Self-adhesive, bulk-fill bioactive materials as an alternative to silver amalgam in restorative dentistry

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ABSTRACT
Introduction: The disadvantages of silver amalgam fillings and the growing social requirements for the widespread availability of not only durable but also aesthetic dental fillings have contributed to the search for another basic restorative material that retains the advantages of silver amalgam and eliminates its disadvantages.
The aim of the study is to present, on the basis of a literature review, the basic structure, properties and indications for the use of dental materials used in direct restorative dentistry, as well as new self-adhesive hybrid materials with simplified application technique. These are: Activa BioActive Restorative (Pulpdent; AB), Cention N (Ivoclar-Vivadent; CN), and SureFil One (Dentsply Sirona; SO). Basic information on the chemical structure and basic indications for the use of these materials were presented.
Conclusions: The presented new materials are evolutionary products based on conventional glass ionomer cements (GIC),

resin-modified glass ionomer cement (RM-GIC) and composite materials. The chemical structure and reactions that occur during the binding of AB and SO materials are similar to some RM-GIC, while in the case of CN material similar to fluorine-releasing resin-based materials. Previous studies do not confirm that the new materials have mechanical properties necessary to meet the requirements for posterior restorations. Considering limited clinical trials, care should be taken in their systematic application in all patients. There are no unequivocal studies confirming the bioactivity of the materials. Further *in vitro* studies as well as clinical observations to assess their chemical properties and the ability to induce remineralization and bioactivity are needed. The materials show self-adhesion but when included in the protocol of a bonding system, their adhesion to hard tissues is better.
Keywords: GIC; HV-GIC; RM-GIC; compomer; giomer; Activa BioActive Restorative; SurFil One; Cention N; bioactive materials.

INTRODUCTION

The use of silver amalgam as a filling material has a long history. The first records of its use come from a medical text of the Tang Dynasty written by Su Gong in 659 [1]. It appeared in Germany in 1528. In 1833, the English Edward Crawcour and his nephew Moses Crawcour brought amalgam to the United States. In 1844, it was reported that 50% of all restorations in Upstate New York were silver amalgam fillings [2]. In the 19th century, amalgam became the material of choice for dental fillings [3] and maintained its position as the 'basic' restorative material for the direct restoration of cavities in posterior teeth [4] until almost the 21st century. Many decades of using silver amalgam have confirmed its beneficial properties, i.e. durability, cariostatic properties, low cost (the material itself and the equipment necessary for its proper application), simple application without bonding systems, and self-curing. In clinical practice, silver amalgam is a material that is relatively insensitive to the application technique, and its long-term clinical durability is exceptional. Anusavice reports that about 90% of amalgam fillings are still correct after 10 years. Silver amalgam also has disadvantages, such as: the content of toxic metals (mercury), unfavourable colour (important from the patient's point of view), thermal conductivity, discoloration of tooth tissues, lack of biocompatibility and the need for retention

preparation of cavities [5]. The discussion on the safety of mercury use and any relationship to various diseases is one of the oldest controversies in medicine. However, an overwhelming body of scientific evidence shows that amalgam is a safe agent for restoring dental cavities, and its safety in patients has been proven in countless studies. The current concern of European and international bodies is largely about the toxicological burden of mercury in the environment and less about patient safety. The unfavourable features of silver amalgam meant that, in accordance with Regulation (EU) 2017/852 of the European Parliament and of the European Council, the Member States of the European Union were asked to prepare, by 1st July 2019, a national plan to discontinue the use of silver amalgam as a dental restorative material. The European Commission is to present an evaluation on the possibility of a gradual end to the use of silver amalgam in dentistry in the long term by 2030. In July 2018, the EU banned the use of silver amalgam for the dental treatment of children under 15, and pregnant and breastfeeding women [6]. The disadvantages of silver amalgam fillings and the growing social requirements for the widespread availability of not only durable but also aesthetic dental fillings have contributed to the search for another 'basic' restorative material that retains the advantages of silver amalgam and eliminates its disadvantages. Such material

should be characterized by durability similar to amalgam, good aesthetics, low cost of the material itself, and low labor and time consumption (i.e. it should be easy to handle without complicated equipment). Additionally, such material must be self-adhesive, self-curing, setting as bulk-fill, releasing fluorine ions, and bioactive [7].

The aim of this work is to present the basic structure, properties, and indications for the use of dental materials currently used in direct restorative dentistry and new self-adhesive hybrid materials with simplified application techniques, in terms of their suitability as general purpose restorative material.

