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## Review Article

# A comprehensive review of resin luting agents: Bonding mechanisms and polymerisation reactions

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## ABSTRACT

The field of dentistry is constantly evolving and increasingly embracing minimally invasive approaches. One such approach, which is bonding to the tooth structure, particularly enamel, has been shown to offer the most predictable outcomes. However, there are instances where significant tooth loss may limit treatment options for a restorative dentist. In these scenarios, indirect restoration might be the preferred treatment option. This literature review provides a comprehensive examination of the currently available resin luting agents and their bonding requirements. It provides valuable insights for dental professionals seeking an in-depth understanding of the current state of the field and the future prospects of dental adhesion.

## 1. Introduction

Cement firmly bonds two surfaces. In the field of dentistry, there are three categories of luting cement, which are categorised according to their interaction with the underlying surface: (i) luting cements that do not adhere (such as zinc phosphate cements), (ii) cements that form a chemical bond (such as glass ionomer, polycarboxylate and phosphate-modified resin cements), (iii) cements that create a micromechanical bond (such as dimethacrylate-based cements) (Table 1).

Understanding the characteristics of luting materials and their recommended clinical use is crucial to ensuring high-quality cementation. These materials are responsible for creating a seal between the restoration and the tooth, which is important for not only securing the restoration in place but also preventing microleakage (Heboyan et al., 2023; Perdigão, 2020; Perdigão et al., 2021). Consequently, the longevity of indirect restorations is influenced by the quality of the luting materials used. These materials are commonly used in the cementation of various dental restorations such as crowns, veneers, inlays, onlays, orthodontic appliances and endodontic posts (Heboyan et al., 2023). Therefore, it is important for dental professionals to have a comprehensive understanding of the clinical indications of resin cements. Hence, this review seeks to examine the physical, adhesive, chemical and aesthetic characteristics of these materials.

## 2. Bonding mechanisms for adhesive resin cements

To facilitate bonding to dental tissues, many resin cements require the dental substrate to be pre-treated. Depending on the specific characteristics of the cement, the pre-treatment can involve the use of either an etch-and-rinse or a self-etch dentin adhesive system. Recently, self-adhesive resin cements have been developed to substitute multistep resin-based luting cements. Hence, resin cements can be categorised into three groups based on their bonding properties: etch-and-rinse, self-etch and self-adhesive resin cements.

### 2.1. Etch-and-Rinse

For most resin cements, manufacturers recommend using two-step etch-and-rinse adhesives or 'one-bottle' adhesive systems. In the latter approach, the primer and adhesive resin are mixed in a single solution, making it theoretically easier for the user to employ. However, to achieve similar bond strengths as those obtained from multistep etch-and-rinse adhesives, clinicians need to reassess their application technique for two-step etch-and-rinse adhesives.

Phosphoric acid is a component of etch-and-rinse adhesives, mainly because it can simultaneously etch enamel and dentin. When the acid is applied to the dentin, the smear layer is eliminated and the dentin is demineralised by 5–8 μm, enlarging the dentin tubules and exposing

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**Table 1**  
Material properties of different dental cements (Duarte et al., 2011; Leung et al., 2022).

Interaction between substrates	Cement	Film thickness (µm)	Tensile strength (MPa)
Non-adhesive	Zinc phosphate	25	3.1–4.5
	Polycarboxylate	25	3.6–12
Chemical bonding	Glass ionomer	11–35	42–53
	Resin-modified glass ionomer	24	13–25
	Phosphate-modified resin (self-adhesive)	16	34
	Self-cured resin	24–50	62
Micromechanical bonding	Light-cured resin	5–10	77
	Dual-cured resin	16.4	40–56

collagen fibres (Perdigão, 2020). The tiny spaces formed within the network of dentin collagen are permeated by hydrophilic monomers, leading to the encapsulation of collagen fibrils by the resin and the creation of a resin-dentin interdiffusion zone (Nakabayashi, Kojima, and Masuhara, 1982).

