

Self-sealing resin fixators in dentistry

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ABSTRACT

Fixed indirect restorations bond to the prepared tooth surfaces with the use of a variety of luting agents depending upon the purpose of that rehabilitation. Success and failures of these restorations have been attributed to the quality of their bond with the tooth substrate. However, the advent of resin-based and self-adhesive resin luting agents have greatly changed this equation by altering the conventional bonding mechanisms and the durability of bond. The limited literature details of these self-adhesive resin luting agents require further exploration for the benefit of dental professionals. This review provides an overview of the composition, chemical interactions, favourable and unfavourable properties to be known for improving the scope of their utilization in dentistry.

1. Introduction

Rehabilitative appliances fabricated to restore the missing tooth/teeth include removable prostheses and fixed partial dentures (FPD). FPDs mandate preparation of teeth surfaces to a thickness of 1.5 to 2mm involving both enamel and dentin to accommodate the bulk of prosthetic materials and a thin bonding space. This space and the substances filling it determine the quality of bond with natural tooth/teeth and thereby govern the success and durability of FPDs. Dental cements, commonly referred to as 'luting agents', are widely used adhesive agents between fixed partial dentures and the tooth structure. These luting agents not only provides bonding between the FPD and the tooth structure but also prevent the formation of secondary caries and penetration of oral fluids into the prepared surface and insulate the thermal conduction by filling the gap between the tooth surface and the restoration. Further, dental cements are used to bond orthodontic appliances to the teeth and cementing pins and posts to retain dental restorations. Fixed orthodontic appliances are attached to the natural tooth surface without any reduction [1, 2].

Various luting cements used for luting of indirect restorations and orthodontic appliances are zinc phosphate, zinc polycarboxylate, glass ionomer, hybrid ionomer, resin-modified glass ionomer and polyacid modified resin cements [1, 3-6, 11-13]. A group of resin-based cements have been developed with enhanced bonding mechanisms by using the acid-etch technique for adhering to enamel and potential bonding molecules for attaching to conditioned dentin with an organic or inorganic acid. These resin-based cements are used for luting orthodontic

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brackets or resin-bonded bridges [4]. This article reviews the composition, chemistry, properties, advantages, and disadvantages of resin-based luting cements with more emphasis on self-adhesive resin cements.

2. Resin-based luting agents

Resin cements were introduced in the mid-1980s. Bio-mer was the first resin cement marketed by Dentsply/Caulk, in 1987. Resin cements contain resins or polymers as the primary reactive ingredients and to which fillers have been added to modify the coefficient of thermal expansion (CoTE) and water sorption thereby increasing the strength and hardness of polymers [1,4]. These resin-based cements are also possessing anti-cariogenic property as they contain fluoride agents [14]. These resin-based cements are widely used for luting of non-metallic restorations, resin-bonded FPDs, porcelain crowns and veneers, ceramic and resin composite inlays and onlays [1,4]. However, these early resin-based cements do not chemically adhere to enamel and dentin, leading to microleakage and also possess high film thickness. Besides, they cause pulpal irritation due to leaching out of residual monomer [15], and also undergo discolouration due to high residual amine levels after polymerization [1,4,16]. It was reported that the resin-based cements with a dentin bonding agent exhibited superior retention of crowns on teeth compared to using zinc phosphate cement [1,4].

Later, aromatic dimethacrylate-based resin cements, bis-GMA based, have been developed [1,7]. Bis-GMA resin is a multi-functional methacrylate resin developed by Dr Bowen. The bis-GMA (2,2-bis[4-(2 hydroxymethacryloxypropoxy) phenyl] propane) resin can be described as an aromatic ester of dimethacrylate, synthesized from an epoxy resin and methyl methacrylate [1,4,17]. Bis-GMA is extremely viscous at room temperature; hence, a diluent resin, such as triethylene glycol dimethacrylate (TEGDMA) is blended with it to reduce the viscosity. Resin cements are available as powder/liquid, encapsulated, or paste/paste systems and are classified into three types based on the method of polymerization as chemical-cured, light-cured and dual-cured [1,4,17].