Technological progress in the field of dental materials science since the mid-20th century has resulted in the emergence of 2 new groups of materials: glass ionomer cements with later modifications (high-viscosity glass ionomer cements – HV-GIC and RM-GIC) and resin-based composites with hybrid modifications (compomers and giomers) which, it was hoped, would become the new basic materials for restorative dentistry.

CONVENTIONAL GLASS IONOMER CEMENTS

Conventional glass ionomer cements (GIC) were developed on the basis of silicon and polycarboxylic cements in the late 1960s. They were first described by Alan Wilson and Brian Kent in the early 1970s and marketed shortly thereafter. Self-adhesive, self-curing, water-based, and with cariostatic properties, these materials constitute a very extensive group of materials with a diverse composition but with common characteristics. The matrix of the material is a polymer or copolymer of carboxylic acids, while the liquid part of the material, apart from water, consists mainly of polyacrylic acid [8]. Other polyacids, such as tartaric, itaconic, maleic or tricarbalylic acid, can also be added or even replaced with polyacrylic acid to modulate the reaction or rheological properties of the material [9, 10]. The inorganic filler is a fluoro-alumino-silicate (FAS) filler that plays a major role in both the acid-base binding reaction of the powder-fluid mixture and the final mechanical properties of the material. To maintain their reactivity and considering the absence of resin in the GIC formulation, FAS fillers used in conventional GICs on the market are non-silanized. In addition to the basic FAS reactive fillers, the powder may contain other elements, such as strontium, phosphate, zinc, calcium or sodium, depending on the material manufacturer [11, 12]. Conventional glass ionomer cements is characterized by the highest release of fluorine ions among the dental materials. They are also able to replenish ions, especially fluoride, from the oral cavity. Many *in vitro* studies have indicated the induction of tissue remineralization under a glass ionomer cement restoration. Therefore, these materials are considered truly bioactive [9, 10, 11, 12, 13]. Glass ionomer cements, due to the setting only within the acid-base reaction, are considered to be the only materials characterized by a true bulk-fill setting reaction. Despite these advantages, fillings made of conventional GICs are characterized by low flexural properties [14] and a high tendency to wear down [15]. Therefore they are not currently used in restorative dentistry.

HIGH-VISCOSITY GLASS IONOMER CEMENTS

To improve conventional GICs properties the high-viscosity glass ionomer cements (HV-GICs) were developed. The stages as well as the setting characteristics of these materials are the same as those of conventional GICs, therefore they are considered as conventional GICs by many authors [16, 17, 18]. Like GICs, also HV-GICs are self-adhesive, self-curing, water-based materials with cariostatic properties. In order to increase flexural strength of material, reduce the risk of cohesive cracks, and improve wear resistance compared to classic GICs, the powder/liquid ratio was increased in HV-GICs [17, 18], also higher molecular weight polyacrylic acid was used [19]. In addition to the classic FAS fillers, small, surface-modified FAS fillers were also introduced into the powder in order to increase their reactivity. Thanks to chemical innovations, the initial setting time has been shortened to reduce the sensitivity of the material to water [18, 20]. Although HV-GICs release less fluoride than conventional GICs, the mechanism of fluoride release and recharging is similar to conventional GICs. This ion release has been shown to induce remineralisation of the underlying hard dental tissues in a number of *in vitro* studies [13, 21, 22]. Therefore, HV-GICs are considered to be bioactive restorative materials characterized by a true 'bulk-fill' reaction. High-viscosity glass ionomer cements have gained broader indications for use over conventional GICs. High-viscosity glass ionomer cements are a reliable alternative of amalgam in pediatric dentistry due to the short lifetime of deciduous teeth [23]. However, not polymerizable, the polyacid matrix component leads to a weak cohesive network, low strength, and low wear resistance, which does not allow to make posterior filling in permanent dentition. They can be applied as final fillings in adults – in some cervical cavities and in small class I and II cavities of very limited extent. They are still recommended as intermediate base in the sandwich technique.