A wet bonding technique is applied while using etch-and-rinse adhesives to enlarge the acid-etched dentin matrix and to stop the collagen network from collapsing (Kanca 3rd 1992; Perdigão, 2020). However, this technique must be employed carefully, as an excessive amount of water in the spaces between the fibrils can compete with the adhesive monomers, diluting them and hindering optimal polymerisation (Hashimoto et al., 2007; Perdigão, 2020). Additionally, water present in the collagen network can cause the bonded interfaces to degrade quickly. Therefore, this review proposes several techniques to enhance the bonding of dental tissues. (i) Multiple coatings of two-step etch-and-rinse adhesives are required in order to obtain stable micromechanical interlocking between the monomers and the collagen network (Hashimoto et al., 2004; Perdigão, 2020). Moreover, (ii) vigorous application of the adhesive can significantly improve the bond strength and, in turn, clinical retention (Perdigão, 2020). (iii) Thorough drying of the solvent is necessary following the application of the dentin adhesive. If the solvent is not completely evaporated, the bond strength decreases and permeability increases (Perdigão et al., 2021; Van Landuyt et al., 2007). Inadequate evaporation can result in water being trapped in the collagen network, preventing the adhesive monomers from fully polymerising. The manufacturer's recommended duration for solvent evaporation may not be sufficient, and complete removal of the solvent is difficult to achieve (Van Landuyt et al., 2007; Cadenaro et al., 2009). Simplified adhesives allow fluids to pass through the cured adhesive layer (Tay et al., 2004; Perdigão et al., 2021; Feitosa et al., 2012). This effect has been observed both in teeth that have undergone root canal therapy and those that are still vital (Schwartz, 2006). If water is trapped at the interface, it can cause the polymer to become soft and lead to failure (Feitosa et al., 2012). To prevent this, (iv) a layer of hydrophobic resin coating (such as flowable composite) can be applied over the simplified adhesive, which may reduce the permeability of the adhesive and improve the bond's strength (Vinagrea et al., 2019; de Carvalho et al., 2021; Reis et al., 2009; Fuentes et al., 2023).

When an adhesive system is polymerised, satisfactory mechanical and physical properties are achieved. The success of this process depends on the composition of the adhesive and the distance from the light source (Perdigão et al., 2021; Van Landuyt et al., 2007). However, particularly in the case of indirect restorations, it may be necessary to use a self- or dual-cured adhesive if effective light polymerisation cannot be guaranteed. As a solution to this issue, certain etch-and-rinse resin cements now contain chemical co-initiators or activators to enable a light-polymerised adhesive to become self- or dual-cured. Unfortunately, using an activator has limited effectiveness in terms of enhancing the coupling of dual-cured adhesives with self- or dual-cured resin cements (Tay et al., 2003; Perdigão et al., 2021). It is also not advisable to

rely solely on self-polymerisation, as it results in significantly lower conversion rates than the dual-cured mode (Aldhafyan, Silikas, and Watts, 2022). It is, therefore, recommended to light-polymerise dentin adhesives when they are utilised with resin cements, regardless of the activation mode employed, and to increase the curing time to > 20 s to ensure proper polymerisation (Aldhafyan, Silikas, and Watts, 2022, 2021).

## 2.2. Self-etch

To mitigate the adverse effects associated with the use of phosphoric acid as a dentin-conditioning medium, which include a reduction in the cohesive strength of dentin and an elevated risk of post-operative sensitivity, an alternative conditioning approach has been suggested. Self-etch adhesives contain acidic monomers that etch and prime dentin and enamel simultaneously without the need to rinse. They are available in one-step or two-step options. One-step self-etch adhesives contain everything combined in one solution, while two-step self-etch adhesives have a separate self-etching primer and adhesive resin. Self-etch adhesives both demineralise and infiltrate the dental substrate. The degree of etching depends on the acidity of the solution. Ultra-mild self-etch adhesives (pH > 2.5) interact at the nano level with dental substrates. Mild self-etch adhesives (pH ≈ 2.0) create a submicron hybrid layer with less obvious resin tags, and strong self-etch adhesives (pH ≤ 1.0) create an interfacial morphology similar to the one formed by total-etch adhesives (Van Landuyt et al., 2007).

Self-etch adhesives work differently from etch-and-rinse adhesives in that the former do not require rinsing and drying, which means that the smear layer is not taken away but is instead infused with the acidic monomers. This process exposes the intertubular collagen, and resin monomers assume the place of the subtracted minerals, creating a micromechanical interlocking effect within the collagen spaces (Perdigão, 2020). Unlike with total-etch adhesives, the collagen fibrils are not completely devoid of hydroxyapatite (Van Meerbeek et al., 2011; Perdigão, 2020). Therefore, limited chemical interactions can occur between functional monomers (such as 10-methacryloyloxydecyl dihydrogen phosphate (10-MDP)) or certain acids (such as polyalkenoic acids) and hydroxyapatite, which may lead to improved bond durability (Perdigão, 2020; Carrilho et al., 2019; Fehrenbach, Isolan, and Münchow, 2021). Micromechanical interlocking remains the primary bonding mechanism for self-etch adhesives despite the fact that chemical bonding also occurs (Duarte et al., 2011; Perdigão, 2020).