3. Self-adhesive resin cements

Self-adhesive resin cements were introduced in 2002 to overcome some of the disadvantages of both conventional (zinc phosphate, polycarboxylate, and glass-ionomer cements) and resin cements [18].

Self-adhesive resin cements have a wide range of clinical applications as they have favourable characteristics of conventional luting and resin cements [18,19]. They possess good esthetics, best mechanical properties, good dimensional stability, and micromechanical adhesion as shown with resin cements. Unlike conventional resin cements, no pre-treatment of the tooth surface is required prior to luting with self-adhesive resin cements. The application procedure of self-adhesive resin cements is simple and is accomplished in a single clinical step, similar to the application procedures used with zinc-phosphate and polycarboxylate cements. Furthermore, patients do not experience any postoperative sensitivity as the smear layer is not removed. They are also moisture tolerant compared to the earlier luting agents. These self-adhesive resin cements also exhibit anti-cariogenic properties as they release fluoride ions in a manner comparable to glass ionomer cements [18-20].

3.1 Composition of Self-adhesive resin cements

Self-adhesive resin cements are usually dispensed in individual syringes. The most popular dispensing system is a two-paste system with dual-barrel syringe dispensers. One paste contains the predominant functional acidic monomers, conventional di-methacrylate monomers (e.g., bis-GMA, UDMA, and TEGDMA), and initiator systems for both light and self-cured reaction. The other paste contains fillers like fluoro-alumino-silicate, silanated barium glasses, or both, and silanated silica particles. Further, this paste also contains activator-initiator systems, and methacrylate monomers [4,20, 21]. The composition of various contemporary materials was described in table 1.

3.2 Setting reaction of self-adhesive resin cements

The self-adhesive resin cements undergo a free-radical addition polymerization, which is either self-activated or dual-cured. The initial pH is low and it is necessary for the adhesion mechanism. The acidity is neutralized by the reaction between phosphoric acid groups and the alkaline glass as the polymerization reaction proceeds [20,21]. Currently available self-adhesive resin cements are dual-cure resin materials, which depends on both light and self-curing mechanisms [16]. Literature reported that the overall degree of conversion of dual-cure resin cements might be compromised as the self-curing mechanism is relatively slow, and it can be interrupted by the formation of a first polymer network, which is triggered by light activation [22-24]. The set material is mainly a cross-linked polymer, which is covalently bonded with silane coupling agents.

Table 1. Self-adhesive resin cements and their characteristics

Product	Delivery system	Working and setting time	Shades	Composition
BisCem® (Bisco, Schaumburg, IL, USA)	Paste/paste dual syringe; direct dispensing through a mixing tip.	1min/6min at 22°C	Translucent Opaque	Bis (hydroxyethyl metha-crylate) phosphate (base), tetraethylene glycol dimethacrylate, dental glass.
BeautiCem SA, Shofu Inc, Japan	Paste/paste dual Auto-mixing syringe; direct dispensing through a mixing tip and also available for manual mixing material			
Bifix SE, Voco, Japan	Dual curing system	20 sec – light curing	3 shades	Glycerine dimethacrylate-based resin
Breeze™ (Pentron Clinical Technologies, Wallingford, CT, USA)	Paste/paste dual syringe; direct dispensing through a mixing tip	1min/4min at 22°C	A2 Translucent Opaque White	Mixture of Bis-GMA, UDMA, TEGDMA, HEMA, and 4-MET resins, silane-treated barium borosilicate glasses, silica with initiators, stabilizers and UV absorber, organic and/or inorganic pigments, opacifiers
Calibra Universal, Dentsply, Milford	2-paste system	10 sec/45 sec		
Clearfil SA (Kuraray, Tokyo, Japan)	Dual-barrel syringe	1min/5min	A2 White	Bis-GMA, TEGDMA, MDP, barium glass, silica, sodium fluoride
Embrace WetBond resin cement (Puldent; MA, USA)	Automix or standard syringe packaging	Completely autocures in 7min	One shade	Di-, tri-, and multi-functional acrylate monomers into a hydrophilic, resin acid-integrating network (RAIN).
G-Cem™ (GC; Tokyo, Japan)	Capsules	2min/4min	A2, A03, Translucent, B01	Powder: fluoroaluminosilicate glass, initiator, pigment. Liquid: 4-Met, phosphoric acid ester monomer, water, UDMA, dimethacrylate, silica powder, initiator, stabilizer
G-Cem LinkAce, GC America, USA	dual-cure self-adhesive resin delivered in double barrel automix syringe		A2, Translucent, Opaque (A03) & (B01)	
iCEM® (Heraeus Kulzer)	Double syringe			
Maxcem Elite™ (Kerr; Orange, CA, USA)	Paste/paste dual syringe; direct dispensing through a mixing tip	2min/3min	Clear White White opaque Yellow Brown	GPDM (glycerol dimethacrylate dihydrogen phosphate), comonomers (mono, di, and tri-functional methacrylate monomers), proprietary self-curing redox activator, photo-initiator (camphorquinone), stabilizer, barium glass fillers, fluoroaluminosilicate glass filler, fumed silica (filler load 67%wt, particle size 3.6µm)
Multilink Sprint Ivoclar Vivadent, Schaan, Lichtenstein	Paste/paste dual syringe; direct dispensing through a mixing tip	Working time : 130±30s, Setting time: 270±30 s (based on oral temperature)	Transparent Yellow Opaque	Dimethacrylates and acidic monomers. The inorganic fillers are barium glass, ytterbium trifluoride and silicon dioxide. The mean particle size is 5 µm. The total volume of inorganic fillers is approx. 48 %

