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Review

Modifications of Glass Ionomer Cements Using Nanotechnology: Recent Advances

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Abstract

Glass ionomer cements (GICs) are dental materials that were invented by Wilson & Kent in 1972. They can chemically bond to enamel and dentin and can exhibit anti-cariogenic activity that allows the release and uptake of fluoride ions. They also possess the ability to render color. The setting reaction of GICs is a neutralization reaction that results in the formation of polycarboxylate salts. The most important GIC modification process involves the addition of resin components, resulting in the development of resin-modified glass ionomer cements (RMGICs), which contain self-and photo-curing systems. Modification of conventional GICs and RMGICs can be achieved by the incorporation of nano-sized fillers into the materials. Conventional GICs and RMGICs can also be modified by introducing nano-sized bioceramics to the glass powder. It has been previously reported that the incorporation of nano-sized particles helps improve the mechanical properties of conventional GICs. Conversely, the commercially available nano-filled RMGICs do not hold any significant advantage over conventional RMGICs as far as the mechanical and adhesive properties are concerned. Glass carbomer is a novel glass ionomer material, and the bioactivity of which is better than the bioactivity of the conventional GICs. However, it is more brittle and less strong than the

modern conventional GICs. Additionally, clinical techniques that can be used to transfer external energy on the surface of a GIC have also been used for modification. These techniques can be used to reduce the duration of the initial setting stage and improve the rate of the setting reactions, resulting in faster development of the mechanical properties. Premature failure of the restorations can be avoided under these conditions. The lack of long-term clinical studies limits the use of nano-modified glass ionomers and glass carbomers in daily clinical practice. More randomized clinical trials are required to justify the use of these modern modified materials.

Keywords
Bioactive materials; glass ionomer cements; modifications; nanofillers; nanotechnology

1. Introduction

Glass ionomer cements (GICs) are dental materials that were invented by Wilson & Kent in 1972 [1]. They can chemically bond to enamel and dentin. The origin of the anti-cariogenic activity of the materials can be attributed to the release and uptake of fluoride ions. The materials can be used to render color effectively [2-4]. Glass ionomers exist in powder and liquid form. The powder consists of fluoro-alumino-calcium-sodium-silicate glass particles, usually in the form of SiO-AlO_2-CaF_2-$AlPO_4$-Na_3AlF_6. Some formulations contain strontium (Sr) and barium (Ba) compounds that improve radiopacity and remineralization properties. The liquid is an aqueous solution of various polycarboxylic acids, which are primarily polyalkenoate acids. The low viscosity of the acids facilitates the handling of cements [5-7]. Tartaric acid is also added to the liquid to improve the ease of handling and increase working time [8].

The setting reaction associated with GICs is a neutralization reaction, resulting in the formation of polycarboxylate salts [9]. Initially, the hydrated protons (H_3O^+) of the polyacid react with the basic particles in glass. This promotes the movement of Na^+, Ca^{2+}, and Sr^{2+} ions, and later Al^{3+} ions, from glass to the polyacid solution [10-12]. These ions react with the polyacid molecules and form ionic bonds. Thus, the formed insoluble polysalt network causes the cement to harden [10]. Water is an essential component of glass ionomers as it is the solvent of polymeric acid. It contributes to the release of protons. It functions as the matrix for the setting reaction and is also a structural component of cement [13]. The loss of water from freshly hardened cement creates an unsightly chalk surface due to the formation of microcracks (Figure 1). To prevent dehydration, it is important to coat the surface of the cement with a hydrophobic material such as Vaseline or a suitable resin varnish [14].