The effectiveness of self-etch adhesive systems can vary due to factors such as composition (Cuevas-Suarez et al. 2019; Ageel and Alqah-tani, 2019) and shelf life (Iliev et al., 2021; Perdigão et al., 2021). The annual failure rate of one-step self-etch adhesives has been noted to be higher than that of two-step self-etch and etch-and-rinse adhesives (Perdigão et al., 2009). However, the clinical performance of more recent one-step self-etch adhesives has shown some improvements (Josic, Mazzitelli, et al. 2022; Perdigão et al., 2021). Therefore, it is important to exercise caution while using these adhesives to bond with chemically activated resin cements (either self-cured or dual-cured) due to the potential negative chemical interaction between the acidic adhesive and the resin cement (Cheong et al., 2003; Silva et al., 2011). Studies have demonstrated that the bond strength between self-cured cement and dentin decreases with lower pH values of the bonding agent used (Sanares et al., 2001). When a simplified adhesive is applied to a self-cured cement, the bond strength reduces by 10–50 % compared to when the same adhesive is utilised with a cement that requires light curing (Sanares et al., 2001). These decreased bond strength values result from the interaction between the residual acidic monomers in the adhesive inhibition layer and the binary peroxide-amine catalytic components present in chemically cured resin composites (Sanares et al., 2001). This interaction results in the neutralisation of the tertiary amine of the resin cement and a lack of reaction with the initiator, which reduces the strength of the bond at the adhesive-cement interface. To

ensure the maximum performance of resin cements, it is recommended to use dual-cured or self-cured cements only when they are combined with three-step total-etch systems or with self-etching primer systems that contain a separate bonding agent. For all other adhesive systems, it is wiser to use only photo-activated resin cement.

Applying a hydrophobic resin coating can enhance the sealing ability of one-step self-etch adhesives and limit the negative interaction with dual-cured or self-cured cements (de Carvalho et al., 2021). However, their application is still reliant on the use of the proper technique. Despite the latest developments in bonding with self-etch adhesives, satisfactory bonding to enamel can only be achieved in the long term by pre-treating with phosphoric acid.

### 2.3. Self-adhesive resin cements

Resin cements that can bond to dental tissues without requiring etching procedures or bonding adhesives are available and popular in clinical settings due to their one-step application. These cements contain phosphoric acid methacrylate, which is capable of demineralising hard tissues after being mixed. Although the initial pH level is low (pH < 2.0), only superficial demineralisation of the enamel and dentin is achieved (Perdigão, 2020). A reaction between the phosphate groups, alkaline fillers and hydroxyapatite from enamel and dentin neutralises the acidity of the resin and leads to an increase in the pH level up to 7.0 (Perdigão, 2020).

Chemical bonding, as opposed to micromechanical retention, is the main bonding mechanism of newly developed resins. Acid groups in the resins promote chemical adhesion by chelating the calcium ions of hydroxyapatite (Perdigão, 2020; Fukuda et al., 2003).

Self-adhesive resin cements can dissolve a portion of the smear layer without completely eradicating the smear plug in the dentinal tubules. However, a thick smear layer can be detrimental to the bond strength of such cements, as hydroxyapatite is essential for the chemical bond. Using phosphoric acid to etch dentin before the application of self-adhesive resin cement is not recommended, as it can harm the bond strength (Hikita et al., 2007; Manso and Carvalho, 2017). On the other hand, adhesion can be enhanced with the use of mild acidic agents such as 25 % polyacrylic acid as a dentin conditioner, as it may take away any loosely bound portions of the smear layer (Pavan et al., 2010; Scholz et al., 2021). Nonetheless, the interaction between mild acidic conditioners and self-adhesive resin cements needs further validation in clinical practice. It is highly recommended to use a strong acid, such as 37 % phosphoric acid, to pre-treat enamel (Perdigão et al., 2021).

