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CONTEMPORARY CONCEPTS ON COMPOSITE MATERIALS

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Summary

Composite materials are a tridimensional combination of at least two different materials mutually connected with a clearly recognizable coupling agent. In the development of composite materials, an outstanding place belongs to Michael G. Buonocore, who suggested etching the enamel surface with orthophosphoric acid; Rafael L. Bowen, who created composite resin, and to Nobuo Nakabayashi, who suggested hybridization of the dentin substrate and accomplished the promotion of adhesion by the infiltration of monomer into the tooth structure. Composite material consists of three fundamental parts: an organic resin matrix with a complimentary initiator of polymerization, an inorganic filler and a coupling agent.

Composite materials were primarily developed for fillings on anterior and posterior teeth, but materials with similar composition are also used for an extremely large number of indications: pit and fissure sealants, adhesive cementation of ceramic and indirect composite restorations, for crown build-ups, temporary crowns and bridges, the bonding of brackets in orthodontics, making splints and root canal sealers.

Contemporary composite materials are being constantly upgraded and have significantly improved physical and mechanical characteristics in comparison with previous generations, especially concerning the hardness, firmness, elasticity, resistance to bending, breaking, torsion and wear. However, since cross linking in net formation during polymerization leads to volumetric shrinkage and, consequently, polymerization stress that can affect the creation of a marginal gap and also compromise the longevity of the restoration, stress compensation represents the biggest scientific and clinical challenge.

The future of composite materials is mirrored in several directions. The first one is finding low shrinking or expanding composite materials, the second one is the optimization of composite materials based on amorphous calcium phosphate which is a direct precursor of hydroxyapatite, the basic unit of tooth structure. Others include the incorporation of antibacterial agents into composites as well as the development of materials with self-adhesive properties.

Key words: composites; adhesives; polymerization; shrinkage; remineralization.

INTRODUCTION

Improvements in tooth-coloured restoratives and bonding technology have made dental procedures more palatable and feasible [1]. Patients are attracted to a restoration that matches the color of natural teeth. Resin composites meet this demand and have become the most frequently used esthetic material in dentistry [2]. In addition, resin composites avoid the mercury controversy, and bond to tooth structure by using adhesive systems.

Composite is a multiphase material that exhibits the properties of both phases (organic and inorganic) where the phases are complimentary, resulting in a material with enhanced properties [3,4].

The composition of resin-based dental composites has evolved significantly since the materials were first introduced to dentistry more than 50 years ago. In 1951, a Swiss chemist Oscar Hager developed the first dimethacrylate molecule, which allowed for a cross-polymerized matrix. In 1962, Rafael Bowen developed a large-molecule, hydrophobic dimethacrylate monomer (Bis-GMA or Bowen's resin), a key advance in resin chemistry. Bis-GMA forms the basis of present-day composites because of its limited shrinkage and fracture resistance. Bowen's resin possessed the viscosity of honey, and therefore limited the amount of filler particles that could be incorporated. Subsequent experiments incorporated triethilene glycol dimethacrylate (TEGDMA) as a diluent to reduce viscosity. This monomer combination has become one of the most widely used matrix monomer combinations for dental composite to date. Both of these monomers contain two reactive double bonds, and when polymerized, form covalent bonds between the polymer chains known as a cross-link. Cross-linking improved mechanical and physical properties [5]. It was first used in a composite in 1969.

Resin composites are primarily used as anterior and posterior filling materials. Products with similar composition are also used as pit and fissure sealants, luting composites, for cores and buildups, inlays, onlays, temporary crowns and bridges, root canal sealers, root canal posts, and the bonding of brackets and orthodontic bands [6].

It is obvious that the use of resin composites will continue to grow due to their versatility.

DENTAL COMPOSITE FORMULATIONS

Resin-based composite materials are very complex mixtures composed of an organic phase, an inorganic filler, a coupling agent that improves filler/resin interactions and an initiator [2,7].

The organic phase (matrix resin) consists of a mixture of various polymerizable monomers such as Bisphenol A-glycidyl dimethacrylate (Bis-GMA) and/or urethane dimethacrylate (UDMA) as well as of various modifications of these molecules with double C=C bonds which, after light activation of free-radical-forming photoinitiators, convert to the highly cross-linked polymer with C-C bonds [6,8,9].