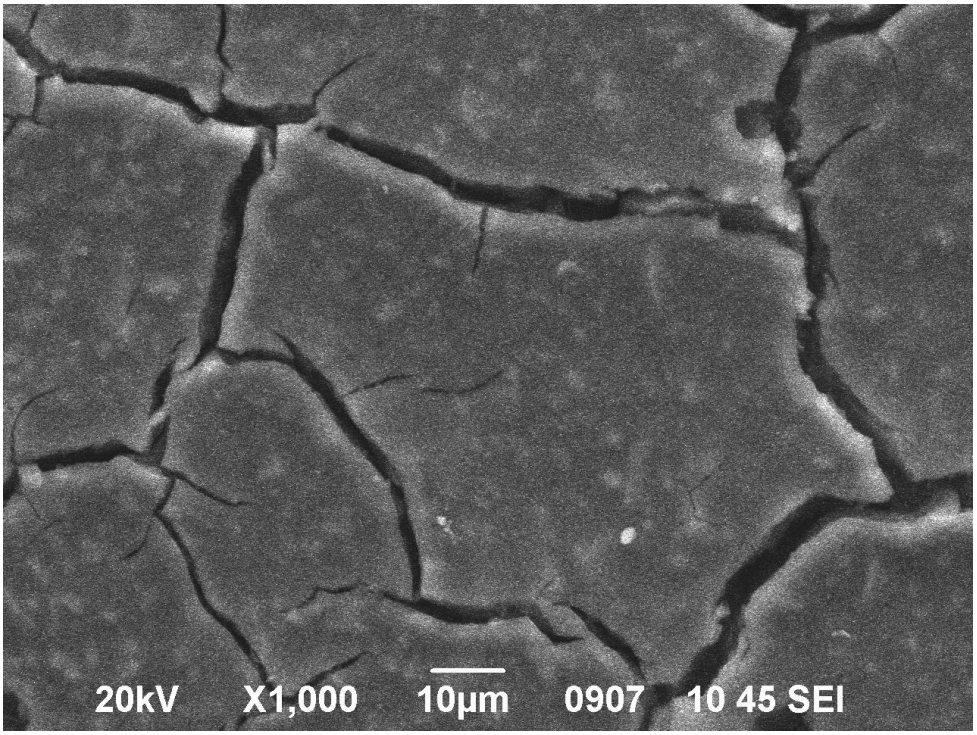

Figure 1 Representative scanning electron microscopy (SEM) image of the surface of a high-viscosity glass ionomer cement Equia Fill after desiccation presents microcracks.

The setting reaction has been studied by various spectroscopic methods, and it has been observed that the reactions proceed over two phases [15]. Ionic bonds, which are responsible for the immediate hardening of the cement, are formed in the first phase. Ionic bonds involving Al^{3+} ions are formed in the second phase, and the formation of these bonds starts approximately 10 min after the initial setting. The process continues at a slow rate for approximately 24 h [11, 12]. This is followed by the process of maturation, which takes several weeks or months. During this process, minor changes such as an increase in the compressive strength and degree of translucency occur. The process is accompanied by a decrease in toughness and degree of opacity. The content of bound water increases to a limiting value, and the extent of bonding (attributable to the process of continuous ion exchange) to the tooth surface increases [16].

Depending on their clinical application, glass ionomers can be classified into four categories [10]: a) GICs for bonding bridges, crowns, inlays/onlays, posts, and orthodontic rings; b) GICs for fillings (these are further divided into two subcategories: the first includes aesthetic cements for anterior teeth, which have a variety of shades and translucencies [17, 18] and the second includes reinforced glass ionomers which are used in posterior teeth); c) GICs for tooth cavity bases and liners [19, 20]; and d) GICs for dental sealants [21].

There are several factors that limit the application of GICs under certain clinical conditions. The mechanical properties of the GICs are poorer than those of the resin-based materials [22]. The limiting factors also include low resistance to abrasion [23] and high sensitivity to moisture in the oral cavity [24]. Various modification methods have been used to tune the composition of the GICs to address the problem of reduced physical-mechanical properties. The most prominent modification method included the addition of resin components in the GICs. This resulted in the development of the resin-modified glass ionomer cements (RMGICs), which contain self-and

photo-curing systems [25, 26]. Zinc [27, 28], stainless steel [29], strontium oxide [30], silicon particles [31], bioactive apatite [32], a mixture of bioactive apatite and strontium [33, 34], synthetic fibers [35] polyacids containing N-vinylpyrrolidone [36], and amino acid monomers [37] have been used over the years as additives to improve the mechanical properties of the materials. In recent years nanotechnology has been used to produce new composite resins. It has been reported that the method can be used to effectively improve the mechanical properties of the materials [38, 39]. Similar efforts have been made to improve the physical and mechanical properties of both conventional and resin-modified GICs. Glass Carbomer, a modified GIC,contains modified glass particles, nano-hydroxyapatite, and silicone oil [40, 41].

