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XXVII CICLO DEL DOTTORATO DI RICERCA IN NANOTECNOLOGIE

Laboratory evaluation of several nanofilled dental resin composites: mechanical and chemical properties

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To my family, for their continuous support and patience

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Summary

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1. Composite materials

The precursor of resin-based composite materials were acrylic resins, particularly polymethyl-methacrylate (PMMA), which was introduced to the dental profession in 1936 as Vernonite and was employed for inlays, crowns and fixed partial dentures [Rueggeberg 2002]. However, the use of PMMA-based restorations was limited due to several factors: volumetric shrinkage during polymerization, a large difference in the thermal expansion coefficient between PMMAs and the surrounding tooth, color instability, poor adhesion and marginal leakage. As a consequence of these limitations a high incidence of marginal staining and recurrent caries was identified at the restoration/tooth interface [Paffenbarger et al 1953; Rueggeberg, 2002].

Bowen in the 1950s developed novel organic high molecular weight epoxy resin and methacrylate derivatives that incorporated inorganic filler particles and sought to reduce the detrimental polymerization shrinkage of the preceding PMMAs. This work resulted in a patent in 1958 of a material composed of 75% by weight of quartz or aluminosilicate glass filler and 25% by weight polymerizable resin monomer, namely the dimethacrylate formulation 2,2-bis[4-(2-hydroxy-3-methacryloxypropoxy)phenyl] propane (bisphenol-A glycidyl methacrylate; BisGMA). Subsequently, the large molecular size and chemical structure of the bifunctional BisGMA resulted in decreased polymerization shrinkage compared with PMMAs and improved the elastic modulus, tensile and compressive strengths [Bowen 1956].

The high viscosity of BisGMA limited the filler particle loading necessitating the introduction of a lower molecular weight monomer, namely triethylene glycol dimethacrylate (TEGDMA) to reduce the viscosity of the paste and allow for increased filler loading and appropriate handling characteristics. A silane coupling agent was used to coat the glass filler particles prior to incorporation into the resin matrix to promote adhesion between the glass filler and the BisGMA/TEGDMA co-monomer.

Early composite resins were chemically cured via a reduction-oxidation reaction to initiate free radical polymerization [Bowen 1956; Bowen 1958; Bowen & Rodriguez 1962; Bowen RL. 1964]. As composite resins were developed, light-activated polymerization was introduced and subsequently a photo-initiator, such as camphoroquinone, was added to promote the curing reaction, whilst the addition of an inhibitor, such as hydroquinone, was also required to increase both the shelf-life of the material and working time available to the dental practitioner during placement [Rueggeberg, 2002]. UV lights were first used but had a limited depth of cure due to their low power light sources. The development of catalysts triggered by visible light solved this problem and allowed greater depth of polymerization compared with UV light [Rueggeberg, 2002; Minguez et al., 2003]. One of the main advantages of light activated materials was that it increased working time for the dentist, allowing the placement of the material inside the cavity through appropriate layering technique before exposure to the light and initiation of the polymerization reaction [Rueggeberg, 2011].

Classification of resin based composites

Many classification has been proposed over years. To date, dental composite materials are commonly classified according to the mean size of the inorganic filler particles or volume percent of filler [Lang et al.1992; Willems et al.1992]. The first classification system was based on the mean size of filler particles, manufacturing techniques and chemical composition of the filler [Lutz & Philips 1983]. The classification of composites according to filler type has produced a wide variety of classifications and sub-classifications as new composites have been developed and existing materials refined, although the system developed by Lutz & Philips (1983) remains the most widely accepted.

Macro-filled Composites

Macro-filled composites, also referred to as conventional or traditional composites, are constituted by large reinforcement particles, being that the more common materials used are finely ground amorphous silica and quartz. These composites contain glass filler particles with average particle size of 10 µm to 20 µm and the largest particles of 50 µm, and are characterized by a wide distribution in particle size. Inorganic filler loading ranges from: 70% to 80% in weight or 60% to 70% in volume. Due to the inclusion of such large particles surface finishing is poor and in sliding contact, resin could be removed along with these protruding filler particles.

Micro-filled Composites

Micro-filled composites contain silica particles in the range 0:01 µm−0:1 µm with a typical average particle dimension of 0:04 µm (40 nm). This value is one-tenth of the wavelength of visible light and 200 to 300 times smaller than the average particles in macro-filled composites. Due to average particle sizes these composites exhibit smooth surfaces very similar to that obtained for unfilled acrylic resins. Colloidal silica particles tend to agglomerate during mixing, agglomerates account for particle sizes ranging from 0:04 µm to 0:4 µm. The very small particle size produces a massive increase in available surface area for a given volume of filler (typically 103 − 104 times more surface area). Consequently, it is not possible to incorporate very high filler loadings for small particle size and products which are available contain only 30%−60% filler by weight. Even at these lower levels, calculations show that many filler particles must be present as agglomerates and not as individual particles surrounded by resin.

Hybrid Composites

Hybrid composites combine the features, and particularly the advantages of both micro-filled and macro-filled composites. Hybrid composites cover a broad range of particle sizes. This wide range of particle sizes may cause high filler loading with resultant high strength. Typically, hybrid composites contain a filler with an average particle size of 15- 20 µm and 0.01- 0.05µm.

Nano-filled Composites

Nanotechnology has led to the development of a new resin composite. This is characterized by the inclusion of nanoparticles, 20 or 75 nm in size, and nano-aggregates of approximately 0.6-1.4 µm, which are made up of zirconium/silica or nanosilica particles. In order to ensure that the aggregates bind to the resin, they are treated with silane. The distribution of the filler, aggregates and nanoparticles gives a high load, up to 75% in weight.

Nano-composites are available also as nano-hybrid types. An increased filler load is achieved by the reduced dimensions of the particles, along with their wide size distribution. This consequently reduces the polymerization shrinkage and increases the mechanical properties, such as tensile strength, compressive strength and fracture resistance. These characteristics are higher than those of conventional composites and significantly superior to those of micro-filled composites [Beun et al 2007, Kim et al 2002].

The presence of nano-sized filler particles in composite materials have been identified to produce distinct improvements to the material itself, such as increased filler loading in hybrid-type materials as nano-sized particles pack more efficiently between larger particles and also a subsequent reduction in polymerization shrinkage [Grandio Product Specification, 2006]. An extensive study conducted by Beun et al. (2007) compared the flexural strength, elastic modulus, Vickers microhardness and degree of conversion of several nanofills with universal and microfill composites. The study concluded that the nanofills Filtek™ Supreme

(3M ESPE) and Grandio (Voco) exhibited superior flexure strengths, surface hardness values and elastic moduli compared with the other Composites tested, with the exception of Filtek™ Z100 (3M ESPE). Subsequently, both nanofill materials were indicated for posterior and anterior placement [Beun et al., 2007].

The addition of even small quantities of nano-sized silica particles has been identified to improve the mechanical properties. Tian et al. (2008) highlighted that the addition of 1 and 2.5% mass of nano-sized fibrillar silica to a BisGMA/TEGDMA resin significantly improved the flexure strengths (128 and 130MPa) compared with conventionally filled Composites, (110 and 120MPa respectively). This was suggested to occur as a consequence of the reinforcing effect of highly separated and uniformly distributed nano-fibrillar silica, whilst the formation of agglomerates of fibrillar silica may weaken the resulting material [Tian et al. 2008]. Nanoparticles produce a more homogeneous filler distribution in low viscosity materials, such as bonding agents. The incorporation of nanosized filler in bonding agents also produced a more structured bond at the tooth/bonding agent interface as filler penetrates the dentine tubules to reinforce the hybrid zone [Breschi et al. 2008].

A further phenomenon contributing to the aesthetic appearance of nanofill composites was that such materials appear translucent as a consequence of the small size of the dispersed nano-sized filler particles [Grandio Product Specification, 2006]. This occurs as the particle size is smaller than the wavelength of incident light (400-700nm), the subsequent scattering coefficient is reduced enabling light to pass through the material without refraction at the interface between the resin matrix and inclusions, such as filler particles and porosity voids [Ruyter & Oysaed 1982; Lee 2007].

Modern micro- and nano-filled have also been described as ‘universal’ or ‘all-purpose’ composites and have been indicated for both anterior and posterior placement [Cobb et al 2000; Manhart et al 2001]. Universal composites possess appropriate filler distributions to attain a maximum loading in excess of 80% in weight with a non-uniform size distribution of less than or equal to 1µm, providing flexural strengths of up to 160MPa [Lohbauer et al. 2006; Lu et al 2006]. In addition, Cobb et al. (2000) identified that universal composites exhibited an increased resistance to wear and improved surface polishability compared with preceding materials.

Composite limitations

Despite the continuing development of composites and subsequent improvement of clinical behaviour [Mjör 1997], optimum mechanical and physical properties of dental composites remain compromised by several factors such as: polymerization shrinkage stress [Davidson et al 1997; Palin et al 2005a; Marchesi et al 2010], limited depth of cure [Jandt et al 2000; Fleming et al 2008], decreased monomer conversion [Palin et al 2003], insufficient wear resistance [Hu et al 2002; Palin et al 2005b], hydrolytic instability [Palin et al 2005c.] and technique sensitivity of application [Lucarotti et al 2005; Opdam et al 2004; Opdam et al 2007]. Of these limitations possibly the most detrimental is polymerization shrinkage and the subsequent generation of polymerization shrinkage stresses.

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2. Bulk-fill resin composites

The early years of composite resins created challenges because of material composition, bonding, layering, curing, finishing and polishing techniques. After years of development a predictable success with composite restorations could be achieved [Manhart et al 2004]. There have been many advances to composite resins in terms of strength, shrinkage, polishability, durability and esthetics. However, for most resin-based materials, a methodical layering technique is strictly required for success, above all in high C-factor cavities [Kwon et al 2012, van Dijken 2010].

In some direct composite restorations, the use of a horizontal flowable composite layer on dentin has been suggested, due to its greater ability to internal flow and adaptation which partially compensates shrinkage stress, thus going to be an "elastic layer" between the substrate and the restorative material [Aggarwal et al 2014; Oliveira et al 2010]. To be successful with closed/open sandwich technique, the flowable composite resin should have certain properties that will guarantee an adequate long-term performance. The use of flowable composite in the high C-Factor cavities below the composite ensures a better marginal integrity [Chuang et al 2002; Haak et al 2003] and reduced enamel fracture [Haak et al 2003]. It also improves the fit between adhesive system and composite material creating less voids [Campos et al 2014].

Recently, with the attempt to overcome some composite limitations, a new type of light-curing resin composite have been introduced, the so-called bulk fill resin composites, which can present low and high viscosity. These materials should present an increased maximum increment thickness and thus could be placed in layers up to 4mm thick without compromising the polymerization and the degree conversion [Czasch & Ilie 2013; Ilie et al 2013a], resulting in a need for fewer increments. In any case, the bulk-fill flowable composite should be covered with at least a 2mm layer of conventional composite [Burgess & Cakir 2010; Roggendorf et al 2011; Ilie et al 2013]. To date there are few randomized clinical studies that evaluated in vivo behavior of these materials: Van Dijken & Pallesen reported comparable Annual Failure Rate between bulk fill composite (class 1: 1.2%; class 2: 2.2%) and conventional composite (class I: 1.0%; class 2: 1.6%) after 3-years of clinical function (Van Dijken & Pallesen 2015).

However several in vitro studies focused on bulk fill composites and they confirmed that micro-mechanical properties and degree of conversion are satisfactory in layers of 4 mm polymerized for 20 seconds (Ilie et al 2013a; Zorzin et al 2015), thus they can be cured in large increments. This is due to several characteristics: the high translucency of these materials, in which the amount of filler decreases but increase its size; the presence of particular photoinitiators and accelerators of the polymerization, more reactive towards curing lights than camphorquinone and leucerin TPO [Ilie & Hickel 2011]. For example, Tetric EvoCeram Bulk Fill contains Ivocerin, a germanium-basedphotoinitiator particularly efficient with a high sensitivity to wavelengths between 400 and 450nm and which does not require the presence of amine as co-iniziators (Moszner et al 2008). Alshali et al (11) showed that some bulk fill flowable composites, immediately after curing, presented a degree of conversion inferior than traditional composites, but nevertheless they reached a similar degree of conversion after 24 hours. This particular behavior could be advocated to the capacity to reduce shrinkage stress during polymerization [Alshali et al 2013].

Manufacturers also claim that contraction stress in these new composites is even lower than that found either in flowable either in non-flowable composites [Venus Bulk Fill Technical Information (2011); Tetric EvoCeram Bulk Fill Technical Information (2012)]; a recent study [Moorty et al 2012] showed that minor contraction stress exerted by bulk fill flowable composites translates into a lower cuspal deflection compared to traditional composites placed with oblique layering technique.

However because of poor mechanical properties (Ilie & Hickel 2011) (hardness and modulus of elasticity are closely related to the amount of filler [El-Safty et al 2012]), the use of low viscosity bulk fill composite is not recommended in situations where high mechanical stress is present, such as in direct contact with occlusal loads. Previous findings [Ilie et al 2013b] showed that Young modulus, Vickers hardness and Indentation modulus classify some bulk fill materials (SureFil SDR, Venus Bulk Fill and Filtek Bulk Bulk) as between hybrid and flowable composites. Moreover, bulk fill composites with increased viscosity were also produced to overcome mechanical limitations and increase clinical indication. Within high viscosity bulk fill composites, Sonic Fill (Kerr) presents a sonic activation through a specific handpiece that allow a transitory viscosity and hardness reduction, which should assure an easier composite adaptation to cavity walls during placement (SonicFil Technical Information 2013).

The classification of bulk fill materials in low and high viscosity reflects mechanical properties [El-Safty et al 2012] and determines clinical procedure: the low viscosity material

(SureFil SDR, Venus Bulk Fill, X-tra Base, Filtek Bulk Fill) must be finalized by placing above them a layer of traditional composite, while the high viscosity bulk fill composite (Tetric EvoCeram Bulk Fill, SonicFill) do not need such finalization [Ilie et al 2013b].

If the bulk fill composites are to provide a true clinical advantage, then they require high depth of cure while simultaneously demonstrating a decrease in internal stress, and subsequent decreased incidence of internal gap formation. However, a recent study by Furness et al. [2014] showed that bulk fill materials, either flowable either non-flowable, resulted in a similar proportion of gap-free marginal interface if compared to a conventional composite.

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3. Resin Cements

The increasing demand of patients for aesthetic treatments has challenged the use of metal-free restorations [Hooshmand et al 2012]. Aside from poor aesthetics, metal-based crowns have some disadvantages such as galvanic and corrosive side effect [Möller 2002] as well as causing gingival discoloration (Christensen 1994). As a result, posterior tooth-colored adhesive restorative techniques have grown considerably over the last decade (Magne 2006). All-ceramic crowns were routinely placed not only in the anterior region but also in the posterior were they were subjected to greater occlusal forces and stress from cyclic loading (Snyder & Hogg 2005). The ceramic system technology has developed very fast in the last years and has become a definite option in the restoration of anterior and posterior teeth that require indirect rehabilitations either because it offers the possibility of a double adhesion of the resin cement to the tooth structure and the restoration [Peixoto et al 2007] either because it bases its clinical success to a great extent on the reliable bonding between ceramic and dental hard tissues provided by the luting materials [Zhang & Wang 2011]. Further, the grater attention in preserving the higher amount of dental sound tissue, even in case of big reconstruction, has contributed to the success of adhesive ceramic, especially on the anterior teeth.