Compared to Resin modified glass ionomer cement (RMGIC) and glass ionomer cement (GIC), one advantage of self-adhesive resin cement is that it causes less postoperative sensitivity (Shetty et al., 2012). However, compared to conventional multi-step resin cements, self-adhesive resin cements exhibit lower adhesive performance and bond strengths to both enamel and dentin (Miotti et al., 2020), making them unsuitable for cementing restorations with minimal retention and resistance forms such as resin-bonded bridges. Additionally, they are unsuitable for veneer cementation due to their weaker enamel bonding and a greater tendency to discolour (Manso and Carvalho, 2017). While a two-year study showed similar clinical outcomes for self-adhesive and conventional resin cements (Taschner et al., 2012), a five-year prospective clinical study demonstrated that total-etch resin cement had better marginal continuation and adaptation (Eltoukhy et al., 2021).

## 3. Polymerisation reaction

In the context of resin cements, dimethacrylate resin monomers undergo a series of chemical reactions to achieve polymerisation. This results in the formation of a cross-linked polymer network that incorporates filler particles. The polymerisation process can be elucidated through a series of steps, commencing with the creation of free radicals via chemical reactions or the application of light or heat (*Activation*).

These radicals then initiate the reaction by attacking carbon–carbon bonds (*Initiation*), leading to the formation of a covalent bond with one of the carbon atoms and leaving the other with an unpaired electron. This unpaired electron enables the propagation of the reaction, ultimately leading to the formation of a polymer chain (*Propagation*). The process may terminate for various reasons, including increased polymer viscosity that limits chain movement (*Termination*) (Cadenaro et al., 2019).

The degree of conversion (DC) achieved by resin cements, or the proportion of aliphatic C = C (double) bonds converted into C–C (single) bonds to establish the polymeric network, is generally around 60 % (De Souza et al., 2015; Fidalgo-Pereira et al., 2023). This is because the polymerisation reaction increases the viscosity of the cement, making the reactive species less mobile (Moraes et al., 2009). Incomplete polymerisation of the cement can lead to higher sorption and solubility values, which may accelerate cement degradation at the interface (Aldhafyan, Silikas, and Watts, 2022; De Souza et al., 2015). This degradation can result in a reduction in bond strength between the cement and the substrate (Aldhafyan, Silikas, and Watts, 2022; De Souza et al., 2015), leading to debonding, secondary caries or fracture (De Souza et al., 2015). Moreover, unreacted monomers, which are not bound to the polymeric chain, can also aggravate the pulp and trigger an inflammatory response (Chang et al., 2014).

Several factors can impact the degree of conversion of resin cements and potentially decrease the lifespan of indirect restorations. They include the material composition, such as the type of monomers and activation system components, as well as the potential interactions between the bonding system and the cement (Pegoraro, da Silva, and Carvalho, 2007). The characteristics of the restoration being cemented, such as optical properties and thickness (Mendonça et al., 2019; Fidalgo-Pereira et al., 2023), can also affect the degree of conversion, as can the properties of the photoactivation process (Aldhafyan, Silikas, and Watts, 2022, 2021).

### 3.1. Chemically activated resins

Chemically activated resin cements are typically delivered in a dual-tube system; one tube contains the initiator (benzoyl peroxide), and the other contains the co-initiator (tertiary amine, mostly N, N-bis (2-hydroxyethyl)-p-toluidine). The peroxides used can produce enough radicals to be mixed with the tertiary amine, causing a *charge-transfer* interaction that initiates polymerisation. When these two components are mixed, a chemical reaction occurs, triggering the polymerisation process and causing the resin cement to harden and set. Such cements are suitable for use in thick restorations and for bonding posts and crowns made of opaque materials – for example, highly opaque ceramics or metallic copings. Their use aims to ensure long-term maximum properties in areas that cannot be reached by light. However, the working time of these cements is limited compared to their extended setting time, and they tend to become more yellowish in colour due to the high concentration of activators (Ferracane, Moser, and Greener, 1985). Moreover, while refrigeration can extend the limited shelf life of these resins to some extent, the primary hurdle remains the uniform amalgamation of the two pastes, resulting in a homogenous mass that achieves even setting (De Souza et al., 2015; Ferracane, Moser, and Greener, 1985; Pegoraro, da Silva, and Carvalho, 2007).

### 3.2. Light-activated resins

Photo-activated resin cements are a recommended option in cases where the translucency of the restoration necessitates the passage of curing light, such as in translucent veneers. Light-cured resins, which contain all of the necessary chemical constituents, including initiators and activators, in a single tube, are associated with advantages such as time efficiency and reduced air inclusion risk, as no mixing is required.