Most recent versions of GICs typically consist of powders that contain some of the polymeric acids in dried form, resulting in the formation of a low-viscosity acid solution. The freshly mixed cement prepared under these conditions contains high amounts of acid that promote the rapid setting of the material. The process also imparts good strength. These types of materials are labeled as “high-viscosity” GICs, a term typically applied to materials characterized by high powder/liquid ratios of at least 3.6:1 [16]. In 2015, a novel GIC material known as the Equia Forte (GC Inc., Kyoto, Japan) was introduced for application in high-load-bearing areas in posterior teeth. It is a glass hybrid restorative material containing a multifunctional monomer and reinforced with ultrafine, highly reactive glass particles [42, 43]. The time frame for the development of glass ionomer materials is presented chronologically in Table 1.

Table 1 Developments of glass ionomer materials.

Date	Glass ionomer developments
1972	The invention of conventional GICs
1977	Metal (silver)-reinforced GICs
1980	RMGICs self-polymerized
1990	RMGICs photo-polymerized
1991	RMGICs (photo+self)-polymerized
2003	Glass Carbomer
2007	Nano-modified RMGICs
2008	Nano-modified conventional GICs
2008	High-viscosity conventional GICs
2015	Hybrid restorative GICs

Therefore, the purpose of this literature review is to present the current data for the latest modifications of GICs, emphasizing the modifications involving nanotechnology.

2. Resin-Modified Glass Ionomer Cements (RMGICs)

RMGICs were introduced in the field of dentistry in the late 1980s. These are hybrid materials with combined properties of conventional GICs and composite resins. The components present in the powder are almost the same as the components present in conventional GICs. The liquid methacrylate monomers and a photoinitiator system are also present in the system [44]. The monomer is typically 2-hydroxyethyl methacrylate (HEMA), and the photo initiator is usually camphorquinone (CQ)[45].

Two different chemical reactions occur during the process of setting of RMGICs. The acid-base reaction is initiated immediately after the process of powder/liquid mixing. The polymerization of the methacrylate monomers is stimulated using a dental light-curing unit such as light-emitting diode (LED) devices. The properties of the material can potentially degrade due to the simultaneous progress of the two antagonistic reactions [46]. The method of mixing and the light-curing should be conducted following the instructions provided by the manufacturer to avoid deleterious effects on the structure of the cement [46].

Post photopolymerization, the material is exposed to conditions of a fast initial hardening process to form the polymer network. However, the acid-base reaction continues after light-curing and is completed within 10-12 min of mixing [4]. Unlike conventional GICs, moisture-protecting substances need not be used immediately after application, and this can be attributed to the formation of the polymer network. They also show greater resistance to compression, diametrical tensile strength, degree of bending, and modulus of elasticity than the conventional GICs [22, 47]. They present lower water sorption ability, a lesser degree of solubility, and higher translucency than conventional GICs. These improve the aesthetic performance of the materials. The process of polymerization shrinkage during setting limits the application of RMGICs. The extent of fluoride release recorded for the RMGICs is lower than that recorded for the conventional GICs. This can be attributed to the low solubility (attributable to the less hydrophilic nature) of the material and the release of unreacted monomers to the surrounding tissues. Fluoride is released in two phases in conventional GICs. A large amount of fluoride is released during the first phase (burst effect). This is followed by the steady release of a small amount of fluoride ions during the second phase. The second phase is longer than the first phase [48, 49]. Small amounts of Na^{+}, Al^{+3}, PO_4^{-3}, and Ca^{+2} ions are also released during the process. They exhibit buffer properties and increase the pH of the oral fluids in an acidic environment [50, 51].