The resin phase in most commercially available composite resins comprises the aromatic base monomer bisphenol-A glycidyl dimethacrylate (Bis-GMA). Bis-GMA is a long-chain monomer with two methacrylate groups available for cross-linking polymerization. However, due to its large size, it is very viscous and it quickly reaches the gel point of photopolymerization, resulting in a relatively low degree of conversion (DC) due to the retardation of the diffusion of the monomer to the radical sites on the relatively immobilized network structure [10]. Also, the high viscosity limits the filler loading capacity of dental composites [4].

Bis-GMA is often combined with low-molecular weight diluent monomers like triethylenglycol-dimethacrylate (TEGDMA). TEGDMA enhances the molecular mobility in the polymerization process and delays the gel point of photo-polymerization because of its low viscosity. At Bis-GMA levels up to 40% in Bis-GMA/TEGDMA copolymers, Bis-GMA governs the final DC via controlling the diffusion-controlled termination process. At higher levels, DC is expected to diminish due to the reduction in monomer mobility. Composite formulations with higher amounts of TEGDMA usually exhibit higher DC and allow increased filler concentrations, but also exhibit higher polymerization shrinkage [8]. This lower viscosity monomer may comprise 10-50% of a composite resin’s content [4].

Ethoxylated bisphenol-A dimethacrylate (EBPADMA, Bis-EMA), a base monomer utilized in some dental composite resins, is a more hydrophobic analog of Bis-GMA, with a relatively flexible structure, lower vinyl group concentration and lower viscosity than Bis-GMA systems [11]. Dental polymers based on EBPADMA usually exhibit higher DC and lower polymerization shrinkage than the typical Bis-GMA/TEGDMA resins [10]. Lower polymerization stress was also reported for experimental composites where TEGDMA was substituted by EBPADMA with Bis-GMA as a base monomer [12].

The properties of composite restorative materials are considerably influenced by the included fillers. Fillers are most often added to polymers to improve tensile and compressive strength, abrasion resistance, toughness, dimensional and thermal stability, and other material properties [13]. Modern composite systems contain fillers such as quartz, colloidal silica, and silica glass containing barium, strontium, and zirconium [14]. By increasing the filler content, polymerization shrinkage, linear expansion coefficient and water absorption are reduced. On the other hand, by increasing the filler content, compressive and tensile strength, the modulus of elasticity and wear resistance are generally increased [15,16]. Fillers used in dental composites directly influence their radiopacity, abrasion resistance, flexural modulus, and thermal coefficient of expansion [9]. Polymerization shrinkage largely correlates with the volumetric amount of the filler in the composite [17].

A silane coupling agent that has functional groups to chemically link the filler and the matrix is utilized to achieve bonding of these two phases. A typical coupling agent is 3-methacryloxypropyltrimethoxysilane (MPTS). One end of the molecule can be bonded to the hydroxyl groups of silica particles, and the other end is capable of copolymerizing into the polymer matrix [14]. Surface modification of most fillers used in dental composites is necessary to reduce the filler surface energy so that composite paste consistency and hydrophilicity are reduced while filler dispersion within the resin is enhanced; and to provide a functional interface that permits covalent attachment between the polymer matrix and the reinforcing higher-modulus filler [8].

Autocured resin composite restorative materials largely disappeared from clinical practice in the 1980s because of the popularity of the light-cured materials [2]. While there have been attempts to develop different polymerization promoting systems, most composites are light-activated, either as the sole polymerization initiator or in a dual cure formation containing a chemically cured component. The most common photoinitiator system is camphorquinone (CQ), accelerated by tertiary amine, typically an aromatic one [18,19]. Some commercial formulations have included other photoinitiators, such as 1-phenyl-1,2-propanedione (PPD), monoacylphosphine oxid (Lucirin TPO), and bisacylphosphine oxid (Irgacure 819) which are less yellow than CQ.

ADHESIVE TECHNOLOGY

However, it is unthinkable to talk about resin composites without mentioning resin bonding. Definitively, one of the most significant developments in dentistry is the ability to bond materials to tooth structure. Bonded restorations have a number of advantages over traditional, non-adhesive methods. Adhesive techniques have expanded the range of possibilities for esthetic dentistry. Adhesion or bonding is the attachment of one substance to another. Adhesive system or bonding agent is defined as the material that, when applied to a surface or substances, can join them together, resist separation, and transmit loads across the bond [20,21]. Adhesion refers to forces or energies between atoms or molecules at an interface that hold the two phases together. Adhesive or bond strength is the measure of the load-bearing capability of the adhesive.