Contd...

Table 1. Self-adhesive resin cements and their characteristics

Product	Delivery system	Working and setting time	Shades	Composition
Monocem™ (Shofu Dental; San Marcos, CA, USA)	Paste/paste dual syringe; direct dispensing through a mixing tip	Unlimited working time (7min in anaerobic conditions)	Translucent Bleach white	
Panavia SA, Kuraray Noritake Dental				
RelyX™ Unicem (3M ESPE; St Paul, MN, USA)	Capsules (Aplicap: 0.001ml; Maxicap: 0.36ml)	2min/5min at 22°C	A1, A2, Universal Translucent, White opaque A3 Opaque	Powder: glass fillers, silica, calcium hydroxide, self-curing initiators, pigments, lighth-curing initiators. Liquid: methacrylated phosphoric esters, dimethacrylates, acetate, stabilizers, self-curing initiators, lighth-curing initiators
RelyX™ Unicem 2 (3M ESPE; St Paul, MN, USA)				
SeT (SDI, Australia; SE)	Capsules	5min	Translucent, A1, A2, A03 White opaque	UDMA, phosphate, fluoroaluminosilicate glass, silica.
SmartCem® (Dentsply-Caulk- Germany)	Dual-barreled syringe	2min/6min	Translucent Light Medium Dark Opaque	Urethane dimethacrylate; di- and trimethacrylate resins; phosphoric acid modified acrylate resin; barium boron fluoroaluminosilicate glass; organic peroxide initiator; camphorquinone photoinitiator; phosphene oxide photoinitiator; accelerators; butylated hydroxy toluene; UV stabilizer; titanium dioxide; iron oxide; hydrophobic amorphous silicon dioxide.
SpeedCEM™ (Ivoclar, Vivadent)	Double syringe	Working time: Self-cure: 100 – 140 Seconds, Dual-cure: 100 – 140 seconds Setting time: (37 °C) Self-cure: 150 – 220 seconds, Dual-cure: 150 – 220 seconds	Transparent Opaque Yellow	Dimethacrylates, ytterbium trifluoride, co-polymer, glass filler, silicon dioxide, adhesive monomer initiators, stabilizers and pigments

Formation of ionic bridges between carboxylic groups and ions released by the glass may also be observed [20].

3.3 Properties

Self-adhesive resin cements are not biocompatible due to their higher cytotoxicity compared to resin and acid-base cements. However, dual-cure self-adhesive resin cements possess reduced cytotoxicity [20]. Also, the degree of polymerization of dual-cure adhesive resin cements is less. de Souza Costa CA *et al.* (2006) [25] demonstrated no pulpal response with RelyX Unicem cements even after 60 days of their placement. It can be attributed to its chemical adhesion to tooth structure, low solubility, and a self-neutralizing mechanism during the polymerization reaction. On the other hand, Variolink II with the bonding agent, Excite demonstrated severe effects on the pulp-dentin complex.