In terms of biocompatibility, RMGICs lag behind conventional GICs because they release the monomer HEMA, especially during the first 24 h. It can penetrate dentinal tubules and is considered potentially cytotoxic to pulpal cells [52-54]. It has been previously reported that low cytotoxicity (determined by conducting MTT assays) values were recorded for all the tested materials (conventional GICs, RMGICs and resin composites) and low extraction times were involved, indicating minimal cytotoxicity of the materials (less than 30% inhibition). One RMGIC presented significantly higher cytotoxicity compared to the other materials [54]. RMGICs should always be light-cured for at least the manufacturers' recommended time at thicknesses no greater than the maximum recommended value to minimize HEMA release [52]. Efforts have been made to modify RMGICs with nanoparticles and bioceramic particles to address the persisting issues [55, 56].

3. Modifications of GICs using Nanotechnology

Nanotechnology involves the production of functional materials and structures whose dimensions are in the range of 1-100 nm. The materials are produced using various physical and chemical methods [57, 58]. The introduction of nanotechnology in restorative dentistry led to the development of nano-filler particles. The physical, chemical, and biological properties of a particle in the nanoscale dimension are different from the properties of the particles at the atomic/molecular level. The properties of nanomaterials are also different from the properties of

the bulk material [59]. Tooth tissues are composed of nanoscale structural units [60]. Hence, synthetic nanoparticles of similar nature are needed to mimic the properties of natural teeth. Two primary approaches in the field of nanotechnology are used for developing small or improved materials. These methods are also used to form complex assemblies from small components. The first approach involves the solid-state processing of materials. The processing methods include the processes such as milling, machining, and lithography. Approaches such as chemical vapor deposition, monolithic processing, wet etching, and plasma etching are used to fabricate functional structures at micro and nano levels [61]. The second approach includes the fabrication of materials via edifice-up particles by harvesting atomic elements [62]. The methodis based on highly organized chemical synthesis methods and the growth of materials [63].

In the field of dentistry, nanotechnology has been used to modify the surface of bone implants [64], improve the mechanical properties of resin composites [38, 65, 66], and prevent caries [67]. Efforts have also been made to improve the mechanical properties of both conventional and resin-modified GICs. The aim is also to significantly improve physical properties and address issues associated with wear resistance, hardness, and elasticity. Researchers have also aimed to achieve patient satisfaction in terms of aesthetic appearance. They have attempted to improve the translucency and polishing ability by incorporating nanoparticles into GICs [68].

3.1 Modifications of Conventional GICs with Nanoparticles

Hydroxyapatite and fluorapatite exhibit significantly high chemical affinity toward bone and dental tissues and for this reason they have been used in the field of implantology [69] and prevention of caries [57, 67]. Nano-hydroxyapatite crystals have been found to contribute significantly to the remineralization of enamel [70, 71]. It has been reported that the addition of nano-hydroxyapatite to resin composites significantly improves their mechanical properties [72]. Nano-hydroxyapatite or nano-fluorapatite, when used as additives in conventional GIC powder, significantly improves the compressive strength, tensile strength, and flexural strength of the materials [73]. Glass ionomers containing nano-fluorapatite have better mechanical and adhesive properties than those containing nano-hydroxyapatite. This can be potentially attributed to the low solubility of nano-fluorapatite [36, 73]. The improved mechanical properties of GICs that contain nano-apatite are apparent due to the formation of ionic bonds between polyacrylic acid and apatite crystals [36]. It has been claimed that when GIC powder containing nano-hydroxyapatite is used with a liquid containing a mixture of polyacrylic acid, itaconic acid, and polymers of N-vinylpyrrolidone (instead of the commonly used polyacrylic copolymer), the mechanical properties of GICs are further improved. This may be explained by the formation of strong chemical bonds between N-vinylpyrrolidone and apatite crystals [36]. Nano-apatite-containing GICs exhibit a better degree of adhesion (with dental tissues) than the other materials. This can be attributed to the ability of apatite crystals to form strong ionic bonds with Ca ions in dental tissues [74]. The small nano-apatite particles significantly increase the surface area of the particles and improve the ability of the particles to penetrate demineralized enamel and dentin. This results in an increased adhesion to the tooth surface [75].