RESIN-MODIFIED GLASS IONOMER CEMENTS

In order to shorten the setting time, improve mechanical properties and reduce the sensitivity of the material to early fluid contamination, compared to GICs, the modification of glass ionomer cements was developed by adding composite resins. The new chimeric material was named resin-modified glass ionomer cement (RM-GIC). Monomers – usually 2-hydroxyethyl methacrylate (HEMA) – and photoinitiators such as camphorquinone were added to the fluid. Classic FAS fillers are subjected to silanization, which theoretically allows the binding of these particles with the resin matrix, further increasing the crosslinking of the resin, improving the final mechanical properties of the material and modulating the solubilization of reactive fillers [24, 25, 26, 27]. However, the stability of silanization of FAS fillers and its effect on ion release in parallel with the acid-base reaction is unclear and has not been investigated [4]. During RM-GIC setting, the same acid-base reaction takes place as in classic GIC, combined with the radical polymerization reaction of

methacrylate monomers [4, 28]. Despite the coexistence of both types of reactions, there is also competition between them. As soon as the resin polymerization begins, the acid-base reaction is reduced [29]. The polymerization reaction is also influenced by the acid-base reaction, and unreacted HEMA monomers cause higher water absorption than in HV-GIC due to their hydrophilicity [30]. This effect increases the sensitivity of the material to hydrolysis [31]. The ion release and RM-GIC charging mechanisms are similar to those described for conventional GICs. However, RM-GIC seems to release less fluoride than conventional GIC and HV-GIC [32, 33], as the polymerized resin matrix limits ion exchange with the external environment. However, this ion release has been shown to induce remineralization of the underlying hard dental tissues in a number of *in vitro* studies [34, 35]. Therefore, the first RM-GICs can be considered bioactive restorative materials. The mechanical properties of RM-GIC, especially flexural properties, are similar to conventional GIC and HV-GIC [36]. However, their wear resistance in areas of mechanical stress remains low [37]. Despite many years of availability on the market, RM-GICs have not achieved the expected clinical success. The indications for their use are subject to constant restrictions. They are still recommended as an intermediate base in the sandwich technique [38], for the reconstruction of some cavities in the cervical region [39], and for filling cavities in deciduous teeth under certain conditions or when the operator wants to control the hardening time of the filling, which is not possible with conventional GICs and HV-GICs.

RESIN BASED COMPOSITES

Resin based composites (RBCs) turned out to be a real alternative to silver amalgam fillings, in terms of mechanical resistance and aesthetics. The development by Raphael Bowen in 1956 of the monomer Bis-GMA from bisphenol A and diglycidyl methacrylate and the related introduction in 1964 of the 1st commercial resin-based material (Addent (3M)) deserved the name – the revolution in restorative dentistry [40]. The beneficial properties of composite materials induced their dynamic development. The progress in the production of composites was manifested both in the improvement of structure of inorganic filler molecules, the organic matrix as well as connecting agents and polymerization initiators [41, 42]. Modern composite materials with new bonding materials have displaced silver amalgam, providing an excellent alternative to restoring missing tooth tissue in the posterior region and advancing in aesthetics and minimally invasive dentistry. Resin based composites, despite their excellent aesthetics, high resistance to abrasion and crushing, enabling the execution of posterior restorations with long-term durability, also have features which prevent their use as new basic materials. These are time-consuming and cost-consuming materials, particularly sensitive to technique of application (including moisture), requiring the use of intermediate systems of bonding with tooth tissues [41]. The introduction of the Bulk-Fill High Viscosity RBCs in the last few years, despite the shortening of treatment time, did not eliminate the necessity to use bonding systems and considerable

sensitivity to application techniques [43]. Resin based composites are also not materials that release fluorine ions in amounts that are sufficient for remineralization, and the necessity to use bonding systems prevents their bioactivity towards the tissues under the filling [41, 42].

In order to enrich the properties of resin composite materials with the desired properties of glass ionomer cements, e.g. the ability to release fluorine ions supporting remineralization, hybrid materials known as compomers and giomers have been developed.