The clinical success of an indirect restoration is partially related to the material and technique used for the luting procedures (Hickel & Manhart 2001). An inadequate marginal adaptation of the cement on the bonding interfaces and a decreased retention mainly cause the premature failure of a restoration [Mijör & Gordan 2002a; Mijör et al 2002b]. Several products are available in the dental market for the cementation of indirect restorations such as single crowns, bridges, fiber posts and screws. The selection of the luting agent should be based on the specific clinical situation, the type of the restoration and the physical, biologic and handling properties of the luting material itself [Jivraj et al 2006]. However, it cannot be possible to indicate one single product to be universally recommended in multiple situations. An ideal luting material should provide an effective marginal seal, it should possesses good mechanical and physical properties, it should be insoluble in the oral fluid, it should set in a short period of time and it has to be esthetic.

According to their chemical composition, dental cements can be divided into five main classes: zinc-phosphate cements, polycarboxilate cements, glass-ionomer cements, hybrid cements (resin-modified glass- ionomer cements and compomer) and resin cements [Diaz-Arnold et al 1999]. Clinicians should be aware of each material's characteristics, its advantages and disadvantages, its chemical compositions and mechanical properties as well as the substrate to be bonded and the type of material used for the restoration (i.e. ceramic, zirconia, composite) should also be taken into consideration. Different types of luting agents vary considerably in solubility, strength, and ability to adhere to tooth structure. Thompson et al (1998) cited that the clinical failure rate for resin bonded ceramic restorations had been found to be lower than when traditional were used.

Resin cements are gaining popularity in the dental profession because they are strongly recommended for cementation of all-ceramic systems [Blatz et al 2003; Hill 2007; Pegoraro et al 2007]. The vast majority of non-metallic restorations, which are also utilized more at the present time than before, can be cemented only with resin cements. These restorations include ceramic and resin composite inlays and onlays as well as ceramic crowns and porcelain veneers. Resin cements are also the only cement material that can be used for cementation of resin-bonded fixed partial dentures.

The early resin cements were primarily poly-methyl methacrylate powder with various inorganic filler and methyl methacrylate liquid. Resin cements are methyl methacrilate-, Bis-GMA dimethacrylate-, or urethane dimethacrylate-based, with fillers of colloidal silica or barium glass 20% to 80% by weight [Hill 2007] The composition and characteristics of most modern resin-based cement are similar to conventional composites and consist of inorganic fillers embedded in an organic matrix such as Bis-GMA, TEGDMA and UDMA (blatz 2003a). Filler particle size is kept very small [Spinell et al 2009], and recently nano-fillers have been introduced even in resin cements [Babannavar & Shenoy 2014]. Finally, initiators of polymerization are added to change the setting mechanism and pigments are added to aid in tooth color matching [Hatrick et al 2003]

Typically, resin cements are used in conjunction with enamel and dentin bonding agents and, as a result, are capable of micro-mechanical attachment to both structures through the bonding agent. They can also bond to appropriately treated surfaces of restorations. This bonding is usually micro-mechanical in nature and occurs when the fitted surface of the restoration —ceramic, resin composite or metallic — has been micro-etched or sandblasted and silanized. Some resin cements are formulated in such a way that they possess an additional chemical agent to enable them to bond chemically to cast restorations made of non-precious metal alloys. Unlike resin cements, non-polymeric cements, such as zinc phosphate cement, generally cannot bond to either the tooth structure or the fitted surface of the restoration. One exception is glass ionomer cement, which can bond chemically to both dentin and enamel; however, the strength of the bond is far less than what can be achieved with resin cements. A previous study stated that a resin cement used in conjunction with a dentin bonding agent to lute crowns to teeth with short clinical crowns achieved approximately 3 times the bod strength effected by phosphate cement [El-Mowafy et al 1996]. For teeth with crown preparations with less-than-ideal angle of convergence, the placement of crowns bonded with one resin cement was more than 6 times higher than the attachment achieved with zinc phosphate cement [El-Mowafy et al 1996]. This implies that bonded resin cements can be useful as alternative cement material in clinical situations where retention of crowns or fixed partial dentures is compromised. In the case of a short clinical crown, the standard treatment would typically involve surgical intervention to lengthen the clinical crown; however, the use of a resin cement in conjunction with a dentin bonding agent should be considered as a viable alternative. It would enable the dentist to avoid the surgical procedure and reduce the overall cost and complexity of the treatment, which might help to convince some apprehensive patients to accept the treatment.

Another use of resin cements that has evolved and been adopted by dentists is the cementation of posts, both metallic and non-metallic. One study recommended the use of resin cements with dentin bonding agents when the length of the post space is less than ideal or when the hole is not rounded [El-Mowafy et al 1994] When the canal is short, the extra retention that the bonding produces compensates for the reduced length (Scotti et al 2011), even if nowadays post-retained restorations are always bonded to radicular dentin to provide retention and stability. Moreover, when the canal is not rounded, the resin cement fills in the spaces and eliminates the need for a cast post [Scotti et al 2014].

Resin luting cements possess high compressive strenght, increase the fracture resistance of ceramic materials and resist tensile fatigue [Attar et al 2003; AL-Makramaniet al 2008]. They have good aesthetic qualities, ability to adhere to multiple substrates, increased retention, low solubility, improved marginal wear resistance and less micro leakage in comparison to conventional cements [Piwowarczyk et al 2005; Terry 2005; Kuybulu et al 2007]. Controversially, resin luting cements offer no fluoride release or uptake, short working time, greater film thickness and post-operative sensitivity from polymerization shrinkage. They require more complicated clinical procedures that involve multiple steps that are technique sensitivity and more expensive [Haddad et al 2011; Pospiech 200].

Metal-free indirect restorations cementation is mostly performed with two different materials, based on a light-curing or a dual-curing activation. Light-curing cements have a polymerization mechanism that allows hardening only in presence of a source of light that activate photo-initiators and starts the polymerization reaction [Pick et al 2010]. A great advantage of these materials is their ease of use due to their set-on-command and unlimited working time [Hofmann et al 2001]. However, the absence or reduction of light irradiance caused by the thickness, the shade and the translucency of the composite or ceramic material could reduce the quality of the polymerization reaction [Arrais et al 2008]. Dual-curing cements, on the other hand, have been introduced in an attempt to overcome this problem. In fact, these materials combine a light-curing mechanism of polymerization with self-curing components that initiate the polymerization reaction also in the absence of light [Arrais et al 2008; Giraldez et al 2011]. However, even if polymerization process takes place also when a source of light is not available allowing a uniform set of the materials[10], dual-curing materials require a setting reaction slow enough to allow sufficient working time and quick enough to permit the finishing of the restoration [10] In other world, the polymerization reaction is not controllable from the moment the base and the catalyst paste are mixed together and the polymerization starts [Pick et al 2010].

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Aim of the thesis

The aim of this thesis was to analyze properties of several dental nanofilled resins. During the three year of PhD School in Nanotechnology the research activity focused on different nanofilled materials: resin composites the first year, bulk fill composites the second year and photo-cured nanofilled cements the third year.

Study #1

Evaluation of Depth of Cure: ISO 4049 vs. Micro FT-IR Analysis

Introduction

Composite materials are widely used in restorative dentistry due to their aesthetic quality, ease of handling, and effective bond with dental tissues (Stansbury et al. 2005; Peutzfeldt 1997). The polymerization of composite resins starts through the absorption of light with an appropriate wavelength (440-480 nm) which allows the activation of a photoinitiator (Lindberg, Peutzfeldt, and van Dijken 2005) that initiates a free radical polymerization process of the methacrylate groups. The result is the opening of the aliphatic C=C double bonds, and the subsequent formation of a cross-linked polymeric matrix (Caughman, Rueggeberg, and Curtis 1995; Park, Chae, and Rawls 1999). The degree of conversion describes the percentage of double bonds involved in the reaction, which may vary from 55% to 75% on average (Ferracane and Greener 1986; Silikas, Eliades, and Watts 2000). Several factors can influence the degree of conversion, such as light source used, power density, wavelength, irradiation time, light-tip size, photo-activation method, distribution, quantity of inorganic fillers, the type and quantity of the photoinitiator, shade and translucency of the composite, and pre-heating of the composite (Rastelli, Jacomassi, and Bagnato 2008).

Clinically, in addition to achieving a degree of conversion as high as possible, a further problem in the light-curing process is the attenuation of the light beam through to deeper layers of the composite. Indeed, the UV radiation is partly absorbed by the organic matrix and partly refracted by the filler particles (Cook 1980), thus gradually decreasing the degree of conversion in the deeper layers of the composite resin (Cook 1980; Nomoto et al. 2006; Ruyter and Oysaed 1981). This degree of conversion decreases with depth from the surface, which is indicated by the term Depth of Cure (DoC) (Leloup et al. 2002). A high

DoC is necessary to obtain the necessary physical properties and chemical stability, as well as high wear resistance (Halvorson, Erickson, and Davidson 2002) of the composite material. DoC can be tested through the use of indirect techniques such as scraping test (Koupis et al. 2004), hardness test (Leung, Kahn, and Fan 1984)and penetrometer test (Mills, Jandt, and Ashworth 1999). However, it is possible, through an analysis of FT-IR spectroscopy, to directly assess the composite resin DoC. To measure the degree of conversion of dental resin composites, Fourier transform infrared spectroscopy (FTIR) has been widely used and is considered a reliable method due to the availability of equipment and numerous sampling techniques (Imazato et al. 2001; Stansbury and Dickens 2001; Amirouche-Korichi, Mouzali, and Watts 2009). This method detects the (C C) stretching vibrations, centred around 1638 cm−1, directly before and after curing of materials (Imazato et al. 2001; Stansbury and Dickens 2001; Amirouche-Korichi, Mouzali, and Watts 2009). The ratios of the infrared spectra of aliphatic (1638 cm−1) to aromatic (1608 cm−1) C=C double bonds absorption peaks are used to calculate monomers conversion (Silikas, Eliades, and Watts 2000).

This method involves the study of the interaction between the material and a radiation field in the mid-infrared (400-4000 cm^{-1}) range and quantification of the number of double C = C bonds present in the resin (Camilotti et al. 2008; Shadman et al. 2012; Imazato et al. 2001; Stansbury and Dickens 2001).

Research on the composition of composite materials is focused on the resin matrix monomers to improve properties such as polymerization shrinkage (Dauvillier and Feilzer 2005) and stress (Calheiros et al. 2004), viscoelastic and thermal properties (Kim et al. 2004), biocompatibility (Eick et al. 2002) and the filler content (Beun et al. 2007), which play a major role in mechanical properties. One of the most recent advances in restorative materials is the incorporation of nanotechnology. Nanofilled composites, with a filler size ranging from 5 to 100 nm, have been produced in recent years (Moszner and Klapdohr 2003), and are claimed to have improved aesthetics and mechanical performance (Beun et al. 2007; Lohbauer et al. 2006).

Composite pre-heating has been shown to improve flowability and handling characteristics without altering physical properties (Daronch et al. 2006). Recent studies demonstrated a strong correlation between composite temperature and monomer conversion (Daronch, Rueggeberg, and De Goes 2005; Trujillo, Newman, and Stansbury 2004), thus reducing the amount of unreacted monomer leaching into the oral cavity (Daronch, Rueggeberg, and De Goes 2005).

The aim of this *in vitro* study was to compare two methods of assessing the DoC of nanohybrid composite resins. The null hypothesis is that the DoC is not influenced by (1) testing methods, (2) curing light energy density, or (3) composite temperature.

Materials and methods

For this *in vitro* study a nanohybrid resin composite (Venus Diamond, Heraeus Kultzer, Hanau, Germany), shade A2, was selected. Prior to the confection of the samples, resin composites were pre-stored at different temperatures: 25°C (room temperature/ group A) and 50°C (Calset, AdDent Inc., Danbury, CT, USA/ group B). The composite was placed with a bulk-fill technique inside semicircular metal molds with a diameter of 10 mm and a depth of 6 mm (Fig.1). The bottom surface of the mold was in contact with a plate of glass, which simulated the floor of an ideal first-class cavity. Composite was irradiated with a halogen curing unit (Swiss Master Light, EMS, Nyon, Switzerland), with different energy density regimens according to the group (n=12 per group):

G1: 4J/cm^2 (400 mW/cm^2 × 10 seconds)

G3: 16J/cm^2 (400 mW/cm^2 × 40 seconds)

G5: 20J/cm^2 (2000 mW/cm^2 × 10 seconds)

G7: 80J/cm^2 (2000 mW/cm^2 × 40 seconds)

The tip of the curing light was placed in contact with the upper surface of the sample, which had been coated with a transparent Mylar strip with the aim of preventing the formation of an oxygen inhibited layer. After 24 hours of storage, the mold was opened to expose the lateral surface of the samples (Fig. 3), which were then polished with 1000-grit SiC paper to remove the resin-rich layer formed against the matrix.

DoC was accomplished with a micro-ATR technique, matching a FT-IR microscope with germanium crystal tip (Hyperion 2000, Bruker Optics SpA) with a FT-IR spectrophotometer (Tensor 27, Bruker Optics SpA) and MCT detector, under the following conditions: range 4000-600 cm^{-1} resolution and 2 cm^{-1} at 25°C +/- 1°C. DoC was calculated on the lateral surface of each sample at the level of the smooth side surface of the composite, along the direction of polymerization, at each 0.25 mm increment from the surface layer of the sample. DoC was considered the depth value, expressed in µm, which corresponded to 80% of the maximum DoC of each sample. After the FT-IR analysis, the sample was carefully extracted from the metal mold and any uncured material was gently removed using a plastic spatula ("scraped away"), leaving a hard cylindrical specimen. Finally, the absolute length of this hard specimen was measured with a digital caliber and divided by two. The resulting value is recorded as the DoC and defines the maximum increment thickness.

Statistical Analysis

A three-way analysis of variance (ANOVA) was performed to evaluate the influence of temperature, curing intensity, curing time and their interactions on ATR-FT-IR values. Furthermore, a one-way ANOVA followed by Bonferroni *post hoc* analysis was performed to compare test methods (ATR-FT-IR vs. ISO 4049). Statistical significance was set at $p<0.05$. All statistical analyses were performed using the software STATA (StataCorp, 4905 Lakeway Drive, College Station, Texas 77845 USA).

Results

Mean DoC values and SD, expressed in μm, of the groups obtained using the ATR-FT-IR and ISO 4049 methods are listed in Table 1.

One-way ANOVA showed a significant difference between test methods employed in the present study since ISO 4049 tended to overestimate the DoC.

Three-way ANOVA test (Table 2) showed a significant influence on DoC of curing intensity (p=0.00001) and curing time (p=0.00001), thus the energy density of curing light is proportional to the DoC. Temperature did not significantly influence the DoC of nanohybrid resin composites (p=0.1049), but the interaction with both curing intensity and curing time significantly influenced the results (p=0.0011).

Discussion

The testing methods employed to evaluate DoC showed different reliabilities, thus the first null hypothesis could not be accepted. ISO 4049 has not been demonstrated to be precise because it tends to overestimate DoC when compared with ATR FT-IR spectroscopy. Previous studies identified that the hardened composite that remains after scraping possesses low mechanical properties (DeWald and Ferracane 1987) because it is not optimally cured (Ferracane and Mitchem 2003; Davidson and Feilzer 1997). Additionally, previous studies showed that the ISO 4049 test does not provide a direct indication of the degree of conversion and tends to overestimate the depth of cure when compared to other test methods, such as hardness evaluation or IR spectroscopy (DeWald and Ferracane 1987). Furthermore, a recent study conducted by Nomoto *et al.* (Nomoto et al. 2006) confirmed that FT-IR provided a higher DoC accuracy than the indirect techniques. The ISO 4049 method was developed using a microfilled resin composite (Durafill, Kulzer & Co GmbH, Bad Homburg, West Germany)

(Cook 1980), one of the first visible light-curing resin composites. Since its development, the principle of the ISO 4049 method has remained basically the same (Nomoto et al. 2006).