Apart from nano-apatite, other types of nanoparticles have also been used to improve the mechanical properties of GICs. More specifically, in some GIC products, nanoparticles (3-5 wt %) of titanium dioxide (TiO_2) have been added to the powder to improve the mechanical properties and

increase the antimicrobial activity of the cement [76, 77]. Although TiO_2 is considered to exhibit toxic effects, results from in vitro studies did not reveal that the toxicity of the nano-TiO_2-containing GIC was higher than the toxicity of the conventional ones [78, 79]. GICs can also be modified by adding a mixture (4 vol %) of nano-hydroxyapatite and zirconia (ZrO_2) particles to the powdered samples. This also results in improved mechanical behavior. This improvement may be attributed to the uniform distribution of the glass and the mixture of nano-apatite and zirconia particles within the matrix of the cement [33]. Fractures in the cement structure were also observed. The origin of the fractures was attributed to the weak bond between the glass and the zirconia. Therefore, the content of the mixture of hydroxyapatite and zirconia should not exceed 4 vol% [33].

3.2 Modifications of RMGICs with Nanoparticles

The property of chemical adhesion is considered to be the most important property of GICs. GICs can effectively adhere to dental tissues. RMGICs bond to dentin both micromechanically (the resin penetrates the collagen network) and chemically (by forming a chemical bond between the carboxylic acid groups and the Ca ions of the crystals of hydroxyapatite of partially demineralized enamel and dentin through ionic reactions) [9, 80]. Nano-RMGICs show a similar bonding mechanism. It has been observed that minimal penetration of the resin into the dentin occurs in these cases, indicating that the strength and efficiency of bonding depend more on the ionic bond than on the micromechanical retention. This is similar to the case of conventional GICs [55]. The commercially available RMGIC Ketac N100/Ketac Nano (3M ESPE) contains nano-agglomerated silicon particles and is accompanied by a primer (Ketac Nano Primer), which is applied to the tooth surface before placement of the cement. However, relevant studies have shown that there is no significant difference in bond strength to dentin between nano-reinforced and conventional RMGICs [55].

It has been demonstrated that the use of 37% orthophosphoric acid before the application of the cement can increase the shear bond strength of nano-RMGICs due to the removal of the smear layer and increase in the surface energy [56, 81, 82]. However, high molecular-weight carboxylic polymers (MW = 8000-15000) present in RMGICs cannot penetrate demineralized dentin. This leaves the dentin collagen network unprotected and exposed to the risk of hydrolytic degradation [83, 84]. Thus, excessive demineralization of dentin should be avoided when RMGICs are used [74, 85] as the polyalkenoic polymers cannot penetrate the collagen of the dentin [86]. Therefore, it is suggested that weak acidic primer or aqueous solutions of polyacrylic acid (usually 25%) should be used for pretreatment of the tooth surface to improve the adhesion ability of nano-RMGICs. A recent clinical study has compared a nano-RMGIC with a conventional RMGIC and a composite resin. It was found that after 1 year there were no differences among the materials in terms of retention of the restorations. However, the nano-RMGICs exhibited higher discoloration and lower marginal integrity than the conventional ones [87]. In another in vitro study, it was reported that the marginal integrity of nano-RMGIC restorations was lower than that of the conventional ones. This presumably is explained by the lower bond strength that present the nano-RMGIC especially to and enamel [88].

Modifications in the shape and size of the fillers can affect the mechanical properties of a glass ionomer material in the same way as happens in resin composites [22, 89]. RMGICs are more

resistant to bending, changes in tensile bond strength, and solubility compared to conventional GICs. This can be primarily attributed to the formation of chemical bonds between the glass particles and the organic matrix [22, 47]. Traditional RMGICs have been found to be more resilient to bending and fatigue than commercially available nano-RMGICs [89, 90]. Additionally, nano-RMGICs exhibit inferior mechanical behavior under acidic conditions [89] than conventional GICs.This can potentially influence the longevity of the nano-RMGIC restorations in the oral cavity.