COMPOMERS

The term 'compomer' is the combination of 'composite' and 'ionomer'. Apart from this general term, these materials are also called polyacid modified composite resins [44, 45]. Compomers differ from composite materials both in terms of the organic matrix and the inorganic fillers. As in RBCs, in compomers, the main components of the matrix are dimethacrylates (Bis-GMA, UDMA, TEGDMA) and photoinitiators (camphorquinone). The differences are the addition of a small amount of carboxylic acid (-COOH) functional monomers. Hence the name of the compomers – polyacid modified composite resins [45]. As the material does not contain traces of water, the acid groups are dehydrated and, after polymerization, they integrate into the resin matrix. Despite the addition of dehydrated acid, the final material is hydrophobic. The modification of the inorganic part, in relation to the composite materials, also consists of silanized reactive FAS fillers which are able to bind with the resin matrix, improving the mechanical properties and releasing fluorine ions under certain conditions. The setting reaction of these materials is a radical photopolymerization reaction, as in a resin composite material [46]. A resin network is formed and covalent bonds are formed with silanized FAS fillers and silanized non-reactive fillers. The mechanical properties of the compomers, immediately after inserting the material, are similar to those of RBCs [46, 47, 48]. However, as a result of hydrolysis and solubilization of fillers, they deteriorate over time [47]. Since the compomers do not contain water, the release of ions occurs solely through water absorption upon contact with the oral environment and occurs at the periphery of the material. The ion release is very low, much lower than that of the GIC and RMGIC. It does not induce remineralisation of the tissues under the filling [49]. The material requires the use of bonding systems and therefore cannot be considered a bioactive material. Compomers must be placed in 2 mm layers. Although compomers have a lower long-term success rate than composite materials, they can be used as final fillings in the cervical and anterior region, as a base for posterior composite fillings, and as fillings in deciduous teeth [45, 50, 51].

GIOMERS

The term 'giomer' is a combination of glass ionomer cement and resin composite. The organic matrix in the giomer is similar

to that in RBCs, with a base around Bis-GMA and other monomers (UDMA, TEGDMA, HEMA) and photoiniciator. No acid functional groups or dehydrated acid groups are included in the composition. The inorganic part consist of non-reactive silanized glass fillers of the resin composite material and preactivated FAS reactive fillers (i.e. SiO_2 gel-coated), similar to those contained in HV-GIC [52]. The FAS fillers are pre-etched with polyacrylic acid to coat them with silica gel, dehydrated by freeze-drying and functionalized by silanization, which allows them to be copolymerized with resin monomers and makes them suitable for releasing ions (fluorine, calcium, and aluminum) in contact with water absorbed by the material [52, 53]. The fillers obtained at the end of such treatment are called pre-reactive glass monomer particles. The release of fluorine ions is very low, comparable to the compomers and much lower than in the case of GIC and RM GIC, without the release peak typical for these materials. The giomers are only slightly rechargeable with fluorine ions. They require the use of bonding systems. They are not bioactive materials. Giomers, as compomers, have a lower long-term success rate than composite materials. They can be used as cervical final fillings, small posterior fillings, and as fillings in deciduous teeth. Their aesthetics as anterior restorations are questioned by some authors [54].

The review of the properties of GICs and their hybrids as well as RBCs and their hybrids presented above shows that none of these materials exhibits all the features desired for an ideal basic restorative material: low cost, fluoride release, bioactivity, self-adhesion, easy and quick to handle, durable at the level of amalgam, and high aesthetic value (Tab. 1). In search of such material, new products were presented by manufacturers, which were a continuation of previous experiences of associating the beneficial properties of glass ionomer cements and resin-based composites. In recent years, 3 hybrid materials have been introduced which can become new basic materials in economic restorative dentistry. These are Activa BioActive Restorative (Pulpdent; AB), Cention N (Ivoclar-Vivadent; CN) and SureFil One (Dentsply Sirona; SO). General information on the chemical structure and indications for the use of these materials are presented in Table 2.

ACTIVA BIOACTIVE RESTORATIVE (PULPDENT, WATERTOWN, MA, USA)

The group of materials with the common name Activia Bio-Active includes 4 materials with different applications: BioActive Base/Liner, BioActive Restorative, BioActive Cement and BioActive Kids. Activia BioActive Restorative was introduced in 2013. The material was defined by the manufacturer as a hydrophilic, bioactive composite [55]. However, its structure and the double bond reaction show similarities to subsequent RM-GICs [4]. The material differs significantly from the 1st generation RM-GIC due to its fortified formula. It is distinguished by the use of dimethacrylate phosphate monomer, which, after ionization, is theoretically capable of cross-linking the resin and acid networks through aluminum cations.