There is no general consensus on the adequate curing light exposure time required for proper polymerization of a resin-based material because the susceptibility to variation in irradiance under simulated clinical conditions is often dependent on the material (Musanje and Darvell 2003). For this *in vitro* study a nanohybrid composite was selected (Venus Diamond, Heraeus Kulzer, Hanau, Germany). The organic matrix is formed from monomers with low viscosity (UDMA) and from monomers with high molecular weight, which results in a slower cure rate and very low shrinkage stress values (Marchesi et al. 2010). In contrast, the high filler content should reduce light transmission through the material during irradiation (Arikawa et al. 2007; Emami, Sjödahl, and Söderholm 2005)and, thus, influence the final depth of cure. For this reason, the present study evaluated DoC of a nano hybrid resin composite treated with different energy densities. According to the results of this *in vitro* study, DoC was proportional to curing light energy density. Irradiance indirectly expresses the rate of delivery of photons, and thus the rate at which free radicals are generated. With a varying irradiation time, at a constant irradiance, determines the total number of free radicals generated, although not necessarily proportionally in either case. For photoactive dental materials, the total energy principle promotes the common assumption that varying combinations of curing irradiance and exposure time provide similar material properties at constant radiant exposure. This is the principle known as the "exposure reciprocity law"(Halvorson, Erickson, and Davidson 2002; Price, Felix, and Andreou 2004; Leprince et al. 2011), which was partially confirmed by the results of the present study; i.e., either curing intensity or curing time significantly affected nano hybrid composite DoC. Indeed, an energy density between 16 and 20 J/cm^2 was necessary to cure a 2-mm layer of nanohybrid composite, thus the second null hypothesis could be rejected. Moreover, among G3 (400 mW/cm^2 × 40 sec = 16J/cm^2) and G5 (2000 mW/cm^2 × 10 sec = 20 J/cm^2) any statistically significant differences were found, which supports the hypothesis that the use of high irradiance could be accompanied by a reduction in the exposure time necessary to obtain a sufficient depth of cure. Despite this evidence, the irradiance of modern curing units continues to increase, in keeping with the assertion that adequate polymerization might be achieved using short exposure times (5 s or less) with high irradiances. This topic is still controversial, since Price *et al.* affirmed that use of high-powered curing lights for 3 or 5 s did not deliver sufficient energy to cure 1.6-mm-thick composite specimens (Price, Felix, and Andreou 2004).

Composite pre-heating is not thought to increase the DoC of nanohybrid composites, and the results led us to accept the third null hypothesis since temperatures up to 50°C did not significantly influence DoC. It is widely accepted that temperature has a significant effect on the degree of conversion of resin composites, thereby affecting the properties of the polymer. Radical mobility increases with temperature, and additional polymerization occurs as a result of the lower viscosity (Lovell, Newman, and Bowman 1999; Muñoz et al. 2008). The results of the present study are in contrast with Munoz *et al.* (Muñoz et al. 2008), who affirmed that there was an increase in hardness as the temperature of the composite was increased from 70° to 140°F for composites at either the top or bottom location. Inconsistencies could be related either to sample preparation technique, to the curing light employed, to the testing methods used, or to the composite materials tested. Above all, it is well known that composite resins disperse the light of curing units, thus when the light passes through the composite its intensity is reduced due to light scattering by filler particles and the resin matrix (Conti et al. 2004; Braga and Ferracane 2002). In the present study a low-shrinkage nanohybrid composite was selected, which should have a reduced scattering effect compared to microhybrid composites due to the decreased filler content.

Conclusion

Within the limits of this *in vitro* study, we can affirm that the scraping test is not a reliable method for the evaluation of the DoC of composite resins, while direct analysis with ATR FT-IR spectrometry seems to be more effective.

The increase in the energy density supplied to the material significantly increased the depth of cure of the nanohybrid composite nano-hybrid tested in this study, while composite preheating did not increase the DoC. Further studies are necessary to confirm this findings.

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Service Rendered Survey of 1999 by the ADA Health Policy Resources Center; 2002

GROUP	ENERGY DENSITY	COMPOSITE TEMPERATURE	ATR FT-IR (μm)	ISO 4049 (μm)
1	4 J/cm2	25°C	623	1816.6
2	4 J/cm2	50°C	835.6	1833.3
3	16 J/cm2	25°C	1922.5	3466.6
4	16 J/cm2	50°C	1615.6	3360
5	20 J/cm2	25°C	2255.6	3780
6	20 J/cm2	50°C	2148.3	3456.6
7	80 J/cm2	25°C	3071.3	5230
8	80 J/cm2	50°C	4011.1	5398

Table 1: Mean DoC values of the groups using the ATR FT-IR and ISO 4049 test methods.

```
                          Number of obs =      48      R-squared     =  0.8974
                          Root MSE      = 385.391      Adj R-squared =  0.8794

                 Source |  Partial SS    df       MS            F     Prob > F
------------------------+-----------------------------------------------------
                  Model |  51937396.7     7    7419628.1      49.95     0.0000
                        |
            temperature |  408852.083     1   408852.083       2.75     0.1049
            curingint~y |  31586830.1     1   31586830.1     212.67     0.0000
temperature#curingint~y |  644033.333     1   644033.333       4.34     0.0438
             curingtime |    16978923     1     16978923     114.32     0.0000
 temperature#curingtime |  208824.083     1   208824.083       1.41     0.2427
 curingint~y#curingtime |   269100.75     1    269100.75       1.81     0.1859
           temperature# |
 curingint~y#curingtime |  1840833.33     1   1840833.33      12.39     0.0011
                        |
               Residual |     5941053    40   148526.325
------------------------+-----------------------------------------------------
                  Total |  57878449.7    47   1231456.38
```

Table 2: Three-way ANOVA results

Figure 1: semicircular metallic mold

Figure 2: Mold opened to expose lateral sample surface

Figure 3: Composite lateral surface

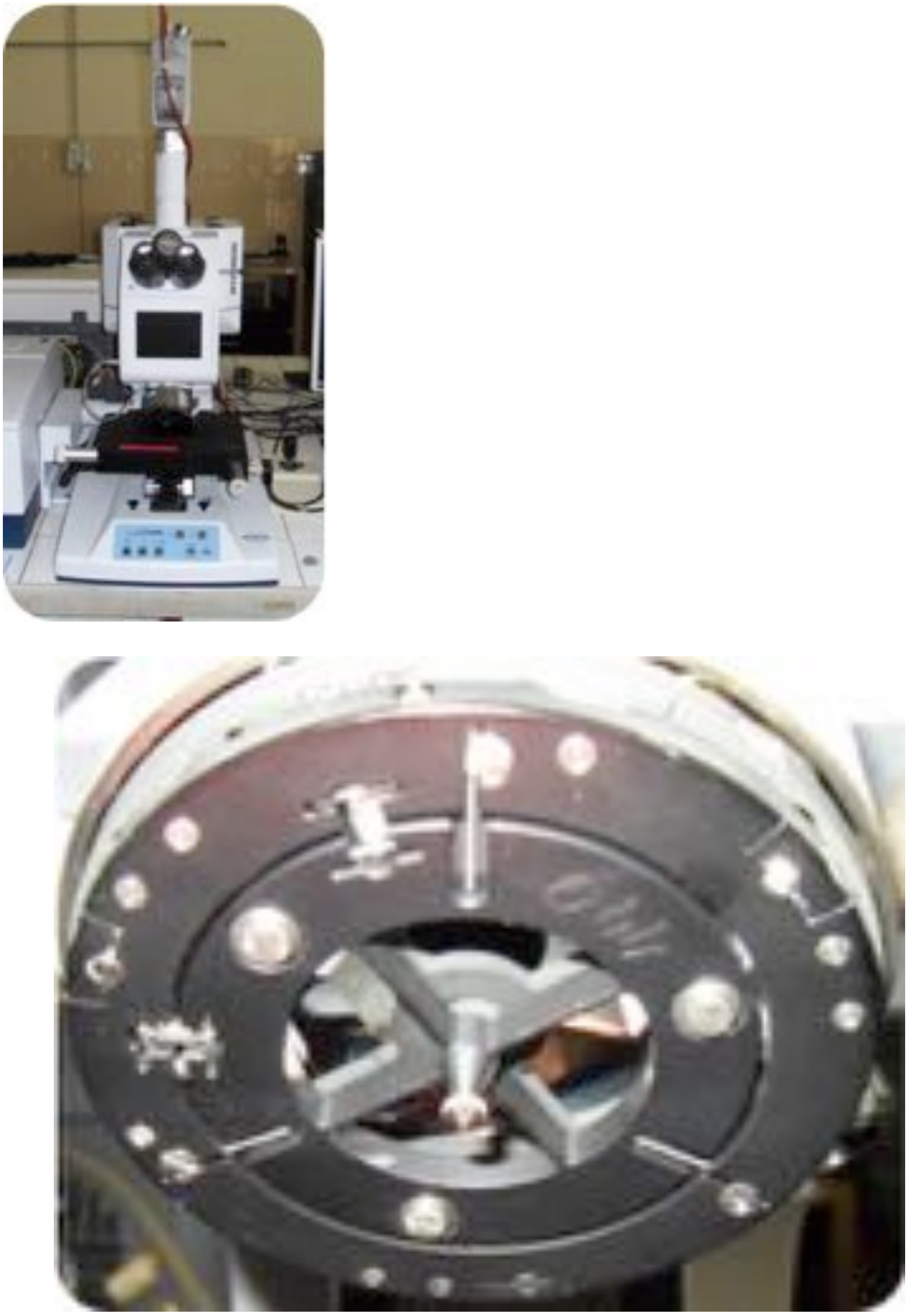

Figure 4: micro-ATR technique, matching a FT-IR microscope with germanium crystal tip (Hyperion 2000, Bruker Optics SpA) with a FT-IR spectrophotometer (Tensor 27, Bruker Optics SpA) and MCT detector

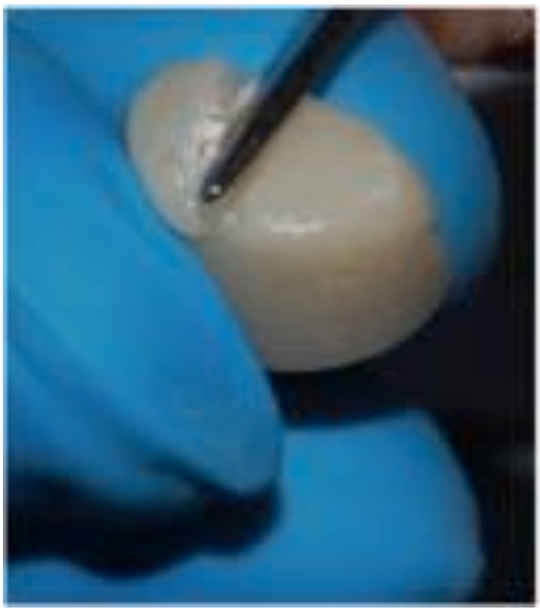

Figure 5: ISO 4049 test: uncured composite removal

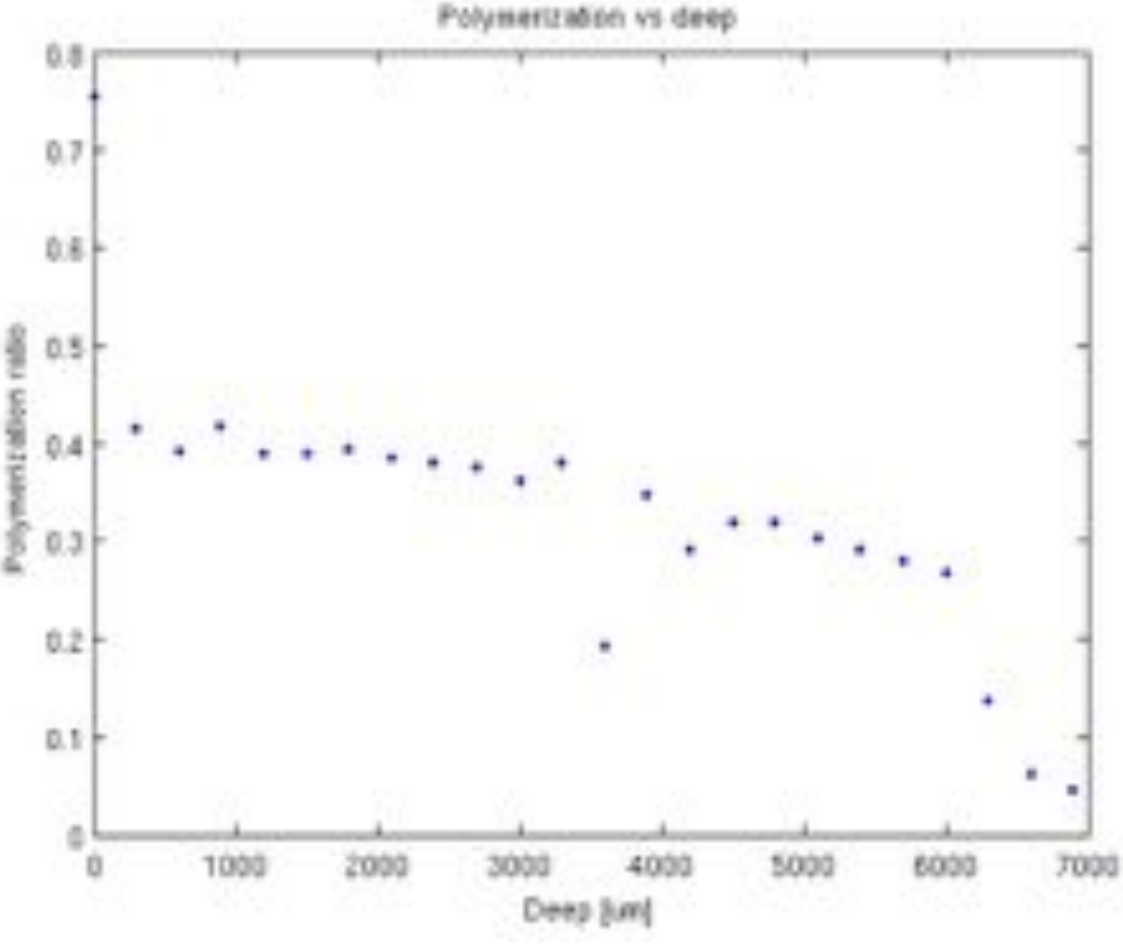

Figure 6: Degree of Conversion correlated to sample depth.

Study #2

Evaluation of Depth of Cure in Nanofilled Composites

Introduction

Adequate photo-polymerization is the crucial factor to obtain optimal physical properties and clinical performance of resin composites[2-6]. Composites are partly translucent and scatter light. Light penetration decreases with increased material thickness (McCabe 1985), due to the absorption and scattering of light by fillers and other additives (Suzuki et al 1991). Unfortunately, light scattering leads to limited depth of cure (Watts & Cash 1994), which has been pointed out by several researchers (Onose et al 1985; Rueggeberg & Craig 1988) as a major clinical drawback with light-cured resin composites, because unpolymerized or partially polymerized material can lead to poor mechanical properties, poor dentin bonding and eventually initiate pulp reactions (Emami et al 2003).