As mentioned before, the addition of nano-hydroxyapatite, nano-fluorapatite, and nano-fluorohydroxyapatite particles can improve the surface properties of the RMCIGs. The improvement can be attributed to the increase in the content of the inorganic phase at the surface [91]. On the other hand, the use of nano-hydroxyapatite particles significantly extends the setting time of the material up to 800 s. This is significantly higher than the time range outlined in the ISO specifications (90-480 s) [92]. Although the exact mechanism of this increase in setting time is yet to be well understood, it appears as if the nanoparticles interfere with the process of polymerization of the monomers [93]. The abrasion caused by toothbrushing on the surface of nano-RMGICs has been found to induce less surface loss compared to conventional RMGICs. Nevertheless, under clinical conditions where microbial and chemical activities are observed, no statistically significant differences were found between the two types of RMGICs in terms of surface roughness and hardness [94]. Hence, despite the modifications brought about by the addition of nanoparticles, the surface roughness and hardness of the RMGICs were poorer than those of the composite resins, due to their lower abrasion resistance and their higher solubility [94-96].

The release of fluoride ions from GICs and RMGICs is one of their major advantages, as fluoride is well documented to reduce demineralization, increase remineralization, inhibit the growth of bacterial and inhibit their adhesion to tooth surfaces [97]. Because fluoride is not involved in the setting process of GIC, it can be released in large amounts by an ion exchange mechanism without affecting the structure of the cement. GICs also have the ability to uptake fluoride from the oral fluids that function as fluoride storage, which can be re-released preventing demineralization of the tooth tissues [98]. However, it has not been clinically confirmed whether the amount of fluoride released by GICs is sufficient to prevent the formation of caries [99, 100]. It has been reported that the amount of fluoride release achieved using nano-RMGIC is similar to the amount of fluoride release achieved using conventional RMGICs. However, the amount is lower than that released by conventional GICs [49, 89]. Notwithstanding nano-RMGICs release more fluoride in an acidic environment (pH = 4), the total amount of fluoride they released after 84 days was comparable to the total amount of fluoride released by conventional RMGICs [89]. Results from in vitro studies revealed that nano-RMGICs significantly reduce the development of secondary caries. Unfortunately, there are no long-term clinical trials to confirm these results in vivo.

4. Glass Carbomer

Glass ionomer cements are considered to be bioactive materials as they release biologically active ions (F, Na, Si, and P) in the oral environment, which can beneficially interact with dental tissues. They also present buffer properties under acidic conditions and reduce the pH of the environment. The glass carbomer is a novel glass ionomer cement, which was claimed to be more bioactive than conventional GICs [10]. Despite the fact that the name “glass carbomer” is the

brand name of a product of the GCP Dental company, it has been accepted to be used in literature [10, 40, 41]. Its setting reaction is an acid-base reaction that occurs between the aqueous solution of the polymeric acid and the basic glass containing certain components which are not usually present in other GICs [10]. In particular, these components are (a) glass beads of cement powder that have been treated with strong acids (HCl), (b) silicone oil containing polydimethylsiloxane, and (c) nano-hydroxyapatite and nano-fluorapatite fillers.