TABLE 1. Summary of some basic properties of currently used dental filling materials

Restorative material	Mechanical strength enabling reconstruction in the posterior part of the dentition	Estetics	Fluorine ion release	Self-adhesive/ undemanding bonding systems	Self-curing	Bioactive	Time and cost consuming	Bulk-fill setting	Sensitive to technique of application
Silver amalgam	+	–	–	+	+	-	–	+	–
Glass ionomer cements	–	–	+	+	+	+	–	+	–
High-viscosity glass ionomer cements	–	–	+	+	+	+	–	+	–
Resin-modified glass ionomer cement	–	+/–	+/–	–	–	+	+/–	–	–
Resin based composites	+	+	–	–	–	-	+	–	+
Compomer	–	+	+/–	–	–	-	+	–	+
Giomer	–	+	+/–	–	–	-	+	–	+

TABLE 2. Composition of three new hybrid materials

Name	Composition		Available colors (Vita)	Indications: cavity class according to Black's classifications	Packaged as
	powder	liquid			
Activa BioActive Restorative	silanated bioactive glass and calcium, silanated silica, and sodium fluoride	diurethane modified by the insertion of a hydrogenated polybutadiene and other methacrylate monomers, modified polyacrylic acid, and water	A1; A2; A3; A3,5	I, II, III, IV,V	automixing syringe
Cention N	barium aluminum silicate glass, ytterbium trifluoride, isofiller, calcium barium aluminum fluorosilicate glass, and calcium fluorosilicate glass	urethane dimethacrylate, tricyclodecane dimethanol dimethacrylate, tetramethyl-xylylen diurethane dimethacrylate, polyethylene glycol 400 dimethacrylate, Ivocerin, and hydroxyperoxide	A2	I, II, V	powder and liquid for self-mixing
SureFil One	silanated aluminum-phosphorus-strontium-sodium-fluoro-silicate glass, dispersed silicon dioxide, ytterbium fluoride, and pigments	acrylic acid, polycarboxylic acid, bifunctional acrylate, self-cure initiator, camphorquinone, and stabilizer	BW, A1; A2; A3; A3,5	I, II, III, IV,V	compules for mixing in shaker

The fluid portions of the material contain high molecular weight polyacrylic acid, similar to that used in HV-GIC and RM-GIC, and unmodified by polymerizable methacrylate groups as in Vitremer (3M ESPE) or Ketac Nano (3M ESPE). In addition, the fluid contains UDMA monomers (called Embrace resin by the manufacturer), dimethacrylate phosphates, photoinitiators, chemical initiators, and water. Fillers are silanized FAS fillers and silanized non-reactive fillers that are capable of bonding to the resin matrix; they play a role in wear resistance and material aesthetics [4, 55]. The material is packed in two-chamber, self-mixing syringes. While stirring, the double bond reaction takes place. An acid-base reaction occurs in which the polyacrylic acid and dimethacrylate phosphate monomers attack the silanized FAS fillers. Silicone gel begins to form on their surface and the bonding of material begins [4]. This acid-base reaction releases ions – calcium, aluminum, and fluoride. Calcium and aluminum ions can form ionic bonds with the ionized carboxyl groups. Along with this acid-base reaction, a second reaction is activated – the polymerization of the resin. The monomers can be copolymerized with silanized FAS fillers, silanized non-reactive fillers, and other monomers. At the end of the reaction, we get 2 different interpenetrating networks with theoretical ionic bonds between them due to trivalent ions. In water, calcium, aluminum, and fluorine ions (and possibly other ions) can be exchanged with the oral environment.

Due to the predominance of the glass ionomer component, it is recommended to prepare the cavity before applying the material, as for the restoration of glass ionomer materials. After preparation of caries, the surface of the defect should be etched for 5 sec with 38% orthophosphoric acid, rinsed, and then dried without overdrying. In low retention cavity, it is recommended to use a bonding system. In class V cavities, it is recommended to remove unsupported enamel. Then we place the material inside the defect in portions up to 4 mm thick. If the material binds in the absence of light, the setting time is 2 min (without oxygen, under a layer of glycerin). It is possible to include photopolymerization (20 sec). After setting, the material can be polished. The new protocol proposed by the manufacturer involves the use of an adhesive system prior to the application of AB.

CENTION N (IVOCLAR VIVADENT, SCHAAN, LIECHTENSTEIN)

Cention N is a material classified by the manufacturer as alkasite [56]. Alkasite refers to a new category of restorative materials which, like compomer or giomeric materials, are essentially a subgroup of RBCs [4]. The liquid of the CN consist of 4 monomers, without any acidic monomer or water. So, this part of the material is similar to RBCs. The powder contains: non-reactive silanized fillers, reactive silanized fillers similar to those used in GICs and silanized fillers advertised as highly reactive, particularly in an acidic environment, which strongly resembles FAS fillers. These fillers are the origin of the name 'alkasite' given by the manufacturer [56]. This new category uses an alkaline filler capable of releasing acid neutralizing ions. Cention N is a self-curing material with the possibility of light hardening. The self-curing process is based on the initiating system consisting of copper salts, hydrogen peroxide and thiourea. The liquid portion of the material contains hydroperoxide and the standard product powder filler is coated with other initiator ingredients. Copper salt speeds up the hardening reaction. This initiator system has some advantages over conventional self-curing initiator systems such as benzoyl peroxide/amine systems. The inclusion of hydroperoxide, which is more stable than benzoyl peroxide, makes the material more temperature resistant, i.e. less sensitive to heat, which is an important factor regarding storage stability. The use of thiourea in place of