The recommended maximum curing depth of the majority of composites is 2mm which has resulted in the necessity of incremental placement techniques when the cavity to be filled exceeds this depth. Incremental placement of composite is itself 'technique sensitive' as a consequence of the need for attention to detail and the requirement to achieve adequate bonding between the previous increment and cavity wall (Liebenberg 2000; Fleming et al 2008). Subsequently, improving the achievable depth of cure is vital to producing clinically successful materials, therefore recent developments in modern composites have included packable composites and clinical placement techniques which have sought to increase the depth of cure (Jackson & Morgan 2000).

As previously cited, light polymerization is influenced by several factors: composition and shade of the composite resin, quality of light-curing unit, exposure time[17], curing protocol and composite layer thickness (McCabe 1985; Yearn 1985; Kanca 1986; Yap et al 2003;

Davidson-Kaban et al 1997; Aguiar et al 2005). It has also been shown that the degree of conversion of light-cured materials is chiefly influenced by the light intensity produced by the curing unit (Rueggeberg et al 1993; Rueggeberg et al 1994), exposure time and the distance between composite surface and lamp tip. Higher curing light intensities may lead to superior physical and mechanical properties (Wang & Sang 2001).

The scattering effect is also expected to increase with increasing filler diameter (Born & Wolf 1980). Since only small differences in refractive index were found between different fillers, the scattering behavior is expected to be dominated by the filler diameters. Thus, the aim of this in vitro study was to evaluate the Depth of Cure (DoC) of nanofilled and micro-hybrid resin based composites. The null hypothesis is that DoC is not influenced by filler size of composites.

Materials and methods

For this in vitro study 4 nanofilled and 1 micro-hybrid resin composite were selected:

1: Venus Diamond, Heraeus Kultzer, Hanau, Germany), shade A2;

2: Filtek Supreme XTE (3M ESPE, St. Paul, USA), shade A2B;

3: Empress Direct (Ivoclar, Shan, Luxembourg), shade A2;

4: Amelogen Ultra “experimental version” (Ultradent, …), shade A2.

5: Gradia Direct Anterior (GC, Tokyo, Japan), shade A2.

Composite were placed with a bulk-fill technique inside semicircular metal molds with a diameter of 10 mm and a depth of 6 mm (Fig.1). The bottom surface of the mold was in contact with a plate of glass which simulated the floor of an ideal first class cavity. Composite was irradiated with an halogen curing unit (Swiss Master Light, EMS, Nyon, Switzerland), with different energy density regimens according to their groups (n=12 per group):

G1: 4J/cm2 (400 mW/cm2 x 10 seconds)

G3: 16J/cm2 (400 mW/cm2 x 40 seconds)

G5: 20J/cm2 (2000 mW/cm2 x 10 seconds)

G7: 80J/cm2 (2000 mW/cm2 x 40 seconds)

The tip of the curing light was placed in contact with the upper surface of the sample, which had been coated with a transparent Mylar strip with the aim of preventing the oxygen inhibited layer. After 24 h of storage, the mold was opened to expose the lateral surface of samples (Fig.3), which were then polished with 1000 grit SiC paper to remove the resin-rich layer formed against the matrix.

DoC was accomplished with a micro-ATR technique, matching a FT-IR microscope with germanium crystal tip (Hyperion 2000, Bruker Optics SpA) with a FT-IR spectrophotometer (Tensor 27, Bruker Optics SpA) with MCT detector, under the following conditions: range 4000-600 cm-1 resolution and 2 cm-1 at 25 ° C +/- 1 ° C. DoC was calculated on the lateral surface of each sample, at the level of the smooth side surface of the composite along the direction of polymerization, each 0.25 mm in depth from the surface layer of the sample. DoC was considered the depth value, expressed in μm, which corresponded to 80% of the maximum DoC of each sample.

Statistical Analysis

A two-way analysis of variance (ANOVA) was performed to evaluate the influence of material, energy density and their interactions on DoC. Statistical significance was set for $p<0.05$. All statistical analyses were performed with the software STATA (StataCorp, 4905 Lakeway Drive, College Station, Texas 77845 USA).

Results

Mean DoC valued and SD, expressed in μm, of different groups obtained through ATR-FT-IR and ISO 4049 methods were listed in Table 2.

Two-way ANOVA showed that DoC is significantly related to curing light energy density (p=0.0001) and not to composite material (p=0.119).

Discussion

The null hypothesis of the present study, that the composite depth of cure is not related to filler content, was accepted due the results obtained.

Inadeguate polymerization of resin-based composites could result in a reduction of physical and mechanical properties (Shortall et al 1995). Moreover it could directly affects, solubility, dimensional stability, color stability and biocompatibility (Ferracane et al 1997; Gilbert et al 1994; Yoshii 1997; Issa et al 2004) because the residual non-reacted monomer acts as a plasticizer and alters the mechanical properties of the material (Daronch et al 2005). Consequently, resin composites should be polymerized as completely as possible to achieve long-lasting restorations.

There is no general consensus on the adequate curing light exposure a resin-based material needs for proper polymerization because the susceptibility to variation in irradiance under simulated clinical conditions was often proven to be material dependent (Arikawa et al 2007). Moreover, the cure of the inner layers of composite is not easily accessible to evaluation.

In order to minimize these undesired effects, the monomer in a resin composite should be cured to a high degree and to an appropriate depth as well. A power density of at least 250-300 mW/cm^2 has been recommended as the lower limit for halogen-based light curing units in order to achieve an adeguate degree of conversion (lee sy j dent 1994). Nowadays, a wide range of curing units are available, including conventional quartz-tungsten-halogen (QTH), light-emitting diode (LED) and plasma-arc (PAC) photo-polymerization lamps. All these lights are available with outputs exceeding 800 mW/cm^2, resulting in shorter recommended exposure times (Scotti quint int 2010). However, shorter irradiation times may lead to an insufficient degree of conversion of the composite resin, especially at the bottom of the restoration (Scotti et al 2011; Stansbury et al 2005). Moreover, the use of curing units with light intensity above 1000 mW/cm^2 may be problematic because it might cause failure of polymer chains to grow and cross-link in the desired fashion (Rueggeberg et al 1990).

To date, the use of the high intensity halogen lamp as an activator for the polymerization reaction is very common (Yearn, 1985; Rueggeberg et al., 1994; Obici et al., 2004; Scotti et al 2011). Light of an appropriate wavelength activates photo-polymerization of methacrylate groups producing a highly cross-linked polymer matrix. Light from the curing source should ideally be able to adequately polymerize the top as well as deeper composite regions. However, as light passes through the composite, it is absorbed and scattered, reducing its effectiveness to initiate polymerization, and consequently resulting in variation of degree of conversion with depth (Peutzfeldt et al., 2000; Mendes et al., 2005a; Mendes et al., 2005b). In deeper regions, where significant light attenuation occurs, the curing unit that delivers light at a more specific wavelength and with high enough power should provide higher degree of conversion.

According to the results of this in vitro study, DoC was proportional to curing light energy density. Thus, differences in energy density resulted not in different degree of conversion but, above all, in different depth of cure. This result is in agreement with previous findings (Lindberg et al 2004; Park et al 2002; Price et al 2000) and corroborates the results of the study conducted by Rueggeberg et al (Rueggeberg et al 1994), which stated that power densities between 233 and 800 mW/cm2 resulted in the same degree of conversion of the top surface.

Any statistically significant difference was noticed between 16J/cm2 and 20J/cm2 concerning the depth of cure of resin based composites tested in this study. Energy density is a curing light parameter that takes into consideration either the irradiation time either the power emitted by the curing light. Present findings confirmed the efficacy of high intensity curing units, which let to satisfactory depth of cure even with high power mode and reduced irradiation time. However literature reported possible problems associated with a high intensity irradiation program: increased composite resins shrinkage, that occurs on polymerization, which creates stress at cavity margins and consequently may lead to marginal fracture, gap formation, marginal staining, leakage, post-operative sensitivity and to secondary caries (Kidd 1976; Davidson et al 1997). Secondly, the risk in employing a high power setting of the halogen light for 10 s allows a depth of cure even greater than that obtained by operating the light at a lower intensity for 40 s but at the expense of a greater temperature rise delivered to pulpal chamber (Stewardson et al 2004). Moreover some findings suggested that too high (>1000 mW/cm^2) irradiance values could be detrimental to the polymerization process and lead to poorer micromechanical properties (Musanje & Darvell 2003).

It has been shown that differences in the refractive indices of the organic matrix material and inorganic filler components influence the transmission of visible light through the material. Regardless of whether this increases on polymerization, a refractive index mismatch between the constituent components of the material leads to higher scatter and lower light transmission at the curing wavelength (Fujita et al 2005).

Despite difference in filler dimension and content, the present study showed that nanofilled composites showed quite similar depth of cure than micro-hybrid composites. Absorption and scatter of light within a resin based composite are the major factors associated with light attenuation (Yearn 1985), which are related to filler size, type and content (Ruyter & Oysaed 1982; Campbell et al 1986; DeWald & Ferracane, 1987), light irradiance (Rueggeberg et al., 2000) and exposure time (Halvorson et al 2002) (radiant exposure) and the shade of the material (Atmadja & Bryant, 1990; Tanoue et al 2001). Considering that tested composites presented same shade, it can be assumed that neither filler size and content neither organic matrix did affect depth of cure obtained with halogen curing light. An increase in filler loading has been reported to show a decrease in the degree of conversion (Halvorson et al

2003). Other researchers also found a decrease, but it was of no statistical significance (Amirouche-Korichi et al 2009). The explanation for that may lie in the fact that the influence of fillers is more related to their size than to their volume (Atai and Watts 2006). Turssi et al (Turssi et al 2005) found no effect on degree of conversion with different filler shapes. It could be also speculated that another explanation of the present findings refers to maximum light scatter, which has been shown to occur where the particle diameter is close to half the wavelength of the incident light (Ruyter & Oysaed 1982). The peak wavelength of the curing lights is approximately 470×10^{-9} m. Maximum scattering would therefore occur for particle sizes around 0.24 µm.

Conclusions

Within the limits of this in vitro study, it can be concluded that all composites tested in this study have comparable depth of cure, which is strictly dependent more to curing light energy density than to material composition. Moreover, 16J/cm2 should be sufficient to cure the recommended 2mm depth of either micro hybrid either nanofilled resin composites. Further in vivo study would be necessary to confirm this findings.

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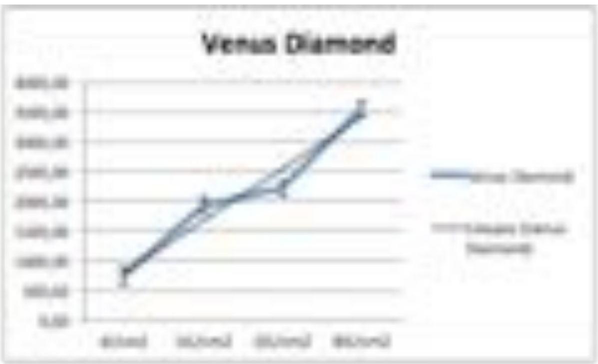
Material	Manufacturer	Fillers	Filler loading	Organic matrix
Venus Diamond **(nano-hybrid composite)**	Haereus-Kultzer	Barium aluminium fluoride glass	81%(wt); 64%(v)	TCD-DI-HEA UDMA
Filtek Supreme XTE **(nano-filled composite)**	3M ESPE	Non-agglomerated/Non – aggregated zirconia Aggregated zirconia/silica cluster (comprised of 20 nm silica and 4 to 11 nm zirconia particles)	78,5%(wt); 63,3(v)	Bis-GMA, UDMA, TEGDMA, BisEMA, PEGMA
IPS Empress Direct **(nano-hybrid composite)**	Ivoclar Vivadent	Barium glass, ytterbium trifluoride, mixed oxide, silicone dioxide and co-polymer	78,15(wt)52-59%(v)	Bis-GMA, UDMA, TEGDMA
Amelogen Plus **(nano-hybrid composite)**	Ultradent	Barium Boron Aluminium particles from 0.4-0.7 m	78%(wt); 61%(v)	Bis-GMA, TEGDMA
GC Gradia Direct Anterior **(micro-hybrid composite)**	GC Dental	Silica, prepolymerized filler	73%(wt); 55,6%(v)	UDMA, dimethacrylate co-monomers

Yoshii E. Cytotoxic effects of acrylates and methacrylates: relationships of monomer structures and cytotoxicity. J Biomed Mater Res. 1997 Dec 15;37(4):517-24.

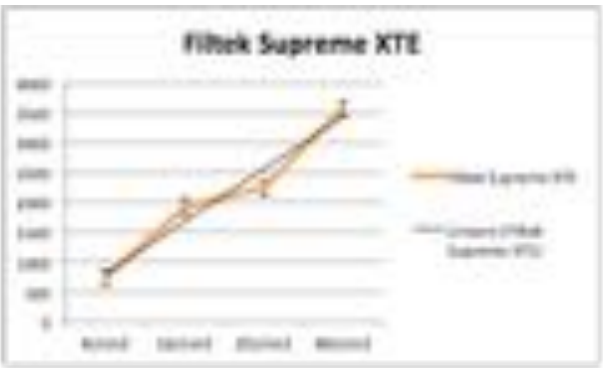
	Venus Diamond	**Filtek Supreme XTE**	**Empress Direct**	**Amelogen Plus Exp.**	**Gradia Direct**
4J/cm^2	737.28 ± 138.81	742.30 ± 136.35	734.43 ± 135.24	744.01 ± 125.59	728.85 ± 135.59
16J/cm^2	1922.53 ± 133.83	1927.47 ± 133.67	1932.23 ± 136.51	1918.05 ± 135.08	1906.03 ± 126.91
20J/cm^2	2216.15 ± 130.66	2238.07 ± 131.41	2236.68 ± 128.81	2247.88 ± 135.40	2200.88 ± 156.49
80J/cm^2	3551.02 ± 124.17	3563.68 ± 122.35	3561.43 ± 127.03	3564.37 ± 130.92	3530.68 ± 143.12

Table 1: materials composition

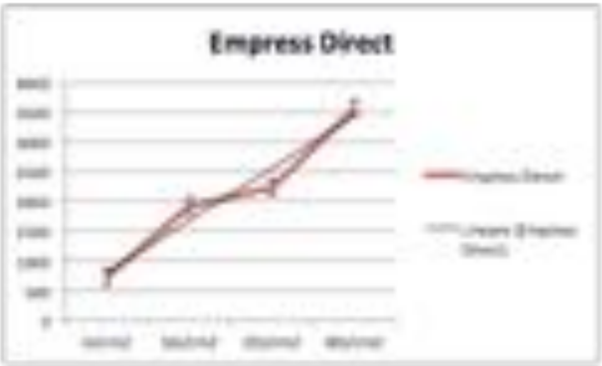
Table 2: Mean DoC obtained in different groups with ATR FT-IR spectroscopy.



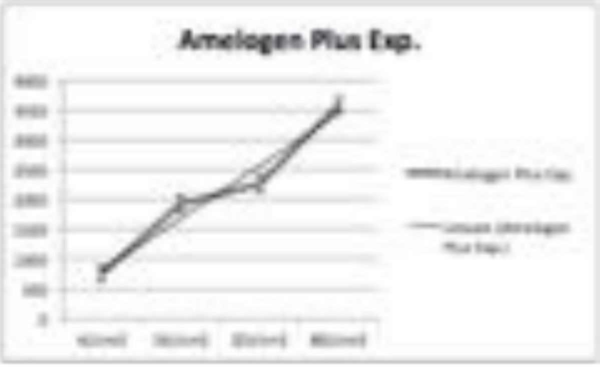
Graph 1



Graph 2



Graph 3



Graph 4

Graph 5

Graphs 1-5: Curves indicating DoC progression of each material at different energy density.