Traditionally, the retention and stabilization of the restoration often required the removal of sound tooth structure. When adhesive principles are used, this is not necessary because adhesion reduces microleakage and consequently the ingress of oral fluids and bacteria along the cavity wall, postoperative sensitivity, marginal staining and recurrent caries [22,23]. Adhesive restorations better transmit and distribute functional stresses across the bonding interface to the tooth and have the potential to reinforce the weakened tooth structure [24].

In 1955 Michael Buonocore was the first to demonstrate that acid-etching enamel with phosphoric acid increased resin-enamel bond strengths and microscopic area available for resin retention [25]. John Gwinnet reported that adhesive resins could penetrate into acid-etched enamel prisms where they could envelop apatite crystallites rendering the acid-resistant [26].

The main challenge for dental adhesives is to provide an equally effective bond to two hard tissues of different nature.

Nakabayashi et al. [27] were the first to demonstrate true hybrid layer formation in acid-etched dentin and the first to prove that resins could infiltrate into acid-etched dentin to form a new structure composed of a resin-matrix reinforced by collagen fibrils named new biocomposite hybrid layer.

Today's adhesives follow either an etch-end-rinse approach or a self-etch (etch-and-dry) approach, which differ significantly in the manner in which they deal with tooth tissue [28]. The fundamental mechanism of bonding to enamel and dentin is essentially based on an exchange process, in which minerals removed from the dental hard tissues are replaced by resin monomers that upon polymerization become micromechanically interlocked in the created porosities [29]. This process called "hybridization" on dentin involves infiltration and subsequent in situ polymerization of resin within the created surface porosities, and thus is a process based primarily upon diffusion.

Etch-and-rinse adhesive systems (ER) are the oldest of the multi-generation evolution of resin bonding systems. In the 3-step version, they involve acid-etching, priming and application of an adhesive. Adhesive bonding begins by acid-etching to increase permeability of resins to enamel and dentin [26]. In dentin, this is a unique form of tissue engineering. Acid-etching with 37wt% phosphoric acid completely demineralizes the surface 5-8 μm of the intertubular dentin matrix to create nanometer-sized porosities within the underlaying collagen fibrillar matrix. This permits the infiltration of solvated comonomers into and around collagen fibrils to gain retention for tooth colored resin-composite fillings. Acid-etching not only simultaneously etches enamel and dentin, but the low pH also kills many residual bacteria. Some etchants include anti-microbial compounds such as benzalkonium chloride that also inhibits matrix metalloproteinases (MMPs) in dentin. Primers serve as actual adhesion-promoting agents and contain hydrophilic monomers dissolved in solvents, such as acetone, ethanol and/or water. Effective primers contain monomers with hydrophilic properties that have an affinity for the exposed collagen fibril arrangement and hydrophobic properties for copolymerization with adhesive resin [30]. The objective of priming is to transform hydrophilic dentin surface into a hydrophobic and spongy state that allows the adhesive resin to wet and penetrate the exposed collagen network efficiently [31]. Primers are usually water and hydroxyethyl methacrylate (HEMA) -rich solutions that ensure complete expansion of the collagen fibril meshwork and wet the collagen with hydrophilic monomers. Water alone can re-expand dried dentin and can also serve as a vehicle for protease inhibitors or protein cross-linking agents that may increase the durability of resin-dentin bonds.

An adhesive resin, also called the bonding agent, consists primarily of hydrophobic monomers, such as Bis-GMA, UDMA, TEGDMA, and more hydrophilic monomers, such as HEMA as a wetting agent. The major role of the adhesive resin is to stabilize the hybrid layer and to form resin extensions into the dentinal tubules, called resin tags.

Each of the three steps can accomplish multiple tasks ending with sealing the bonded interface with a relatively hydrophobic adhesive layer [10].