the amine also improves the colour stability of the product. In order to speed up the self-curing process, it is possible to use the optional light-curing function. Cention N contains Ivocerin® photoinitiator and acylphosphine oxide initiator for optional light hardening. Ivocerin, a dibenzoyl germanium derivative is an amine-free Norrish Type I initiator. The Norrish Type I initiator refers to the fact that only 1 component is responsible for the formation of free radicals. A Norrish Type II initiator, such as camphorquinone, requires 2 components for light induced radical formation to take place [57]. The optional photopolymerization is performed with blue light in the wavelength range of about 400–500 nm – so all standard light curing units can be used.

Cention N is intended for the reconstruction of deciduous teeth and for permanent restorations of class I, II or V. It can be used as a self-adhesive material or with a bonding system. When used in a self-curing mode, the powder and liquid are mixed according to the manufacturer's recommendations, the material should be allowed to set for 4 min after applying to the cavity in 1 layer, compressing and shaping. When this simplified self-adhesive procedure is used, the cavity must be prepared in a retentive shape (i.e. with silver amalgam fillings) and the enamel margins should not be bevelled. When used with a bonding system, the cavity is prepared in accordance with modern principles of minimally invasive dentistry, i.e. with the largest possible natural tooth structure and with the appropriate instructions for use in terms of conditioning and application. Since 2020, the material has been available as Cention Forte in the form of capsules for mechanical mixing with a dedicated self-adhesive bonding system Cention Primer.

SUREFIL ONE (DENTSPLY SIRONA KONSTANZ, GERMANY)

In July 2019, Dentsply Sirona introduced new restorative material – SO. It was presented by the manufacturer as a new concept of self-adhesive restorative material (advanced self-adhesive restorative – ASAR) with properties similar to silver amalgam, but with the aesthetics of composite materials [58, 59]. Basic data on the composition of the material, based on the manufacturer's source materials, is presented in Table 2. An important component of SO is the MOPOS monomer (manufacturer's name) – Modifed Polyacid System, a hydrolytically stable polyacid base with polymerized groups. Thanks to its structure, MOPOS takes part in the initiation of adhesion, creates a network, and contributes to an increase in the strength of material. The 2nd type of monomers is BADEP (manufacturer's name), i.e. bifunctional acrylates (N, N'Bis-acrylamido-N, N'-diethyl-1,3-propandiamine) that serve as a cross-linking agent and are involved in the formation of covalent bonds. These are hydrolytically stable molecules of low viscosity. Both monomers correspond to HEMA and TEGDMA molecules found in RBC. As a result of combining the powder with the fluid, polymerization is initiated. Due to the presence of a photoinitiator – camphorquinone, reducing agents and chemoinitiators, this reaction takes place in 2 ways. Initially, during mixing, the MOPOS monomers are combined into

polymers and the monomers are combined with reactive fillers in an acid-base reaction. After placing the filling at the beginning of the photopolymerization, the photoinitiator is activated under the influence of light and the polymerization process is faster. As a result, a three-dimensional network resembling a composite material is created. Additionally, it is reinforced with double bonds and the presence of carboxyl groups in MOPOS and acid groups. As a result, the structure is strengthened and the mechanical strength of the material increases.

Due to the advantage of glass ionomer components over composite components, it seems appropriate to prepare the cavity just like for fillings made of glass ionomer cements. After selective removal of carious dentine, we can leave demineralized but not infected dentine at the bottom of the cavity (due to the possibility of remineralization of the dentin under the influence of fluoride ions released from the material). The surface-defect angle should be 90–110 degrees. Unsupported enamel must be removed and smoothed. SureFil One does not require a retention shape [58]. After activating the capsule and placing it in a shaker for 10 sec (4200–4600 rpm), 1.5 min are left for working with the material. The cavity should be filled with slight excess. It is recommended that when placing the material into the defect, the tip of the capsule applicator is immersed in the material to prevent the ingress of air bubbles. Cavities up to 4 mm deep enable one-layer reconstruction (the setting time of 1 layer is 6 min), deeper cavities require the use of a 2nd layer. In the case of photopolymerization of the surface layer (exposure time 20 sec, light intensity >800 mW/cm^2), it is possible to immediately and finally finish and polish the surface (in a humid environment), but there is still a time of 6 min for the final polymerization of the deeper layers reconstruction. The material is intended for the reconstruction of cavities from Class I to V according to Black.