Study #3

Micro-hardness and contraction stress of flowable and non-flowable bulk-fill resin materials

1. Introduction

In recent years composite resins have become the material of choice for direct restorations, thanks in part to their aesthetic and biomechanical advantages(Ferracane 2011). However, their correct use requires a strict respect of clinical procedures and a proper curing process to obtain an optimal degree of conversion of the polymer(Baroudi et al. 2007). The majority of the resin composites today are methacrylate-based and cure by means of a free radical polymerization. During the curing of the monomers, a network of polymers is formed, which becomes rigid due to increasing cross-linking of the polymer chains. In the post-gel contraction phase, the shrinkage manifests as a strain on the resin composite and cavity walls(van Dijken and Pallesen 2014). Furthermore, resin irradiation induces a volumetric contraction of the material, which results in a shrinkage stress at the adhesive interface(Chen et al. 2001; Braga, Ballester, and Ferracane 2005). Shrinkage stress can cause deflection of the cusps(Kim and Park 2011), enamel and dentinal cracks, post-operative sensitivity, inflammation of the pulp, and detachment of the adhesive interface(Hannig and Friedrichs 2000). These events, in time, can lead to infiltration and secondary caries, and thus, failure of the composite restoration. Advances in material formulation, including improved filler size and morphology, progress with existing dimethacrylate chemistry and novel monomer technologies may improve the shortcomings of resin composite materials(Leprince et al. 2013). However, simplification of the use of resin composites has not been reported frequently during the last decade(Roggendorf et al. 2011), though clinicians desire to perform high-quality dentistry with minimal chair time.

Incremental layering techniques of resins have long been accepted as the standard and are widely used for light-curing resin composite restorations. Proper light curing is performed when a sufficient energy density is delivered to every composite layer, which cannot be greater than 2 mm in order to be completely irradiated and, thus, cured(Krämer et al. 2008). The main concern when applying thicker increments is whether the resin composite cures enough in the deeper parts to obtain acceptable mechanical, physical and biocompatible properties(van Dijken and Pallesen 2014). However, restoring cavities, especially deep cavities, with multiple increments of resin composite is time-consuming and increases the risk of incorporating air bubbles or contaminants between the increments(Flury et al. 2012).

To overcome the time-consuming incremental cavity filling technique with conventional resin-based composites, bulk-fill materials have been developed. Bulk-fill resin composites, both flowable and high-viscosity, are an innovative class of dental composite materials, which were developed to simplify and shorten the placement of direct composite restorations(Tarle et al. 2014; Par et al. 2014). These newly developed composites claim to allow the use of material increments up to 4 mm in thickness without necessitating a prolonged curing time or a light-curing unit with increased irradiance, while at the same time producing low volumetric polymerization shrinkage and thus a low polymerization shrinkage stress(“Heraeus Kulzer Venus Bulk Fill Scientific Compendium; 2011. ” 2011). Therefore, matrix and initiator chemistry, as well as filler technology, have been optimized. One approach to improve the depth of cure is to increase the material’s translucency(Bucuta and Ilie 2014). Optical properties of resin composite restoratives are of obvious importance in a procedure reliant on photoactivation, since they may affect light transmission and therefore monomer conversion, which influence critical mechanical properties and ultimately clinical performance(Howard et al. 2010). To optimize material properties, manufacturers incorporated new advanced composite-filler technologies, pre-polymer shrinkage stress relievers, polymerization modulators, and highly light-reactive photoinitiator systems(Manhart and Hickel 2014; Czasch and Ilie 2013). Thus, problems related to polymerization shrinkage, such as marginal gap formation leading to secondary caries due to bacterial colonization(Davidson, de Gee, and Feilzer 1984; Leinfelder 1995), pulp irritation, post-operative sensibility when chewing (Carvalho et al. 1996), or cusp deflection when C-factor is high(McCullock and Smith 1986; Alomari, Reinhardt, and Boyer 2001) could be minimized.

1. Aim of the study

The purpose of this *in vitro* study was to evaluate the hardness and shrinkage stress of six bulk-fill resin composites. The null hypothesis was that (1) the decrease in hardness is not directly related to the composite thickness, and that (2) shrinkage stress is not comparable among the various composites tested.

2. Materials and methods

For this in vitro study six bulk-fill resin composites were selected (Table 1).

2.1 Hardness evaluation

Ten samples for every selected bulk-fill composites were prepared, for a total of 60 samples. The composites were placed with a bulk-fill technique inside semicircular metal molds with a diameter of 10 mm and a depth of 6 mm (Fig.1). The bottom surface of the mold was in contact with a plate of glass, which simulated the pulpal floor of an ideal first-class cavity. The tip of the curing light was placed in contact with the upper surface of the sample, which had been coated with a transparent Mylar strip with the aim of preventing the oxygen inhibited layer. Irradiation was performed for 40 seconds with an LED lamp (Bluphase Style, Ivoclar) (Fig. 2). After 24 hours of storage, the mold was opened to expose the lateral surface of the sample (Fig. 3). The molds were then polished with 1000 grit SiC paper to remove the resin-rich layer formed against the matrix. Micro-hardness was measured on the top (in contact with curing tip), bottom and lateral surface of each sample using a Vickers indenter at

100 gf of load, and 15-s dwell time. The mean hardness value for each surface was calculated. For each sample, 4 measurements were performed on the top and the bottom surfaces (Fig. 4) and 12 measurements were performed on the lateral surface, two for every millimeter, starting from the surface in contact with the curing light tip. The size of the impression left by the tip was calculated with the aid of a microscope (Fig. 5); the number in Vickers (HV) is calculated according to the following formula:

$$HV = 1.854(F/D^2)$$

where F is the applied load (measured in kilograms-force) and D^2 is the area of the impression (measured in square millimeters).

2.2 Contraction stress evaluation

Shrinkage stress evaluation was performed with a universal machine (Sun 500, Galdabini, Cardano al Campo, VA, Italy) which takes into consideration the contraction force generated by a bulk-fill composite sample placed between two metal cylinders during and after light curing. The experimental setup consisted of two stainless steel cylinders as bonding substrates with a diameter of 2 mm and height of 25 mm(Par et al. 2014; “Heraeus Kulzer Venus Bulk Fill Scientific Compendium; 2011. ” 2011) (Fig. 6-7). Two metal cylinders were fixed to the upper and lower clamps of the universal machine. Before each measurement, the lateral surface of the stainless steel cylinder was threaded to improve the retention of the testing machine clamps. Before the application of bulk-fill composite, the attachments were sanded with 180-grit sandpaper and air-abraded using a silica-containing abrasive (Cojet, 3M ESPE, St. Paul, MN, USA). A layer of hydrophobic unfilled resin (Optibond FL, Kerr) was applied on the sandblasted surface and polymerized for 20 seconds with a LED curing unit (Bluephase Style, IvoclarVivadent, Shaan, Lichtenstein) before composite application to ensure appropriate bonding to the stress analyzer. The irradiance of the curing unit was 1200 mW/cm^2 as measured using a commercial dental radiometer (100 Optilux radiometer; SDS Kerr, Danbury, CT, USA).

Mylar film was placed around the lower rod and filled with the composite, then the upper cylinder was lowered and inserted into the upper hole of the mold, and the distance between the two cylinders was set to 2 mm (diameter 2 mm, height 2 mm; C-factor = 0.5). An extensometer (model 2630-101, Instron, Norwood, MA, USA) was attached to the cylinders to provide an electronic feedback loop in the system to maintain the specimen at a constant height during the test. Any approximation between the fixation points of the extensometer caused by resin cement shrinkage was immediately compensated for by controlled movement of the crosshead in the opposite direction (within 0.1 μm).

A defined quantity of bulk-fill composite (20 mg) for each tested material was placed in the mold in bulk and polymerized for 20 or 40 seconds (Table 1). The contraction force (N) generated during polymerization to maintain a constant specimen height in opposition to the force exerted by composite shrinkage was continuously recorded for 5 minutes after irradiation. Each experiment was conducted at room temperature (23–24 °C) and repeated six times for each material ($N = 6$). Contraction stress (MPa) was calculated at 5 minutes as the force value (N) per area unit (force value/bonded surface area). Shrinkage stress, expressed in MPa, was calculated using the formula: Contraction Stress (MPa) = Force (N) / Area (m^2).

2.3 Statistical analysis

Micro-hardness values of each material obtained for the top, lateral (1-6-mm depth) and bottom surface were compared using a one-way ANOVA test with *post hoc* Bonferroni correction. To assess *s*hrinkage stress differences among bulk-fill composites, a one-way ANOVA test and *post hoc* Bonferroni correction were performed. Furthermore, a linear regression was performed to compare the trend of MH registered for the lateral surface of each material. The significance level was set at 95% ($p<0.05$). All statistical analyses were performed using the Stata software package (StataCorp, 4905 Lakeway Drive, College Station, Texas 77845 USA).

Results

Mean values and standard deviations of micro-hardness registered in the groups for the top, lateral (1-6 mm) and bottom surface are listed in Table 2. Micro-hardness progression along the lateral surface is shown in Graph 1. Table 3 shows statistical analysis of the curves trend. Mean shrinkage stress, expressed in MPa, and standard deviation of the tested materials are showed in Table 4 and Graph 2.

Statistical analysis of variance showed that all materials had a significant MH decrease between the top and the bottom surface ($p<0.001$). However, the bulk materials tested performed differently when considering lateral depth progression. Using top surface MH values as the reference point, SDR showed a significant difference ($p<0.05$) at 2-mm depth; ExtraBase and Filtek Bulk Fill showed a significant difference ($p<0.05$) at 3-mm depth; TetricBulk at 4 mm ($p<0.05$); SoncFill at 5 mm ($p<0.05$) and Venus Bulk showed comparable MH values between top and lateral surfaces up to 6-mm depth.

The statistical analysis of variance for shrinkage stress evaluation showed that both SDR and Venus Bulk-Fill presented significantly lower stress during irradiation than other tested materials (p=0.001).

Discussion

The results of the present study led us to reject the first null hypothesis, since hardness is always reduced with depth progression along the lateral surface of the materials tested. Thus, in all cases there is a decrease in MH values between the top and the bottom surfaces. Lateral surface MH analysis, although it was depth dependent, showed different behaviors between the materials tested.

Photo-cured resin composites polymerize only to a certain depth, which depends on the penetration of visible light through the bulk of the material(Pianelli et al. 1999). Furthermore, it has been shown that insufficient polymerization can lead to a decrease in the physical/mechanical(Ferracane et al. 1997) and biological properties of resin composites(Caughman et al. 1991).

Hardness is a mechanical property that indicates the resistance of a material to indentation or penetration, which is influenced by several parameters, such as the filler characteristics (size, weight, volume) and the chemical composition of the resin(Scougall-Vilchis et al. 2009). A strong relationship between the amount of filler and the mechanical properties, such as hardness and elastic modulus, has been reported(El-Safty et al. 2012; Taylor et al. 1998; Leprince et al. 2012). The composite hardness is usually measured using the Vickers(Czasch and Ilie 2013) or Knoop(Obici et al. 2004; de Araújo et al. 2008) method. These techniques provide an indentation using a diamond tip, which exert a pre-established force for a certain time. Hardness is then obtained by dividing the applied load by the area of indentation, examined through a microscope, and multiplied by a given coefficient. This method has the advantage of being relatively simple, reproducible and non-destructive(Bouschlicher, Rueggeberg, and Wilson 2004; Watts 2005). Moreover, advances in instrumentation have made indentation a useful research tool for many different systems across size scales (macro to nano) and numerous scientific disciplines. For these reasons, the hardness of the materials tested in this study were evaluated by Vickers test with an applied force of 100 g for 15 seconds(Frassetto et al. 2012).

In this *in vitro* study, the bulk materials tested showed different MH values when considering the top surface of the samples. These findings are in accordance with other studies that compare various bulk fill and traditional resins(Bucuta and Ilie 2014; Leprince et al. 2014).

Stark differences in top surface micro-hardness between bulk fill materials can be attributed to the great variety of filler size and content. In this study, Venus Bulk Fill and SDR are among the materials with lower MH values. These findings are in accordance with other studies showing the reduced filler percentages of these two materials(Par et al. 2014; Alrahlah, Silikas, and Watts 2014). A strong relationship between the amount of filler and the mechanical properties, such as hardness and elastic modulus, has been reported in several studies(El-Safty et al. 2012; Taylor et al. 1998; Leprince et al. 2012). However different materials, such as Filtek Bulk Fill, showed a reduced percentage in filler content and volume, but higher top surface MH. Indeed, MH can also be attributed to other factors not related to filler content, but strictly associated with matrix composition (Ilie, Rencz, and Hickel 2013)and shrinkage behaviors.(Li et al. 2009)

Some authors considered nanoindentation techniques to evaluate MH useful for characterizing homogenous materials, but are inappropriate for determining properties of biphasic materials such as dental resin composites(Alrahlah, Silikas, and Watts 2014).

However, as mechanical properties are directly proportional to the amount of double bonds involved in the polymerization reaction and, therefore, the composite degree of conversion(Tsai, Meyers, and Walsh 2004) micro-hardness could be effectively considered as an indirect method of assessing the polymerization quality of composites(Flury et al. 2012; Alrahlah, Silikas, and Watts 2014). As stated by Leprince *et al.*[20], the micro-hardness could be considered an "indirect approximation" of the depth of cure. Indeed, the degree of conversion evaluation through MH gives results comparable to those obtained with a direct method, such as Fourier infrared spectroscopy (FTIR micro-MIR)(Obici et al. 2004; Tsai, Meyers, and Walsh 2004).

The depth of cure was defined in the literature by Musanje and Darvell(Musanje and Darvell 2006) as the depth at which the hardness is equal to 80% of the surface hardness. The depth of cure of composite resins depends on several factors: the size and type of filler(Leprince et al. 2011), color and translucency(Leloup et al. 2002; Davidson-Kaban et al. 1997; Ferracane et al. 1997), material thickness(Leloup et al. 2002), curing light intensity(Leloup et al. 2002; Unterbrink and Muessner 1995; Shortall 2005), irradiation time and program(Felix, Price, and Andreou 2006), distance between the composite surface and the curing light tip(Leloup et al. 2002). Moreover, the monomer composition and photoinitiator concentration(Ferracane and Greener 1984) affect the depth of cure. This is in accordance with Lambert-Beer law(Hadis, Shortall, and Palin 2012), which states that light energy, incident to the surface of a material, is affected, in an attempt to pass through it, by an attenuation coefficient, which is proportional to the physical characteristics of the material itself(Hadis, Shortall, and Palin 2012). It is known that the degree of conversion of the composite, and thus indirectly its hardness, depends precisely on the energy density received by the material and the material thickness(Yoon et al. 2002; Nomoto et al. 2006). The method most frequently employed to evaluate the depth of cure is ISO 4049(Flury et al. 2012): the composite to be tested is inserted into a mold and cured, and then is pulled out from the mold and the uncured resin is scraped off with a spatula. Finally, the height of the sample is measured and the residual height divided by 2; the value obtained indicates the depth of cure and defines the maximum increase that can be achieved with the composite resin tested. In a study conducted by Flury *et al.* (Flury et al. 2012) ISO 4049 was compared to Vickers micro-hardness test to determine bulk-fill composite depth of cure. Results showed that ISO 4049 tended to overestimates depth of cure when compared to Vickers micro-hardness, which defined the depth at which at least 80% of the maximum hardness was obtained.