The treatment of glass carbomer particles with strong acids results in a significant reduction in the calcium content on the surface of the particles, which is confined to the interior of the particles [101]. The glass used in the glass carbomer contains strontium, large amounts of silicon, and a small amount of calcium. Compared to the other GICs, it contains a relatively larger amount of silicon but a similar amount of aluminum, phosphorus, and fluoride [102]. The treatment of the powder particles with the strong acids results in a reduction in the rate of the reaction between the polyacrylic acid and the copolymer of acrylic-maleic acid. The silicone oil which is added to the powder is absorbed on the surface of the glass particles, preventing their direct reaction with the polymeric acids. Thus, the glass carbomer can be easily mixed in a large powder-liquid ratio, and the high rates of the setting reaction (initiated by the contact between the two components) can be avoided. The rate of the setting reaction lowers following the mixing of the materials. However, it can be accelerated by irradiating the system with a light-curing unit (LCU) for at least 60 s following the manufacturer's recommendation [40]. The LCU emits heat resulting in an increase in the temperature of the cement. This catalyzes the setting reactions and accelerates the process of hardening of the cement. This method has been proposed in various previous studies conducted on conventional GICs [103-105].

As noted previously, the amount of silica in the glass carbomer is higher than the amount of silica present in other GICs and hydroxyapatite fillers. This results in the production of a brittle cement [10]. To address this problem, the manufacturer added silicone oil that bonded with the structure of the material via hydrogen bonds. Under these conditions, the cement becomes more resilient.

Two parallel chemical reactions take place during the setting of the glass carbomer. The first reaction occurs between glass and polyacid, while the second reaction occurs between nano-hydroxyapatite particles and polyacid. Both are acid-base reactions and occur following the process of hardening the cement. Then a polysalt matrix is formed, which encompasses glass particles and hydroxyapatite. The polysalt matrix is similar to the matrix of other GICs except for the fact that it contains polydimethylsiloxane oil [102]. To date, few long-term clinical studies on glass carbomer restorations have been published [106-108]. Therefore, there is no evidence of the effectiveness of the material in oral environment.

5. Thermocuring of Glass Ionomer Cements

As mentioned previously, the mechanical and physical properties of GICs, such as sensitivity to moisture, initial fracture toughness, and resistance to wear, are poorer than those of the resin-based restorative materials, which can be primarily attributed to the slow progress of their setting reaction [109, 110]. Due to these drawbacks of the conventional GICs, it has been suggested to accelerate their initial setting reaction providing external energy, such as radiant heat, by utilizing dental light-curing units (LED or diode lasers) usually for 60-120 s [104, 111, 112] or kinetic energy

by using dental ultrasonic scalers, usually for 55 s [113-115]. The delivery of external energy on the surface of a GIC reduces the duration of the initial stage of the setting process. This also improves the rate of the setting reactions leading to a faster development of the mechanical properties avoiding premature failure of their restorations [116]. More specifically, heat transfer from the light sources to the GIC surface increases ion mobility at the initial stage of the setting process and reduces the viscosity of the material resulting in the enhanced reactivity of the calcium ions in the glass and carboxylate groups of the polyalkenoic acids. This process also helps to improve and accelerate the setting reaction [112].

Various studies have reported that the transfer of external energy to the surface of GICs can increase surface microhardness [117], resistance to abrasion [118], adhesion to tooth tissues [119], and compressive strength [111], while it can reduce water sorption and solubility [120]. On the other hand, it decreases fluoride release from the surface of the material [103-105]. This method in combination with the development of GICs with novel composition is very promising for the improvement of the clinical behavior of the tooth restorations of GICs, especially in areas characterized by high mastication forces, such as the occlusal surfaces of the posterior teeth.

6. Conclusions

In conclusion, modification of conventional GICs with nanoparticles improves their mechanical properties as the structure of the material is reinforced. Under these conditions, these materials become more stable and insoluble and the bond strength with the dental tissues improves. Commercially available RMGICs modified with nanoparticles do not show any significant benefit over conventional RMGICs in terms of mechanical properties and bond strength to tooth tissues. Glass carbomer is considered more bioactive than conventional GICs. The former, is apparently more fragile and less resilient than the latter. These new modified GICs require clinical documentation for their effectiveness, which can be achieved through conduction of more long-term clinical trials.

Author Contributions

Dimitrios Dionysopoulos: Conceptualization, collection of the data, writing the manuscript; Olga Gerasimidou: Data curation, writing the manuscript; Constantinos Papadopoulos: writing-review and editing the manuscript.

Competing Interests

The authors have declared that no competing interests exist.

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