FLUORINE ION RELEASE AND BIOACTIVITY

A desirable property of a restorative material is bioactivity, that is, the ability of the material to induce biomineralization by sufficiently releasing the ions [44]. In this sense of the term, the materials with proven bioactivity include GIC, HV-GIC and older RM-GIC. So far, no composite material has shown proven bioactivity. The producers of AB, CN, and SO postulate that they belong to bioactive and fluorine-releasing materials. According to the data included in the description of the material, AB has an ability to release calcium, aluminum, and fluorine ions (and other ions, e.g. phosphates). The release of fluorine ions has been confirmed in several studies [60, 61]. This release is lower compared to the glass ionomer cements – HV-GIC and RM-GIC [62]. In the study by Poreńczuk et al., HV-GIC (Ketac Molar (3M ESPE)) showed the greatest release of ions, followed by AB [63]. The nanohybrid composite material (Tetric EvoCeram (Ivoclar Vivadent)) had the lowest ability to release fluoride. Also in a 10 day fluoride release study by Garoushi et al. GIC (Fuji II (3M ESPE)) showed significantly higher scores than AB [60]. This study also indicated that the release of fluoride from AB is similar to that from

compomers and giomers, both quantitatively and qualitatively. There was no initial release peak, but the material had the ability to recharge with fluorine ions and subsequently release them into the tissues, which may help to reduce the risk of caries. In addition to releasing calcium and fluoride, the manufacturer states that the material releases phosphates. However, the study by Tiskaya et al. did not indicate that this ion release induced remineralization of underlying hard tooth tissues *in vitro*. Therefore, due to insufficient scientific evidence, this material should not currently be classified as a bioactive material [64].

Cention N, when placed in the oral environment, especially in an acidic environment [62], also releases fluorine ions, hydroxyl ions and calcium ions. In the study by Paul et al., this material showed a lower release of fluorine ions than the Zirconomer (Shofu) material [65]. In a similar study by Rai et al. [66], the best results were obtained by CN, and worse by Zirconomer (Shofu) and GC Gold Label. It was shown that the release of ions in CN was better than in the case of AB [64]. The release of ions, including fluorine ions, occurs by absorption of water, similar to giomers or compomers. An *in vitro* study showed that CN was able to form apatite on its surface and thus remineralize the underlying dentin when used without the bonding systems [64]. If this observation is confirmed by other studies, this material can be considered bioactive. It would be the 1st material derived from a composite resin with proven bioactivity.

According to the manufacturer, SO is also characterized by the ability to release calcium, aluminum and fluorine ions. Based on the tests carried out by the manufacturer, it shows a long-term release of fluoride similar to the long-term release of fluoride by GIC and RM-GIC (even after 450 days) [58]. In the fluoride release study conducted by Densplay Sirona, the highest short-term, an immediate release of fluoride was shown by glass ionomer materials: Equia Forte, Ketac Universal and Fuji II, while SO and Dyract XP had much lower values. On the other hand, all the materials mentioned showed a similar level of long-term fluoride release. This material, partly composed of water, theoretically supports the exchange of water and ions with the oral environment. In particular, this effect leads to the release of fluoride, aluminum and calcium ions (and possibly other ions due to the composition of reactive fillers). This ion release has not yet been investigated, especially in terms of its ability to induce remineralization of underlying hard tooth tissues. Therefore, SO cannot be classified as a bioactive material for now.

SELF-ADHESION

According to the information provided by the manufacturers, the three new materials (AB, CN, SO) can be used as self-adhesive materials. However, in the case of CN, this requires the cavity preparation in retention manner. In the case of low retention cavities, the manufacturers of all materials recommend the use of bonding systems. In order to improve the adhesion of the material to the tooth tissues, the manufacturer proposed a new application protocol, assuming the use of an adhesive system before applying AB. Also in a newer version

of CO – Cention Forte, the manufacturer attached a dedicated primer material (Cention Primer). Numerous studies have shown that the use of a bonding system significantly improves the maintenance time of fillings made of the above-mentioned materials. In a short-term clinical study by Van Dijken et al, AB material was used in class II cavities after a short phosphoric acid etching but without a bonding system [67]. An unacceptable, very high failure rate was achieved after a period of year. On the other hand, the results of the study by Bhadra et al., which compared the clinical efficacy of AB with nanohybrid RBC in class II cavities, did not show a statistically significant difference in the clinical efficacy of both materials after year of follow-up [68]. The study by François et al. also indicated significantly worse results of the obtained bond strength to dentine in the self-cured version, compared to the application of the adhesive protocol with the Scotchbond Universal system [69]. At that time, CN > AB > SO obtained the highest bond strength.