Camphorquinone (CQ)/amine is the most commonly employed

photo-initiator system, with an extensive photo-initiation capability and a peak absorption at 470 nm (Taira et al., 1988; Jakubiak et al., 2003). However, its susceptibility to yellowing has limited its use, resulting in the adoption of alternative initiators such as 1-phenyl-1,2-propanedione (PPD) and Lucirin TPO, which exhibit absorption peaks at 410 nm and 390 nm, respectively (Schneider et al., 2009; Bakopoulou, Papadopoulou, and Garefis, 2009).

The photopolymerisation process involves a CQ initiator that absorbs photons within the blue wavelength range, becoming excited and subsequently reacting with a co-initiator to generate free radicals. Within most dental monomers, methacrylate groups rapidly bind to these free radicals at one end of the (C = C) double bond. This process leads to the other end of the bond becoming a radical itself, initiating a chain reaction that propagates. This chain reaction proceeds rapidly, auto-accelerating until either the available monomer concentration decreases or the densification process restricts monomer mobility, impeding further reactions (Fig. 1).

The optimal polymerisation of light-activated resins requires the light source to be situated as close to the tooth as possible, irrespective of the photo-initiator used. Furthermore, the angle of the light curing unit's tip plays a significant role in the quality of the transmitted light energy; thus, it should be kept at a 90-degree angle over the tooth to optimise light transmission to the depth of the material (Price, Felix, and Whalen, 2010; Marghalani, 2016).

### 3.3. Dual-cured activated resins

The development of dual-cured resin cements sought to merge the benefits of photo- and chemically activated systems to achieve an optimal degree of conversion in the deepest regions of a restoration as well as a controlled working time and a short setting time. These systems consist of two pastes: a catalyst paste containing a chemical initiator, typically benzoyl peroxide, and a base paste containing the photo-cured resin cement and the tertiary amine responsible for activating the self-cured reaction. The polymerisation process is initiated by the physical (photo) and chemical (redox) activations that occur when the two pastes are mixed and exposed to light. The interaction between the tertiary amine and benzoyl peroxide ensures that the cement polymerises in regions with insufficient light. However, inadequate photo-activation of dual-cured resin cements may result in a reduced degree of conversion (Moraes et al., 2009; Fidalgo-Pereira et al., 2023), resulting in reduced hardness, increased solubility, lower flexural and compressive strengths and inferior bond strength to dentin compared to directly light-cured dual cements (Aldhafyan, Silikas, and Watts, 2021, 2022; Vrochari et al., 2009; Fidalgo-Pereira et al., 2023).

## 4. Current advancements and future directions

Recently, researchers have been examining the use of restorative composite resin as an alternative luting material due to its advantages over traditional resin cements. These advantages include higher strength, cost-effectiveness, lower marginal deterioration and a wider range of colour choices (Falacho et al., 2022; Lopes et al., 2020; Magne et al., 2018). Composite resin is distinct from resin cements since it contains a higher proportion of filler particles, making it more viscous and less flowable (Tomaselli et al., 2019). To address this issue, methods such as preheating at temperatures of 55 °C and 60 °C as well as ultrasonic vibration have been explored in order to decrease film thickness and viscosity (Tomaselli et al., 2019; Magne et al., 2018).

Both methods have proved to be successful in decreasing the material's film thickness. However, some of the tested composite resins were unable to achieve a film thickness of < 50 µm, a characteristic mandated by ISO standard 4049:2019 (ISO 2019), after preheating and exposure to ultrasonic vibration (Falacho et al., 2022). When a thin film thickness is not attainable, it can significantly affect the fracture resistance and marginal adaptation of the restoration (May et al., 2012; de Souza et al., 2022). Consequently, additional investigation is needed before a specific composite can be used as a luting agent (Marcondes et al., 2020).

A new class of resin cements, universal resin cement, was recently launched by 3M Dental (3M Oral Care, St. Paul, MN, USA), and it is gaining acceptance by clinicians. With a true 'universal' concept/class, this cement can be utilised in a conventional mode, a selective etch or a self-adhesive mode. The availability of these choices simplifies the clinical decision to select the cementation technique that suits each case. More materials may emerge under this new classification.