The simplified two step version combines the second and the third step but still remains a separate etch-and-rinse phase. However, etch-and-rinse adhesives that utilize three steps are more durable than the two-step etch-and-rinse adhesives because maintaining separate steps enables using each step for multiple purposes. For example, 35-37% phosphoric acid can etch enamel and dentin and simultaneously decimate residual bacteria in carious dentin and inactivate matrix metalloprotease (MMP) [32-35]. Phosphoric acid sometimes contains benzalkonium chloride (BAC) which is a good MMP inhibitor that can withstand the low pH of phosphoric acid and does not lower enamel or dentin bond strengths [36]. The use of primers, originally designed to re-expand dried collapsed dentin and to coat wet collagen fibrils with a hydrophilic monomer, could also inactivate the soluble MMP-2 [37].

The main challenge for dental adhesives is to provide an equally effective bond to two hard tissues of different nature – enamel and dentin.

Self-etch adhesive systems (SE) do not require a separate etching step, as they contain acidic monomers that simultaneously ‘condition’ and ‘prime’ the dental substrate. By avoiding the etch-and-rinse phase they are more user-friendly and less technique-sensitive. A very important advantage is a lower risk of making errors during the application and manipulation and less post-operative sensitivity [29].

They can come as two-step and one-step adhesives. One-step adhesives can be subdivided into two-component or single-component which are the only true "all-in-one" adhesives combining conditioning, priming and application of the adhesive resin without mixing. Depending on the etching aggressiveness, SE adhesives are further divided into "strong" and "mild". Strong SE adhesives usually have a ph of 1 or lower and their bonding mechanism is similar to an ER approach. Mild SE adhesives have a pH of around 2 and demineralize dentin only up to a 1 μm depth. Such superficial demineralization occurs only partially, keeping residual hydroxyapatite still attached to collagen. Sufficient surface porosity is created to obtain micromechanical interlocking through hybridization. The preservation of hydroxyapatite within the submicron hybrid layer may serve as a receptor for additional chemical bonding [38]. Carboxylic acid-based monomers and phosphate-based monomers have a chemical bonding potential to calcium or residual hydroxypatite [28]. Keeping hydroxyapatite around collagen may also protect the collagen better against hydrolysis and, thus, an early degradation of the bond [39,40]. Further optimization of a mild SE approach by synthesis of functional monomers with a high chemical affinity to hydroxyapatite is optimal for dentin with highly recommended selective phosphoric acid etching of the enamel.

CURRENT COMPOSITES AND PROSPECTIVE CHALLENGES

The state-of-the-art composition of dental composites has been changing rapidly in the past few years. Current dental composites have adequate mechanical properties for usage in all areas of the mouth. In general, dental composites have similar flexure strength, fracture toughness and tensile strength as porcelain and amalgam and are superior to glass ionomers. One of the most recent inovations has been the development of „nanofill" composites, containing only nanoscale particles [9,18,41]. New options for reinforcing fillers have generally focused on nano-sized materials and hybrid organic-inorganic fillers, as well as on the novel organically modified ceramics [42]. Significant progress has been made in the development of new monomers for composite formulations with reduced polymerization shrinkage or shrinkage stress. The epoxy-based silorane system [43], provides verified lower shrinkage than typical dimethacrylate-based resins, likely due to the epoxyde curing reaction that involves the opening of an oxirane ring. However, one study has shown that siloran based composite does not produce lower contraction stress than other composites [44].

Others have experimented with tetraoxaspiroundecane (TOSU), added to silorane systems and observed stress reduction, but reduced stress may also be due in part to a reduction in mechanical properties [45].

Other monomers with increased molecular weight have been developed for composites with reduced shrinkage. The modified urethane dimethacrylate resin DX511 is said to reduce shrinkage due to a relatively high molecular weight compared with bis-GMA and traditional UDMA (895g/mole vs. 512 g/mole vs. 471 g/mole, respectively). The urethane monomer TCD-DI-HEA has been shown to produce lower polymerization contraction stress than other low-shrinking composites [44]. The dimer acid monomers have also high molecular weight (673-849 g/mole), exhibit high conversion and lower shrinkage than bis-GMA composites [45,46].

Perhaps the most interesting issue is addressed toward research and development of universal self-adhesive composites. There are already some flowable composites containing adhesive monomers. They are based on traditional methacrylate systems, but incorporate acidic monomers such as glycerolphosphate dimethacrylate (GPDM), capable of generating adhesion through mechanical and possibly chemical interaction [18].