To assess the depth of cure of a composite resin, two studies have assessed the degree of conversion and/or surface hardness along the sample depth(Flury et al. 2012; Alrahlah, Silikas, and Watts 2014). In the present study, hardness was measured on the lateral surface of the sample 24 hours after irradiation (Par et al. 2014), and all the materials tested showed a significant difference from the top surface at a certain depth. X-traBase, Filtek Bulk Fill, SonicFill and Tetric Bulk Fill showed a HM hardness significantly different from the top surface at about 4 mm, confirming the results of previous studies in literature that assess depth of cure(El-Damanhoury and Platt 2014) and, thus, confirming manufacturer instructions (Finan et al. 2013; Alrahlah, Silikas, and Watts 2014). These results generally confirmed the manufacturer's specifications, and a previous report(Alrahlah, Silikas, and Watts 2014), stated that it could be placed in 4-mm-thick bulks instead of the current incremental placement technique, without negatively affecting polymerization shrinkage, cavity adaptation or the degree of conversion (DC).

However, as shown in Graph 1, not all materials had comparable trend curves. SonicFill, Xtra-base, TetricBulk Fill and Filtek Bulk Fill behave in a similar manner, showing a vertical decrease in hardness at 4 mm. Venus Bulk Fill, on the contrary, showed a more linear trend, with a significant difference from top surface hardness only at 6 mm. The behavior of this material can be conducted to its composition and consequently more homogeneous stress distribution(Bucuta and Ilie 2014).

Considering the results of this study SDR was the only material that showed a significant decrease in MH at a depth inferior to that suggested by the manufacturer. The significant decrease for this material was evident at 2 mm depth and the same results is obtained when depth of cure in calculated. This finding is not in agreement with previous reports that confirm manufacturer depth of cure for SDR(Alrahlah, Silikas, and Watts 2014; Ilie, Keßler, and Durner 2013).

When considering contraction stress, statistically significant differences ($p<0.05$) were found between the tested materials, and accordingly, the second null hypothesis was not rejected. On the other hand, there was no statistically significant difference between SDR and Venus Bulk-Fill, which exhibited the lowest shrinkage stress during irradiation. It is worth mentioning that in the setting of this *in vitro* study, we provided a specific environment that allows for comparisons of the behavior of the tested materials under standardized conditions, but the results may vary under different testing conditions, especially increases in the C-factor.

In addition to the hardness of a material, the amount of filler can also influence the elastic modulus of a resin composite(Burgess and Cakir 2010). Several studies have reported that the elastic modulus increases exponentially with increasing filler concentration(Braem et al. 1989; Gonçalves, Kawano, and Braga 2010). Consequently, the volumetric contraction is strictly dependent on the filler amount(Baroudi et al. 2007; Satterthwaite et al. 2012). The amount of filler reduces the volume occupied by the matrix and, therefore, the number of methacrylate groups, leading to a lower volumetric shrinkage. Previous findings(Condon and Ferracane 2000; Kleverlaan and Feilzer 2005) showed a linear relationship between the shrinkage stress and the elastic modulus, thus associating shrinkage stress and filler concentration. The results of this study, however, showed an inverse relationship between shrinkage stress and filler content. This discrepancy is due to the different evaluation methods used to assess shrinkage stress. As shown by Marchesi *et al.*[52](Marchesi et al. 2010) high compliance testing methods are related to low values of shrinkage stress, while low compliance testing methods could lead to overestimation of shrinkage stress. The materials used in the present study that showed a shrinkage stress significantly lower than the other materials tested include SDR and Venus Bulk Fill. The low shrinkage stress of these materials is attributable to their low elastic modulus, due to a reduced amount of filler in volume, which increases the flexibility of the material and, therefore, the ability to internally absorb stresses(Haak, Wicht, and Noack 2003). This viscoelastic behavior is typical of flowable materials. Braga and Ferracane(Braga, Ballester, and Ferracane 2005), in a systematic review in 2005, showed that shrinkage stress is an extremely complex multifactorial phenomenon. It is either related to the volumetric shrinkage during polymerization of the composite material that is bonded to cavity walls, or to its viscoelastic behavior (the ability to flow internally during polymerization), either of which could affect the elastic modulus. Composites with high filler content provide low shrinkage but higher stiffness than materials with lower filler concentration(Braga, Ballester, and Ferracane 2005). On the other hand, the increase in the polymeric matrix degree of conversion simultaneously causes an increase in the volumetric contraction and of the elastic modulus(Braem et al. 1987). In flowable composites, the reduced shrinkage stress is attributable to the fact that the capacity of internal deformation is inversely proportional to the inorganic filler content(J. Vaidyanathan and Vaidyanathan 2001). Moreover, the polymerization kinetics can influence the shrinkage stress(Lim et al. 2002). A previous study conducted by Ilie & Hickel[4] compared shrinkage stress and micromechanical properties of a bulk-fill flowable composite (SDR) to traditional flowable and non-flowable composites. SDR showed significantly lower polymerization stress, as observed in the present study, but lower micromechanical properties than hybrid composites. Within the flowable composites, SDR flow achieved the lowest Vickers hardness, the highest modulus of elasticity, the highest creep and showed a significantly lower elastic deformation. The low polymerization shrinkage for SDR flow results from the addition of the “polymerization modulator”, a chemical moiety in the resin backbone that increases flexibility and thus relaxes the polymerized network without harming DC (SDR^{TM} Scientific Compendium, 2011)(DentsplyInternational).

The results of the present study were in accordance with El-Damanhoury & Platt, who evaluated the polymerization shrinkage stress kinetics of five low-shrinkage, light-cured bulk-fill resin composites (SDR, Tetric Bulk Fill, Venus Bulk-Fill, X-tra Fill Filtek Bulk-Fill). Real-time shrinkage stress of the investigated composites was measured using a tensometer, which showed that Venus Bulk Fill and SDR had significantly lower stress values during irradiation. The findings of El-Damanhoury & Platt(El-Damanhoury and Platt 2014) and the present study are in agreement with the fact that SDR and Venus Bulk Fill, despite being the materials with the lowest concentration of filler (between 38% and 44% by volume, respectively) and with a substantial volumetric shrinkage, compared to other composite flow(Michaud et al. 2014), are designed to greatly reduce shrinkage stress.

Conclusions

- All tested materials had a decrease in MH values along the lateral surface. This MH decrease became significantly different from the top surface at a depth comparable to that proposed by the manufacturers.
- Venus Bulk Fill and SDR showed inferior mechanical properties, but a significant reduced contraction stress. This allows the material to be indicated in cavities with a high C-factor.

Further *in vitro* studies are necessary to assess the behaviors of these materials over time.

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Composite	*Manufacturer*	*Type*	*Resin matrix*	*Filler*	*Filler W% ; V%*
Tetric Evoceram Bulk Fill	Ivoclar Vivadent, Schaan, Liechtenstein	Nano-hybrid	Bis-GMA UDMA	Ba-Al-Si-glass, prepolymer filler (monomer, glass filler and ytterbium fluoride). Spherical mixed oxide	79.5 (including 17% prepolymers); 60-61
SureFil SDR	Dentsply De Trey, Konstanz, Germany	flowable	Modified UDMA, TEGDMA, EBPDMA	Ba-Al-F-B-Si glass and St-Al-F-Si glass as fillers	68; 44
X-tra Base	VOCO, Cuxhaven, Germany	Hybrid, flowable	Bis-GMA UDMA		75;61
SonicFill	Kerr Corp. California USA	nanohybrid	Bis-GMA, TEGDMA, EBPDMA	SiO_2, glass, oxide	83,5; xxx
Filtek Bulk Fill	3M ESPE, St Paul, MN, USA	Nano-hybrid, Flowable	Bis-GMA, UDMA, Bis-EMA, Procrylat resins	Zirconia/silica, ytterbium trifluoride	64,5; 42,5
Venus Bulk Fill	Heraeus Kulzer, Hanau, Germany	Nano-hybrid, Flowable	multifunctional methacrylate monomers (UDMA, EBADMA)	Ba-Al-F silicate glass, YbF_3, SiO_2	65; 38

Table 1: materials composition

	Material					
	Venus Bulk-Fill	SDR	Filtek Bulk-Fill	Xtra Base	SonicFil	Tetric Bulk Fill
Top	32.8±3.4	54±6.6	97.7±4.9	92.5±4.8	92.48±4.8	101.51±4.8
1mm	32.14±6.1	46.24±6.1	95.28±3.3	91.56±3.7	93.46±4.8	100.62±6.4
2mm	29.42±6.1	44.2±6.2	91.46±4.5	89.54±4.6	92.48±5.5	99.7±6.5
3mm	28.9±5.4	36.94±6.4	84.86±7.8	82.26±2.6	88.8±7.1	94.14±6
4mm	27.4±5.1	32.98±5.5	75.06±8.5	76.74±2.6	86.18±6.4	90.18±6.7
5mm	26.06±3.5	31.72±4.7	45.94±8.5	59.4±5.4	60.14±4.7	60.92±8.3
6mm	24.42±4.9	29.54±5.1	44.28±7.5	56.3±3.7	54.6±4.2	58.64±9.1
Bottom	19.1±3.4	30.4±4.5	36.9±9	53±6.2	48.42±6.5	49.73±6.6
80%-Top	26.22±2.0	43.18±5.2	76.10±3.4	74.02±2.9	73.98±2.6	81.21±2.5

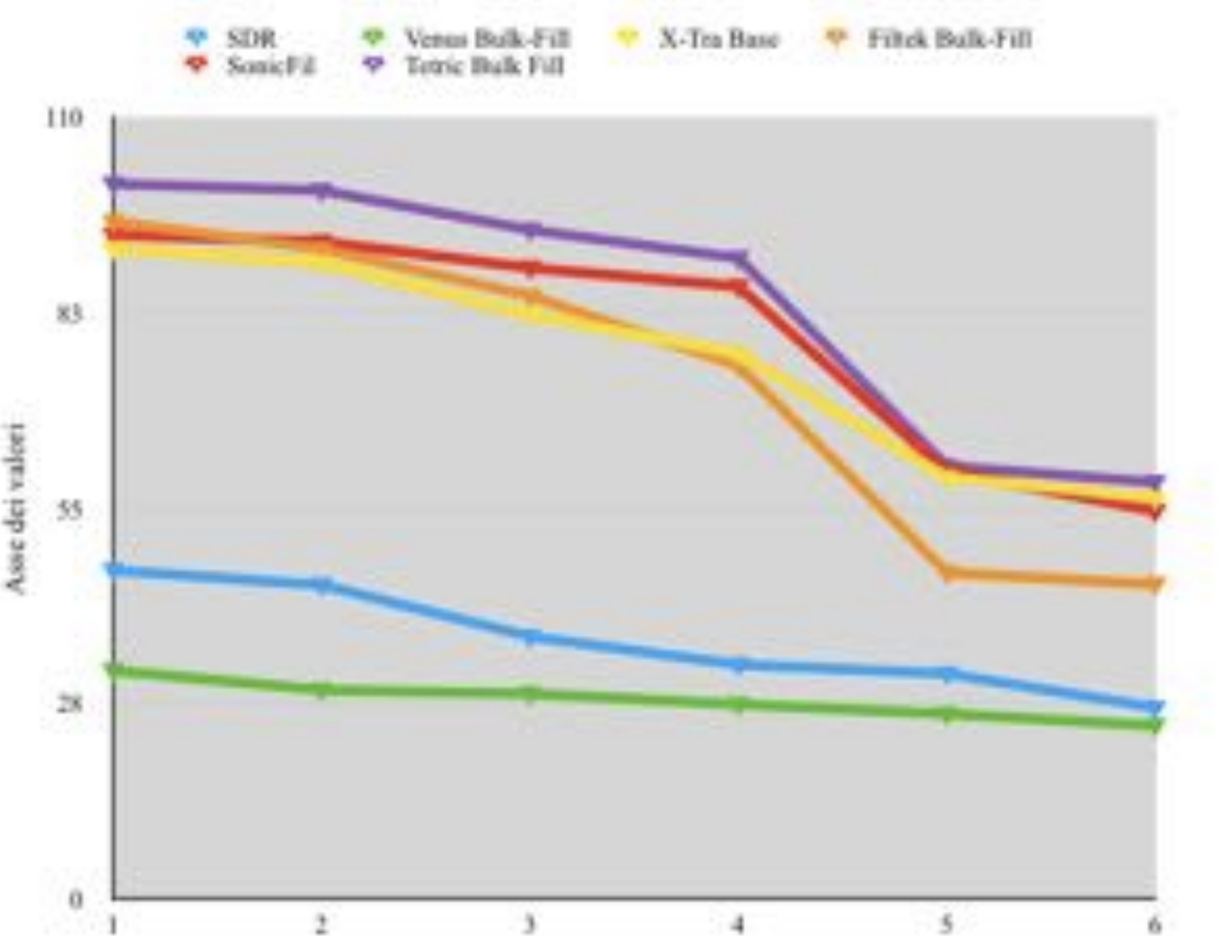
Table 2: Mean values and standard deviation of micro-hardness in the groups for bottom, lateral and top surfaces

	VENUS BULK	SDR	SONICFIL	EXTRA BASE	TETRIK BULK	FILTEK BULK
VENUS BULK	-	-	-	-	-	-
SDR	0.002	-	-	-	-	-
SONICFIL	0.0001	0.0001	-	-	-	-
EXTRA BASE	0.0001	0.0001	0.491	-	-	-
TETRIK BULK	0.0001	0.0001	0.393	0.127	-	-
FILTEK BULK	0.0001	0.0001	0.005	0.0001	0.107	-

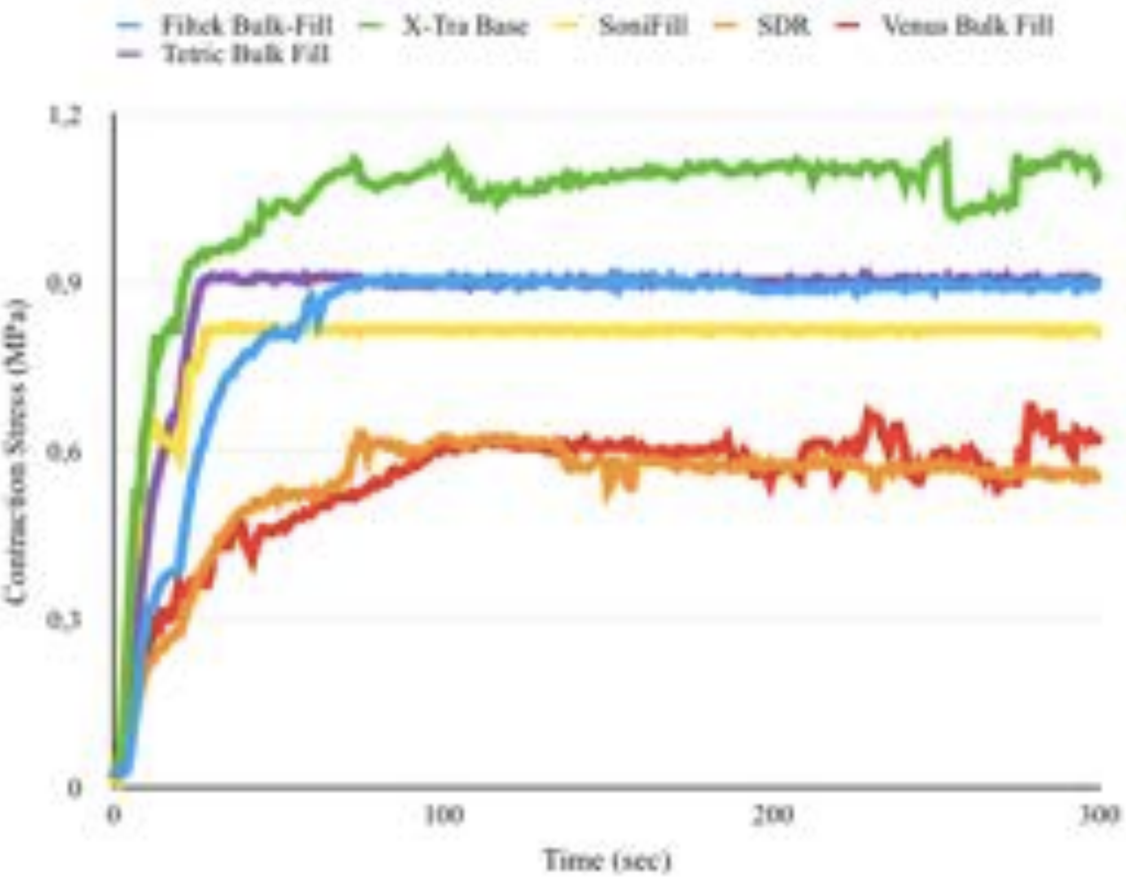
Table 3: P-values obtained comparing materials coefficients obtained by linear regression analysis of the lateral surface MH values.