These cements contain acidic functional monomers, which can neutralise or interfere with the free radicals and retard the polymerization reaction. This delayed polymerization can last from 24 hours to 7 days [26]. The rate of polymerization merely depends on the ratio of self-curing to light-curing components, light exposure time, intensity of the light source, the type and the thickness of the restorations [21]. Also, neutralization of the acidic monomers can significantly affect the rate of polymerization. The presence of residual acidity of these monomers may reduce the curing rate and prolong the final set of the cement. These harmful effects could result in cement with increased water sorption. Storage temperature is another factor that influences the polymerization of self-adhesive resin cements. If the cement is stored at temperatures higher than the room temperature would have a deleterious effect on the curing rate. It is well known that the rate addition polymerization is directly proportional to the temperature. The higher the temperatures, the faster will be the rate of polymerization reactions. However, it may also be influenced by the individual components of the cement and their response to the temperature [27]. The ideal temperature to store self-adhesive resin cements is in the range of 4°C to 18°C, and it is necessary to bring them to room temperature before using [21].

Polymer-based cements tend to absorb water, resulting in swelling of the cement. This increase in size may be considered as an advantage as it compensates the polymerization shrinkage and improves the marginal seal. However, excessive swelling may not be desirable as it creates more stress at the interface of the cement

and the restoration. Generally, the solubility of the polymer-based cements in water is very less. The rate of sorption and solubility depends on the type of the resin matrix that is present in the cement [28-30], the amount of residual hydrophilic components in the set matrix [30], cross-linking density and porosity [31], and amount of residual acidic monomers and type of polar functional groups [31-33].

These cements are initially hydrophilic in nature. The low pH, along with high hydrophilicity, helps in proper wetting and providing bonding to the tooth substrate. The acidic functional monomers are slowly neutralised as they start their chemical reaction. Then during demineralization, the pH of the functional acidic monomers is slowly neutralized with the hydroxyapatite and filler particles. As the pH increases, the material becomes more hydrophobic and becomes less susceptible to hydrolysis [34,35]. The film thickness of these cements is between 15 and 20 µm.

The mechanical properties of self-adhesive resin cements are superior compared to the conventional luting agents and less than the resin cements. However, they vary among commercial materials. It was reported that the light-activated adhesive resin cements exhibit better mechanical properties than the self-cure cements. Kumbuloglu *et al.* (2004) [36] reported more compressive strength and hardness with the RelyX Unicem light-curing cements compared to RelyX ARC, Panavia F, and Variolink cements. On the contrary, Piwowarczyk A *et al.* (2003) [37] reported more compressive and flexural strengths with the three cements than the RelyX Unicem. No significant differences were observed in the fatigue strength and resistance to the fracture among the various commercial materials irrespective of their curing mechanisms [38 - 41].

3.4 Bonding mechanisms

Self-adhesive resin cements do not require the application of a separate adhesive before cementation. However, the performance of various self-adhesive resin types of cement can be improved by additional surface treatments before cementation [42-44].

3.4.1 Bonding with enamel and dentin

Self-adhesive resin cements adhere to the tooth structures via micromechanical interlocking and chemical interaction between the acidic groups and the hydroxyapatite groups in the teeth [20]. On cementation, self-adhesive resin cements first demineralize the tooth substrate and then infiltrate enamel and dentin. However, they interact only superficially with dental hard

tissues [18, 45,46]. The bond strength of these cements with the natural tooth substrates are more compared to the glass ionomer cements and comparable to that of the self-etching adhesives. Therefore, self-adhesive resin cements may be considered as an alternative material to glass-ionomer cement for cementation of metal-based and high-strength ceramic restorations [18].