COMPOSITE RESIN MATERIALS BASED ON AMORPHOUS CALCIUM PHOSPHATE

Dental caries remains a major dental disease in most countries of the world today [47-49]. In terms of therapy of dental caries, restorative dentistry has mostly been limited to procedures by which the carious tissue is removed and replaced by a non-biological substitute. Even though the function and the esthetics of the restorative materials are today regarded to be fairly good, none of them fulfills all the requirements for an ideal replacement material [50] and their longevity is limited [51-53]. Secondary caries has been established as the main reason for the replacement of both amalgam and composite resin fillings [52,53]. Over the last few decades, efforts have been increased to produce bioactive materials being able to reverse the carious process and to remineralize the caries-affected tissue. A variety of calcium phosphate-based, hard tissue restorative materials has been developed based on the similarity of calcium phosphates to the inorganic constituents of teeth and bone [54]. Moreover, the material should be able to actively participate in natural processes of carious tissue repair. Amorphous calcium phosphate (ACP) is unique in the class of calcium phosphates as the direct precursor of biologic apatite in the biomineralization processes of both vertebrates and invertebrates [55].

One of the materials pertaining to the bioactive dental materials is a group of ACP based composite resins. ACP composite materials release calcium and phosphate ions into an aqueous environment, such as the oral cavity, providing supersaturating concentrations sufficient to trigger the apatite build-up. The remineralization was shown in *in-vitro* experiments on demineralized bovine [56] and human teeth [57], or by analyzing the calcium and phosphate ion release concentrations [58,59]. However, ACP is not a reinforcing filler such as silanized glass or silica fillers which are used in most of the commercially available dental composite materials. The consequence is that ACP-based composite resins without a classic reinforcing filler display insufficient mechanical properties. In order to use these materials in clinical practice as a restorative material, it is therefore necessary to enhance the mechanical properties so that the material can withstand the masticatory stresses. Also, similar to other composite resins, polymerization shrinkage, highly correlated to the high degree of conversion, is also an issue that needs to be addressed. Recently, a new generation of ACP composites was developed. The introduction of reinforcing fillers to the ACP composite formulation has improved their flexural strength and hardness, while reducing the polymerization shrinkage and maintaining the high degree of conversion [60].

LOW SHRINKING SILORANE-BASED COMPOSITES

In conventional methacrylate-based composite resin systems, the formation of macromolecular chain network from discrete monomer species involves conversion of intermolecular distances of 0.3-0.4 nm into primary covalent bonds with lengths of about 0.15 nm [61]. This is the background of the polymerization shrinkage (PS) and the consequent occurrence of the closely correlated polymerization stress (PSS), one of the major shortcomings of dental composite materials. There is no proven association between the polymerization contraction of composite restorations and their clinical outcome. However, there are strong indications that the occurrence of the secondary caries around composite fillings, the main reason for their replacement, is related to the occurrence of tooth-composite interfacial debonding, cuspal and enamel fractures, all of which are the consequences of the polymerization stress [62].

The problem of PS and the subsequent PSS of composite resins is still present regardless of the constant attempts to reduce them. PS is an unavoidable consequence of the polymerization process and it is therefore highly dependable on the degree of conversion. The methods to reduce PS can be divided into three groups:

1. the modification of the monomer matrix
2. higher filler load and
3. modifications of curing protocols [63].

One of the most interesting approaches for the reduction of PS and PSS is silorane technology, currently commercially available as the composite material, the so-called „low-shrinkage“ material. The novel matrix system is fundamentally different from methacrylate systems. Whereas methacrylate photopolymerization involves the conversion of C=C double bonds to single bonds, the silorane polymerization is based on the cationic ring-opening reaction [8]. By the virtue of opening the ring structure to facilitate monomer bonding and crosslinking, silorane system is said to exhibit significantly less volume shrinkage after the completion of photopolymerization.

The silorane technology is based on a monomer composed of a cyclic siloxane core appended with four oxirane reactive groups [43]. The cationic reaction is activated by a standard photoinitiator system, which comprises camphorquinone as a photoactivator and tertiary aromatic amine as a photoreductant. Besides them, an iodinium salt as an electron donor is added, and serves as the source of active cationic species. The differences in the composition of the silorane composite as opposed to the methacrylate composites extend to the filler selection and a specific surface treatment of fillers to achieve good interaction with the silorane-based matrix. Due to the cationic chemical reaction, special adhesive system for bonding to the tooth structure has been released [8].