Material	Contraction Stress (MPa)	t-Max (sec)
Sonicfil	0.94±0.05^{b}	30.29±2.02
Tetric Bulk	0.82±0.07^{b}	29.43±1.93
SDR	0.61±0.05^{a}	77.12±2.56
X-tra Base	0.89±0.05^{b}	75.08±2.78
Filtek Bulk	0.88±0.04^{b}	73.34±2.36
Venus Bulk	0.60±0.03^{a}	87.23±2.76

Table 4: Mean values and SD for contraction stress and time to achieve maximum stress rate (t-Max) of the tested materials.



Graph. 1: MH values of different composites registered at each mm of depth progression.



Graph. 2: Comparison of the shrinkage stress development as a function of time for the tested bulk-fill composites.

Figure 1: metallic mold

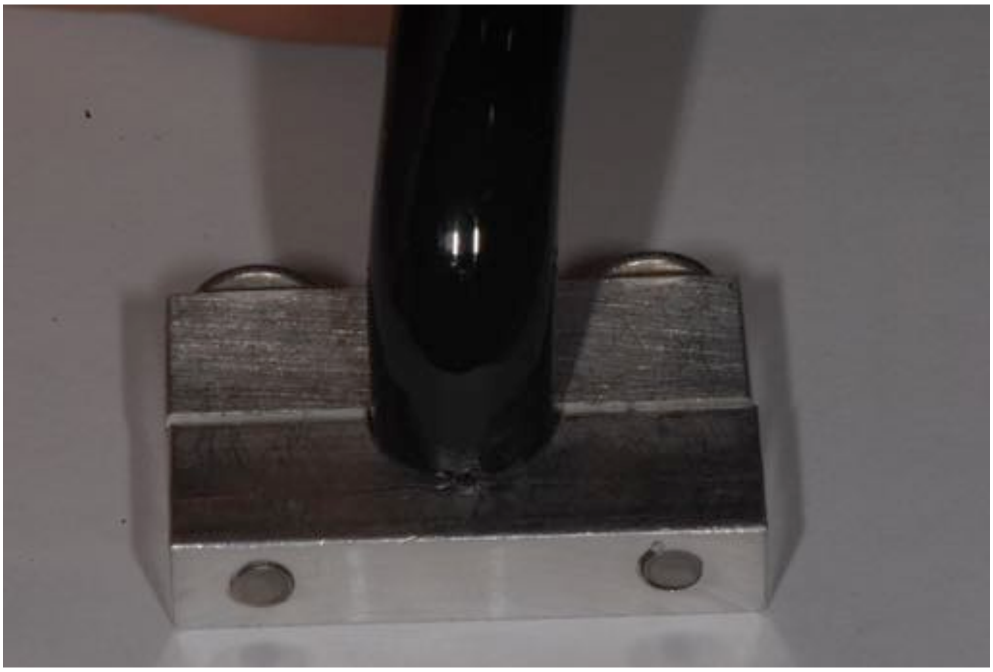


Figure 2: polymerization procedure

Figure 3: composite sample after curing

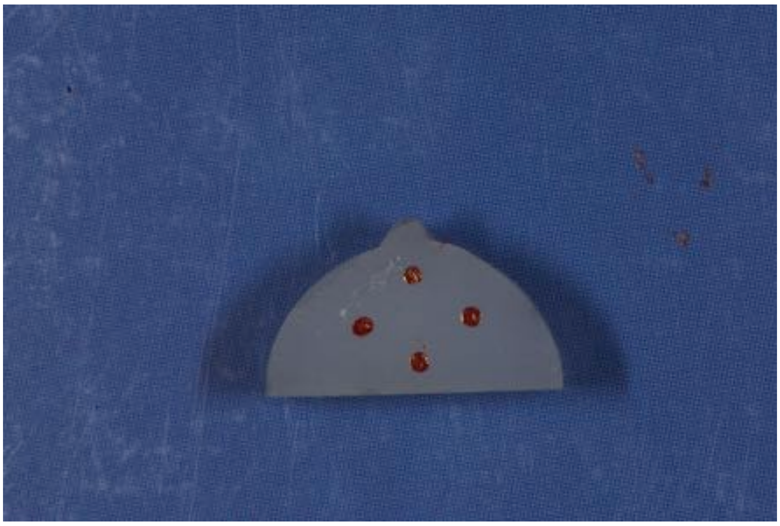


Figure 4: composite sample ready for top surface indetation

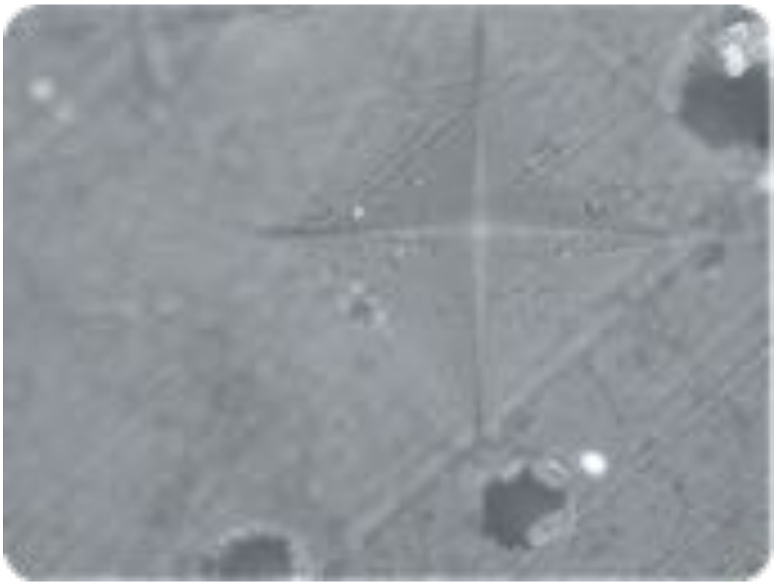


Figure 5:surface indentation

Figure 6: metal rods ready to be filled with composite material

Figure 7: metal rods filled with composite material

Study #4

Effect of lithium disilicate veneers of different thickness on the degree of conversion and micro-hardness of a light curing and a dual curing cement

Introduction

Ceramic system technology has advanced quickly in recent years, and has become a valid option in the restoration of anterior and posterior teeth that require indirect prosthetic rehabilitations. The clinical success of ceramics is mainly due to its reliable bonding to dental hard tissues provided by luting materials.(Piwowarczyk and Lauer 2003; Flury et al. 2013) Moreover, the greater attention given to preserving sound dental tissue has contributed to the success of adhesive ceramic restorations, especially on anterior teeth.

Among ceramic systems, lithium disilicate has gained popularity for anterior and posterior fixed full and partial restorations because of its physical properties.(Niu, Agustin, and Douglas 2013) In fact, while high-strength nonsilica-based ceramic substructure materials, such as alumina or zirconia, have high opacity and require translucent veneering porcelain to achieve adequate shade matches, lithium disilicate is a silica-based adhesive material that guarantees not only superior aesthetics and translucency, but also strength, wear resistance, and chemical durability.(Niu, Agustin, and Douglas 2014)

Various materials and systems to lute lithium disilicate to the tooth substrate are available to clinicians, who can adapt the material to each clinical situation to maximize the performance of indirect aesthetic restorations. An important requirement for an ideal luting agent is its ability to provide superior mechanical properties to resist functional forces over the lifetime of a restoration.(Ilie and Simon 2012) Adequate polymerization is crucial to obtain optimal physical properties and high clinical performance of resin materials. As a result of suboptimal polymerization, a low monomer-polymer conversion rate with a higher residual quantity of double bonds is obtained, causing inferior physical properties and increased water sorption and solubility.(Jung et al. 2001) Various factors may affect resin polymerization, and as a consequence, may also affect the choice of the cement, such as the optical properties, the resin cement activation mode, the light curing unit characteristics,(Pick et al. 2010) and the thickness of the material employed.(Lee et al. 2008) Lithium disilicate veneer cementation may be performed using either light-curing or dual-curing activation. Light-curing cements have a polymerization mechanism that only allows material setting in the presence of a light source that activates photo-initiators and starts the polymerization reaction.(Pick et al. 2010) A great advantage of these materials is their ease of use due to their set-on-command and unlimited working time.(Hofmann et al. 2001) However, the absence or attenuation of light irradiance caused by the thickness, shade, and low translucency of the ceramic material could reduce the quality of the polymerization reaction.(Inokoshi et al. 1993) Thus, dual-cure cements were introduced to attempt to overcome this problem. In fact, these materials combine a light-curing mechanism of polymerization with self-curing components that initiate the polymerization reaction in the absence of light.(Arrais et al. 2008; Giráldez et al. 2011) However, even if the polymerization process does not require a light source, allowing a uniform set of materials,(Hofmann et al. 2001) dual-cure materials require a setting reaction slow enough to allow sufficient working time, but quick enough to permit finishing of the restoration,(Hofmann et al. 2001) because the polymerization reaction is not controllable from the moment the base and the catalyst paste are mixed together and the polymerization starts.(Lee et al. 2008) Moreover, the deficiency of chemical-cure components can result in a higher concentration of unreacted double bonds, lower hardness, and higher solubility of cements, which can influence chemical stability in the oral environment.(Pereira et al. 2010)

To the best of our knowledge, no previous study has compared the behavior of dual-cured and light-cured cement employed under different thicknesses of lithium disilicate. The purpose of this *in vitro* study was to evaluate the degree of conversion (DC) and the micro-hardness (MH) of a dual-cure and light-cure cement under lithium disilicate discs of different thicknesses. The null hypotheses tested were that ceramic thickness does not affect (1) the DC or (2) the MH of the tested cements regardless of the cement-curing mode (light-cure vs. dual-cure).

Materials and Methods

Specimen preparation

Forty-eight Lithium Disilicate core drilled (IPS e.max CAD for CEREC and inLab LOT. R37085, Ivoclar) discs (1 cm in diameter, A2 shade LT) were equally divided into three groups (n=16) according to the thickness of the material: Group A: 0.6 mm; Group B: 1 mm; Group C: 1.5 mm. Precision of discs thickness was checked with a digital caliper and discs with a discrepancy of more than 0,1 mm were excluded. A further group without ceramic, group D, was also considered as a control group. Each group was then randomly divided into two subgroups (n=8) according to the luting cement employed. Samples of subgroup 1 were prepared with NX3 dual-curing cement (Kerr Co, USA); samples of subgroup 2 were prepared with Choice2 light-curing cement (Bisco Inc., Shaumburg, IL, USA) (Table 1).

One side of each ceramic disc was etched with 5% hydrofluoridric acid (IPS Ceramic Etching gel, Ivoclar Vivadent) for 20 s, then rinsed with tap water and immersed in alcohol in an ultrasonic bath for 5 min. Silane (Silane Primer, Kerr Co, USA) was applied to the etched surface, air-dried for 15 sec, and covered with a coat of bonding resin after 30 s (Optibond FL adhesive system, Kerr Co, USA) using a microbrush and thinned with air.

As regard group D, no adhesive procedures were performed, and cement was considered without ceramic apposition.

Degree of conversion measurement.

A ca.170 μm(Öztürk et al. 2012) thick plastic guide with a center hole 1 mm in diameter was placed on the diamond support of an ATR FT-IR (Attenuated Total Reflectance Fourier Transformed Infra Red) spectrophotometer (Thermo Scientific Nicolet IS10) to standardize a layer of luting cement between the sample surface and the FT-IR light beam. The luting cement was applied on the bonded surface of each specimen placed on the FT-IR light beam. The excess cement was eliminated, thereby creating a pressure that simulated the clinical cementation of indirect veneers until the disc contacted the plastic guide. For group D, cement was placed on the FT-IR diamond and thickened with a transparent Mylar strip. Polymerization of the cement was performed using a high power poly wave LED lamp (Valo-Ultradent South Jordan UT USA) for 60 s at 1400 mW/cm^2, with the curing tip contacting the center of the discs and the light beam opposite to the cement layer.

The surface analysis was performed in ATR mode, in which the IR beam penetrated 1 μm into the material. The FT-IR spectra of the curing process were recorded every 2 s with a range between 4000-525 cm^{-1} and a resolution of 6 cm^{-1}. The spectra recorded immediately before activation of the poly wave LED lamp and 10 min after light exposure were fitted and used to evaluate the degree of conversion (DC) of the two tested materials. To determin the percentage of the remaining unreacted double bonds, the DC was assessed as the variation of the absorbance intensities peak height ratio of the methacrylate carbon double bond (peak 1634 cm^{-1}) related to an internal standard of aromatic carbon–carbon double bonds (peak 1608 cm^{-1}) before and after curing of the specimen, according to the following equation(Frauscher and Ilie 2013; Flury et al. 2013):

$$DC\% = \left\{ 1- \frac{(C{=}C\ \text{aliphatic}/C{=}C\ \text{aromatic})_{\text{Polymer}}}{(C{=}C\ \text{aliphatic}/C{=}C\ \text{aromatic})_{\text{Monomer}}} * 100 \right\}$$

Microhardness measurement

Twenty-four hours after DC evaluation, microhardness (MH) was measured using a Leica VMHT microhardness tester (Leica Microsystems S.P.A., Milano, Italy) equipped with a Vickers indenter, at exactly the same location at which DC was analyzed by the FT-IR light beam. A pyramidal diamond indentation was obtained with a load of 100 g for 15 s. Three indentations were obtained for each specimen, and the mean value was considered for the statistical analyses. No indentations were for group D, without ceramic apposition.

Statistical Analysis

To evaluate the effect of lithium disilicate thickness (0.6–1.0 mm and 1.5 mm), luting materials, and their effects on DC a two-way ANOVA was performed. To consider the effect of thickness on Vickers MH one-way ANOVA test and Bonferroni *post-hoc* were performed. The significance level was set at 95% ($p<0.05$). All statistical analyses were performed using the Stata software package (StataCorp, 4905 Lakeway Drive, College Station, Texas 77845 USA).

Results

The mean and standard deviation values for DC obtained from the different sub-groups are expressed in Table 2, while MH mean values and standard deviations are shown in Table 3.