## 5. Clinical recommendations

The durability and success of bonded indirect restorations are related to the quality and strength of the adhesive resin-based cements. The following steps should be considered to improve the bonding effectiveness of adhesive resin cements:

- To reduce the degradation of bonded interfaces, dentin can be pre-bonded with a dentin-bonding agent immediately after being cut (*Immediate dental seal*). Applying a dentin adhesive to freshly prepared dentin can decrease its permeability (Josic, Sebold, et al. 2022; Elbishari et al., 2021; Hardan et al., 2022). Additionally, a hydrophobic resin coat can be applied to improve the bond strength of simplified adhesives (one bottle total etch, one-step self-etch) by increasing the hydrophobicity of the adhesive layer (de Carvalho et al., 2021). This process makes the adhesive interface less

### Polymerization reaction:

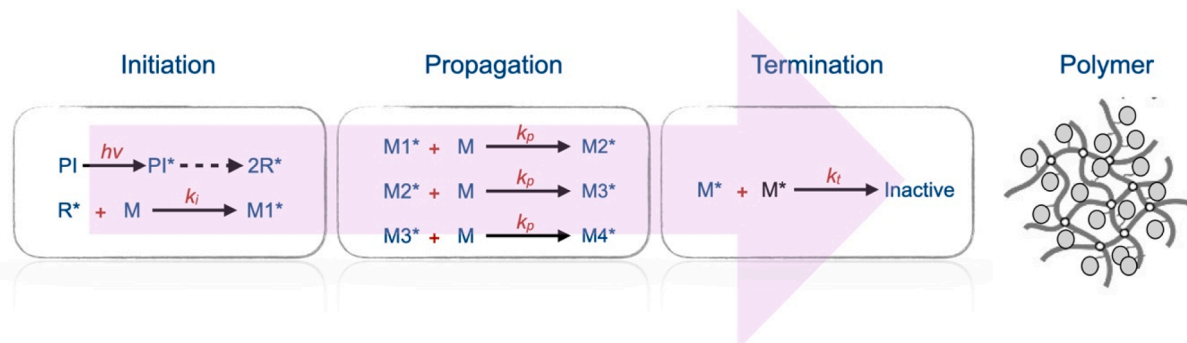


Fig. 1. Free-radical photopolymerisation involves a series of sequential stages. Initiation creates monomer molecules with unpaired electrons. During propagation, these radical entities join with additional monomers, causing the formation of elongating polymer chains. Ultimately, the growth mechanism comes to a halt as a result of one or more termination reactions (Watts and Algamaiah, 2023).

permeable to water and less susceptible to water degradation (de Carvalho et al., 2021).

- Refraining from using temporary cements containing eugenol and ensuring thorough cleaning of the preparation before bonding are recommended (Garcia et al., 2020). Studies indicate that eugenol-free temporary cement can still decrease the bonding of adhesive cements when dentin is contaminated (Carvalho et al., 2014). Therefore, the crucial factor for successful bonding is the proper cleaning of the preparation, which can be achieved through low-pressure and small-particle air abrasion, followed by water spray (Carvalho et al., 2014; Lima et al., 2021).
- To minimise the degradation of the bond interface, chlorhexidine can be applied after the process of acid etching when using etch-and-rinse dentin adhesives (Perdigão et al., 2021). This is because chlorhexidine, an antibacterial agent that also inhibits matrix metalloproteinase, helps preserve the collagen integrity of the hybrid layer that etch-and-rinse adhesives produce, which reduces its degradation (Perdigão et al., 2021). However, the use of chlorhexidine is not recommended with self-etch or self-adhesive resin cements, as it might have a negative effect on their integrity when bonded to dentin (Di Hipólito et al., 2012).
- Applying greater seating pressure during the bonding process can be beneficial. This technique can reduce the amount of water absorption, which, in turn, can decrease water infiltration into the underlying dentin and create a better-quality adhesive interface (Duarte et al., 2011; Chieffi et al., 2007).

## 6. Summary

This review provides valuable insights for dental professionals seeking an in-depth understanding of the current state of the field and the future prospects of dental adhesion. The following conclusions can be drawn from the review:

There are several factors that contribute to the selection of resin cements, including the remaining tooth structure (type of preparation), clinical steps simplification and bond strength needed.

It is important to understand the material composition and possible interactions between different initiator systems in adhesives and resin cements.

Etch-and-rinse resin cements provide the best bond strength compared to other cements.

The utilisation of resin composite materials as cement depends on their composition and can only be utilised if preheating or sonication can reduce film thickness to < 50 µm.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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