The acidic monomers of self-adhesive resin cements provide lower interprismatic hybridization as they are weaker compared to the traditional phosphoric acid etchants. Therefore, enamel may not be effectively demineralized that resulted in weak bond strengths with enamel compared with conventional hybridization techniques that are usually seen with the separate etching and bonding approach [47].

Pre-etching the dentin with phosphoric acid may not provide adequate bonding with self-adhesive resin cements as it results in inadequate resin infiltration into the exposed collagen fibril network [47, 48]. Numerous studies have reported that the use of polyacrylic acid instead of phosphoric acid gives better results, especially with the concentration of 10-25% and at low pH [49,50]. Thermocycling or aging of the restorations in different conditions may also reduce the bond strengths with enamel and dentin [51].

3.4.2 Bonding with the restorative materials

Self-adhesive resin cements not only adheres with the natural tooth but also with ceramics and some metals and alloys.

3.4.2.1 Ceramic restorations

Ceramics are the group of widely used esthetic indirect restorative materials [52,53]. A suitable luting agent such as glass ionomer cements and resin cements may be used to seat the ceramic restoration firmly on the prepared tooth [1]. The durability of ceramic restoration depends on the quality of bonding by the luting agent [54]. In addition, the aesthetics of ceramic restorations also depend on the type of luting agent is used. In general, the internal surface of the ceramic restorations is treated to enhance the bond strength with the luting agent. These treatments include sandblasting or etching the internal surface before the cementation. Silicate-based ceramics achieve good bonding with the self-adhesive resin cements by two simultaneous mechanisms. They include micromechanical retention, which is provided by acid-etching of the ceramic surface, and followed by the chemical coupling with the help of a silane coupling agent [55-60].

Usually, hydrofluoric acid gels are used to etch the surface of the ceramics, followed by silanization [61,62]. The hydrofluoric (HF) acid reacts with the silica that is present in the glassy matrix results in dissolving the surface to the depth of a few micrometres [56] and exposes the crystalline structure [57]. Then, a bifunctional silane coupling agent is applied that promotes a chemical interaction between the silica in the glass phase of ceramics and the methacrylate groups of the resin cement through siloxane bonds [56, 63-65]. Silanization reduces the contact angle and increases the wettability of the ceramic surface [66], making it a suitable substrate for bonding with resin cements. It has been shown that the light-cured cements give better results on cementing the ceramic veneers compared to self-cured resins.

The colour stability of self-cure resins cements is poor as they contain amines activators, which tends to discolour the ceramic veneers.

Shear bond strength has been improved when self-adhesive resin cements are used in conjunction with sandblasted (aluminum oxide) zirconia ceramic restorations [67]. It was also reported that the performance of the zirconia crown cemented with self-adhesive resin was improved when the internal surface of the restoration is pre-treated with light-pressure sandblasting followed by the application of MDP-containing primers [68-71].

Various systematic reviews suggested that physico-chemically conditioned zirconia crowns combined with MDP-based self-adhesive resin cements exhibit favourable results on adhesion with each other [69,70]. Numerous studies reported that the thermocycling improved the shear bond strength with self-adhesive resins cements [72].

3.4.2.2 Bonding to endodontic posts

Self-adhesive resin cements show significantly higher push-out strength to fibre posts compared to zirconia posts [73]. However, limited research was done in this area.

3.4.2.3 Bonding with Titanium abutments

Self-adhesive resin cements exhibited significantly higher with titanium abutments compared with zinc phosphate and glass ionomer cements. However, the bond strength values achieved with the self-adhesive resin cements were incomparable to retention achieved using polycarboxylate cement [74].

4. Conclusion

Self-adhesive cements are promising luting agents and a viable clinical alternative material in indirect restorative procedures due to their simplified technique, reduce the occurrence of postoperative sensitivity and are suitable for a wide range of applications. They can be extensively used for cementation of fibre posts, monolithic zirconia crowns, and PFM crowns when moisture control is challenging for adhesive application. Based on the literature available, RelyX™ Unicem was the most investigated self-adhesive cement and proved to be satisfactory and comparable to other multistep resin cements. However, long-term studies are necessary to evaluate the clinical performance of self-adhesive resin cements prior to making any general recommendation regarding their use.

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