Silorane composite materials have shown many desirable properties such as improved depth of cure, lower polymerization shrinkage, higher strength and hardness in comparison to the Bis-GMA resins [64]. However, another study has determined that the mechanical properties are comparable to the methacrylate composites [65]. Although the majority of the studies has shown that siloranes have lower PS and PSS than methacrylate-based resins [66-68], there are studies which reported the contrary [44,69]. Also, a significantly higher temperature rise during cationic polymerization reaction is noted, when compared to the polymerization reaction in conventional materials [68,70]. Despite the lower polymerization contraction for siloranes reported by *in vitro* studies, the first *in vivo* evaluations did not confirm the supremacy over conventional materials in clinical trials [71].

FUTURE DIRECTIONS IN RESTORATIVE DENTAL MATERIALS

Future developments are aimed at improving composite fillers by adding polymer nanofibres, glass fibres, and titania nanoparticles [41], as well as at developing composites with modified fillers for both enhanced mechanical properties and remineralizing the potential based on calcium and phosphate release [72]. The idea of adding anti-bacterial agents into composites to kill bacteria or inhbit biofilm formation includes fluoride [72-74], chlorhexidine [75], zinc oxide nanoparticles [76], quaternary ammonium polyethyleneimine nanoparticles [77], and 12-Methacryloyloxydodecyl pyridinium bromide (MDPB monomer) [78].

The main point of the research is the development of self-adhesive composites with low polymerization shrinkage and stress, with optimal mechanical and physical properties, capable of releasing remineralizing ions and having an anti-microbial effect.

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Sažetak

Suvremene spoznaje o kompozitnim materijalima

Kompozitni materijali su trodimenzijska kombinacija najmanje dva različita materijala koji su međusobno povezani jasno prepoznatljivom silanskom vezom. U razvoju kompozitnih materijala, iznimno mjesto pripada Michael G. Buonocoreu, koji je predložio jetkanje caklinske površine ortofosfornom kiselinom, Rafael L. Bowenu, koji je stvorio kompozitnu smolu i Nobuo Nakabayashiu, koji je predložio hibridizaciju dentinskog supstrata i tako ostvario promociju adhezije pomoću infiltracije monomera u zubnu strukturu. Kompozitni materijali sastoje se od tri temeljna dijela: organske smolaste matrice i odgovarajućeg inicijatora polimerizacije, anorganskog punila te svezujućeg sredstva.

Kompozitni materijali razvili su se primarno za ispune prednjih i stražnjih zubi, ali se materijali sličnog sastava danas koriste za iznimno puno indikacija: pečaćenje fisura i jamica, adhezijsko cementiranje keramičkih i indirektnih kompozitnih restoracija, za izradu nadogradnji, izradu privremenih krunica i mostova, vezanje bravica u ortodonciji, izradu splintova te za ispun korijenskog kanala.

Suvremeni kompozitni materijali se stalno nadograđuju i imaju znatno usavršena fizičko-mehanička svojstva u odnosu na prethodne generacije, poglavito tvrdoću, čvrstoću, elastičnost, otpornost na savijanje, kidanje, torziju i trošenje. Međutim, kako križno povezivanje u mrežu tijekom polimerizacije dovodi do volumetrijskog skupljanja, a posljedično i polimerizacijskog stresa koji može u značajnoj mjeri utjecati na stvaranje rubne pukotine i kompromitaciju trajnosti restorativnog zahvata, kompenzacija stresa predstavlja najveći znanstveni i klinički izazov.

Budućnost kompozitnih materijala ogleda se u nekoliko smjerova. Prvi je iznalaženje niskoskupljajućih ili ekspandirajućih kompozitnih materijala, a drugi optimizacija kompozitnih materijala temeljenih na amorfnom kalcijevom fosfatu, koji je direktni prekursor hidroksilapatita, osnovne gradbene jedinice zuba. Ostali pristupi uključuju inkorporaciju antibakterijskih agensa u kompozite te razvoj materijala sa samovezujućim svojstvima.

Ključne riječi: kompoziti; adhezivi; polimerizacija; skupljanje; remineralizacija.

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