Considering DC%, two-way ANOVA showed that only the cement factor significantly influenced the results ($p<0,05$), whereas the thickness of the ceramic specimens and the interaction between the two factors had no significant effect. Light- curing cement performed significantly better than dual cement ($p<0,05$). Moreover, the presence of a lithium disilicate disc with a thickness between 0,6 and 1,5 mm did not reduce DC% both for the light-curing and the dual-curing cement.

For Vickers MH ANOVA showed that within the same cement thickness influenced hardness values only between 0,6 mm and 1,5 mm of the light-cured cement.

Discussion

The longevity of indirect adhesive restorations depends mainly on the quality of the dental-cement restoration interface.(Inokoshi et al. 1993; Sjögren et al. 1995) To reach optimal physical and mechanical properties of composite resin cements under ceramic restorations, the conversion rate should be as high as possible.(Jung et al. 2001; Bayne, Heymann, and Swift 1994) The method used in this study to assess the DC was the Fourier Transformed Infrared Spectroscopy (FTIR), a well-established technique that allows direct quantification of unreacted C=C in a resin matrix.(Shadman et al. 2012; Imazato et al. 2001; Stansbury and Dickens 2001)

The present investigation evaluated the effect of lithium disilicate thickness on the degree of conversion of light-cure and dual-cure cement. Several authors have affirmed that the thickness and shade of the restorative material above the cement may affect light transmission and consequently, the DC.(Peixoto et al. 2007) To conduct this study, shade and translucency of specimens were standardized, and the curing process was performed using a continuous light application with a poly wave LED lamp during the entire irradiation time at an intensity of 1400 mW/cm.^{2}

The results obtained in this *in vitro* study support the first null hypothesis, because ceramic thickness did not affect DC values within the same group. The only factor that influenced the quality of polymerization was the material used with the light-cure cement, which yielded a significantly higher DC than the dual-cure cement.

Thickness of the lithium disilicate of 0.6 mm and 1.5 mm had no effect on the DC% of the two cements tested. Previous studies reported controversial findings on this topic. Zhang et al.[1] concluded that ceramic thickness greatly influences polymerization quality, while other authors found that only a thickness of more than 2 mm drastically reduces the degree of conversion either of dual-curing or light-curing resins.(Lee et al. 2008; Acquaviva et al. 2009; Rasetto, Driscoll, and Fraunhofer 2001) Thus, to reach proper polymerization, curing time should be prolonged beyond the manufacturer's recommendation(Lee et al. 2008; Acquaviva et al. 2009; Rasetto, Driscoll, and Fraunhofer 2001) when a 2 mm thick indirect restoration is cemented. The lithium disilicate thicknesses tested in the present study intended to simulate a ceramic veneer with a thickness between 0.6 and 1.5 mm; such a thick layer of ceramic did not significantly attenuate the curing light.(Hofmann et al. 2001)

Our findings also support the hypothesis that immediate photo-activation of the dual-cure resin based material may compromise the final degree of conversion, as recently reported in a study conducted by Pereira et al.(Pereira et al. 2010) The authors also reported that dual-curing resin cements have different polymerization kinetics, and that the extent of polymerization changes considerably among different cements. In particular, the moment of light activation determines the formation of the polymer structure, and consequently, determines the structural integrity of the materials.(Pereira et al. 2010) These results agree with those of a study conducted by Faria-e-Silva et al.,[21] who also hypothesized that light activation may negatively affect the self-curing mechanism. The rationale is that the rapid formation of a cross-linked polymer after light exposure would lead to entrapment of the reactive species, including activators and initiators needed for the self-cure reaction.(Faria-e-Silva et al. 2011)

Conversely, the findings of the present study contrasted with those of a previous report that showed that only the thickness of the indirect restoration affected the DC of the luting materials (two dual-cure cements and a conventional microhybrid resin composite).(Acquaviva et al. 2009) Such controversial findings compared to the present paper could be attributed to the different light-curing materials tested. Moreover, the different thickness and nature of the material employed as indirect restoration could have strongly influenced the DC,(Warren 1990) mostly for light-curing resin composites. In addition, Acquaviva et al.[19] evaluated DC through Raman Spectroscopy 24 h after light curing activation, whereas in the present study, the DC was assessed 10 min after the start of light source irradiance. In addition, in the present study, curing started when cementation procedures were completed and the cement excesses were removed, as takes place *in vivo* during ceramic veneers luting procedures.(Faria-e-Silva et al. 2011)

Deficient polymerization of the resin cement negatively affects its physical and mechanical properties.(Giráldez et al. 2011) However, longevity of a resin cement is influenced, not only by the polymerization degree, but also by the chemical composition of the material itself.(Porto et al. 2013)

Surface microhardness of a restorative resin is one of the most important parameters for assessing physical properties of dental materials, and is defined as the resistance of a material to indentation or penetration. In the literature, microhardness is commonly used as a simple and reliable method for indirectly estimating the degree of conversion of resin-based cements.(Hofmann et al. 2001; Cekic-Nagas et al. 2013; Cekic-Nagas and Ergun 2011) Although it is generally thought that hardness is directly related to DC percentages,(Hofmann et al. 2001) the findings of the current study confirmed that other variables also influence the surface hardness of a material.(Hofmann et al. 2001) Our statistical analysis revealed significant influence on the results, either by the material or by the interaction between the material and thickness variables. These results are in accordance with those of a study by Tantbirojn et al.[26] who stated that microhardness data are comparable only within the same resin system, since they are not linearly correlated with the degree of cure if compared across different materials.

However, within the same cement, the evaluation of thickness influence on MH was taken into consideration and lead to partially refuse the null hypothesis since only light-cure cement MH is influenced by lithium disilicate thickness. The generally significantly better Vickers hardness values of the light-cure cement regard the dual-cement could be explained by an intrinsic characteristic of the material such as its filler load, filler type, resin matrix, or formulation.(Cekic-Nagas et al. 2013; Pilo and Cardash 1992) The filler particles incorporated into the matrix, influence the mechanical properties more than the matrix itself. Therefore, up to a certain limit, a higher filler load may be expected to improve the mechanical properties.(Hofmann et al. 2001) These results are partially in contrast with those of an *in vitro* study conducted by Hofmann et al.(Hofmann et al. 2001) in which dual-cure materials showed better mechanical properties than photo-activated ones, particularly when irradiated through 2.5 mm of leucite-reinforced glass-ceramic. Several studies have shown that the critical thickness of ceramic for a proper curing process is 2 mm or more,(Lee et al. 2008; Acquaviva et al. 2009; Rasetto, Driscoll, and Fraunhofer 2001) whereas the present study tested lower thicknesses. Moreover, Hoffmann et al.[7] tested dual-curing cements in both a dual-activation and light-activation mode without mixing the base and the catalyst paste, thus altering the curing process and the intrinsic nature of the dual curing material. In the present study, light-curing cement was compared to a dual-curing one. On the other hand, a study published in 1995 by Hasegawa et al. studied the setting of three dual-cured cements under resin composite inlays, and reported that chemical curing did not completely harden the cements when light was attenuated by tooth and restoration material,(el-Badrawy and el-Mowafy 1995) which could account for the better performance of the light-curing cement. Furthermore, the composition of the two luting resins tested in the current study suggested that the dual-curing cement (NX3, Kerr Co, USA) has a lower filler content (about 60%) than the light-curing one (about 78%) (Choice2, Bisco, Inc), which could have strongly influenced the material's hardness. Moreover, the light activation of a material with a dual mechanism of conversion may have influenced the polymeric network cross-link density and, consequently, the material mechanical properties.(Pereira et al. 2010)

Conclusion

Within the limitations of this *in vitro* study, both the light cure and the dual cure cement used to lute lithium disilicate veneers with a thickness between 0.6 and 1.5 mm yielded a sufficient polymerization level. Further, the light-cure and the dual cure resins reach a comparable DC%.

Higher MH values obtained with the light-curing resin and the influence of disilicate thickness only in this group of samples may have been the results of a different structure and composition of the two tested materials.

Further studies are needed to validate these results, especially considering the great variability among cements' chemical formulations.

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	Composition
NX3 (Kerr Co, USA)	• BisGMA, UDMA, EBPADMA, and TEGDMA • Proprietary monomers (GPDM) • Proprietary redox initiator • Camphorquinone (CQ)-based photo-initiator • Stabilizers including UV stabilizer • Bariumaluminosilicate glass filler • Nano-sized ytterbium fluoride filler • Colloidal silica Filler by weight 67.5 % (Dual Cure version) Filler by volume 43.3 % (Dual Cure version)
Choice2 (Bisco Inc., Shaumburg, IL, USA)	• Strontium Glass – concentration range <75% • Amorphous Silica – concentration range <25% • BisGMA– concentration range <10%

Table 1: Cement Composition

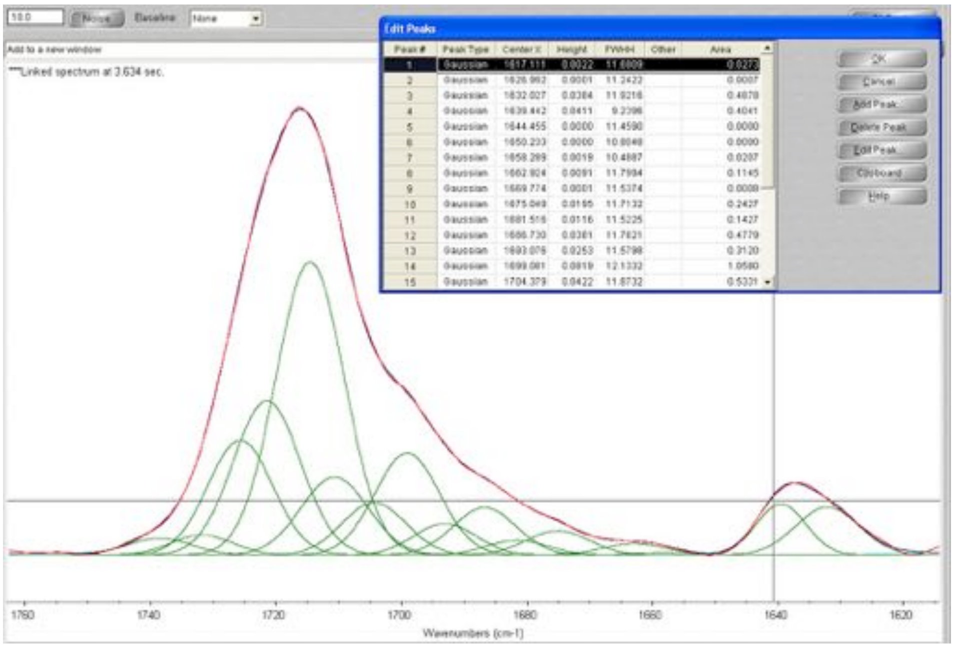
DC%	Dual Cement	Light-Curing Cement
0.6 mm	54.6 ±2.1^{aA}	60.9 ±5.3 ^{aA}
1.0 mm	42.7 ±12.5 ^{aA}	58.4 ±4.4 ^{aA}
1.5 mm	47.4 ±16.2 ^{aA}	53.4 ±7.2 ^{aA}
Control group	53.9 ±10.3 ^{aA}	56,26 ±2.31 ^{aA}

Table 2: Degree of Conversion and standard deviation of light curing and dual curing cements. Different superscript lower-case letters (in rows) indicate statistical differences between cements ($p<0.05$). Different superscript upper-case letters (in columns) indicate statistical differences between different thicknesses within each material ($p<0.05$).

MH	Dual Cement	Light-Curing Cement
0.6 mm	35.8 ±4.6^{a}	61.1 ±14.3^{a}
1.0 mm	31.3 ±2.8^{a}	57.7 ±4.9 ^{ab}
1.5 mm	36.3 ±10.5^{a}	52.2 ±6.6^{b}

Table 3: Microhardness of and standard deviation light curing and dual curing cements.

Different superscript letters indicate statistical differences between different thicknesses within each material (in columns) ($p<0.05$)



Peak #	Peak Type	Center X	Height	FWHH	Other	Area
1	Gaussian	1617.111	0.0022	11.6809		0.0273
2	Gaussian	1626.962	0.0001	11.2422		0.0007
3	Gaussian	1632.027	0.0384	11.9216		0.4878
4	Gaussian	1639.442	0.0411	9.2396		0.4041
5	Gaussian	1644.455	0.0000	11.4590		0.0000
6	Gaussian	1650.233	0.0000	10.8048		0.0000
7	Gaussian	1658.289	0.0019	10.4887		0.0207
8	Gaussian	1662.924	0.0091	11.7984		0.1145
9	Gaussian	1669.774	0.0001	11.5374		0.0008
10	Gaussian	1675.049	0.0195	11.7132		0.2427
11	Gaussian	1681.516	0.0116	11.5225		0.1427
12	Gaussian	1686.730	0.0381	11.7821		0.4779
13	Gaussian	1693.076	0.0253	11.5798		0.3120
14	Gaussian	1699.081	0.0819	12.1332		1.0580
15	Gaussian	1704.379	0.0422	11.8732		0.5331

Figure 1: Polymerization spectra
Fitting of the polymerization reaction spectra in a range between carbon–carbon double bonds (peak 1637 cm^{-1}) and aromatic carbon–carbon double bonds (peak 1608 cm^{-1}).

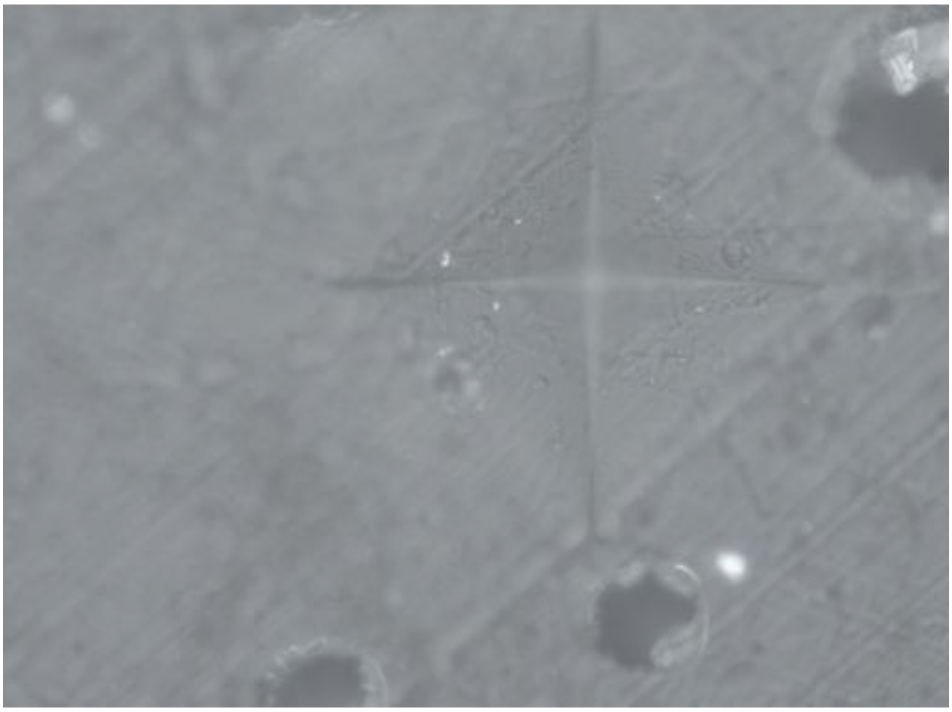


Figure 2: Microhardness test
Indentation of the bottom surface of cement of a ceramic sample