SELECTED MECHANICAL PROPERTIES

The mechanical and adhesive properties of the described materials differ significantly. In the study conducted by François et al., the flexural strength and shear bond strength of the 3 described materials and EQUIA Forte (GC) were compared [69]. The test was conducted for chemically cured materials and with assisted photopolymerization, without a bonding system and with the Schotchbond Universal (3M ESPE) system. It was found that the mechanical and adhesive properties of tested materials differed significantly. Photopolymerization significantly improved the bending resistance of all materials, with the exception of CN. Cention N obtained the highest shear bond strength values after application of the bonding system (33.8 MPa), while SO had the highest value in the self-adhesive procedure (20.9 MPa). The study by Garcia-Godoy and Morrow found that the wear resistance of the AB was comparatively higher than that of flowable RBCs and significantly better than that of GIC and RM-GIC [70]. Interesting results are provided by *in vitro* studies and clinical studies, which compared CN with silver amalgam [71, 72]. The study by Chowdhary et al. has shown that the compressive strength (a property necessary for the lateral fillings transferring occlusal loads) of silver amalgam and CN is almost similar [71]. The study by Minocha et al. showed that there was no significant difference between CN and silver amalgam for selected criteria for clinical class II restorations at 1 week, 3 months and 6 months [73]. Similar results were obtained after year of observation by Dedania et al. who compared both materials in class I cavities [72]. Studies comparing CN properties with RBCs also indicate material properties similar to those of composite materials. In an *in vitro* study comparing the compressive strength of the CN material, it obtained results very similar to two RBCs [74], and better compared to HV-GICs [75]. The material also performed significantly better than GIC and HV-GIC in an *in vitro* study comparing some mechanical properties (compressive strength, diametrical tensile strength and shear bond strength) [76]. In the case of determining the fracture resistance of the materials, the best

results in 2 studies were obtained by CN (CN > Filtek Z 350, Dyract XP > silver amalgamate) [71, 77]. On the other hand, in the study conducted by François et al., CN and AB turned out to be the most resistant, followed by SO and GIC [69]. Frankenberger et al. study evaluated (*in vitro*) marginal integrity, 2-body wear, and fracture behavior of an array of bonded and non-bonded posterior restorative materials (amalgam, GIC, SO, AB, RM-GICs, RBCs) after thermomechanical loading [78]. For marginal quality, SO showed promising behavior close to that of resin composite bonded with a self-etch adhesive. In terms of wear, amalgam and resin composites with recent filler technology were still superior. SureFil One showed stable fracture behavior, good marginal quality, and acceptable wear resistance *in vitro*. In the study of Sahoo et al. the strength of restorative materials: compomer, ormocer, nanocomposite, and AB were compared. There was a significant difference in bond strength among all restorative materials: nanofilled RBC > ormocer > AB > RM-GIC. The results of the study by Sahoo et al. on shear resistance correspond with the aforementioned results [79]. The nanofilled composite was significantly stronger than the ormocer AB, and compomer. The results of generalized and localized volume loss were presented in the study by Latta et al. AB and experimental ASAR-MP4 (SO) materials showed wear values similar to the GICs tested [80].

CONCLUSION

The presented new materials are evolutionary products based on GIC, RM-GIC and composite materials. The chemical structure and reactions that occur during the binding of AB and SO materials are similar to some RM-GIC, while in the case of CN material similar to fluorine-releasing resin-based materials.

Previous studies do not confirm that the new materials have the mechanical properties necessary to meet the requirements for posterior restorations. Limited clinical trials show that caution is required in their systematic application in all patients as no unequivocal studies confirm the bioactivity of the materials. Further *in vitro* studies as well as clinical observations to assess their chemical properties and the ability to induce remineralization and bioactivity are needed. The materials show self-adhesion, but when included in the protocol of a bonding system, their adhesion to hard tissues is better.

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