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Polymer Chemistry of Dental Adhesives

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INTRODUCTION

Dental adhesives are water soluble, non-toxic materials that bind composite resins to dentin and enamel. Adhesive systems are dependent on a polymerization process at the interface and require different moieties to prepare the substrate to effectively interact with the tooth surface. Due to their critical role in restorative procedures, many chemists are interested in strengthening the adhesive bond strength at the interface. This research explores the common issues found in adhesive systems, and how current researchers are working to approach these complications to increase the success rate of dental restorations.

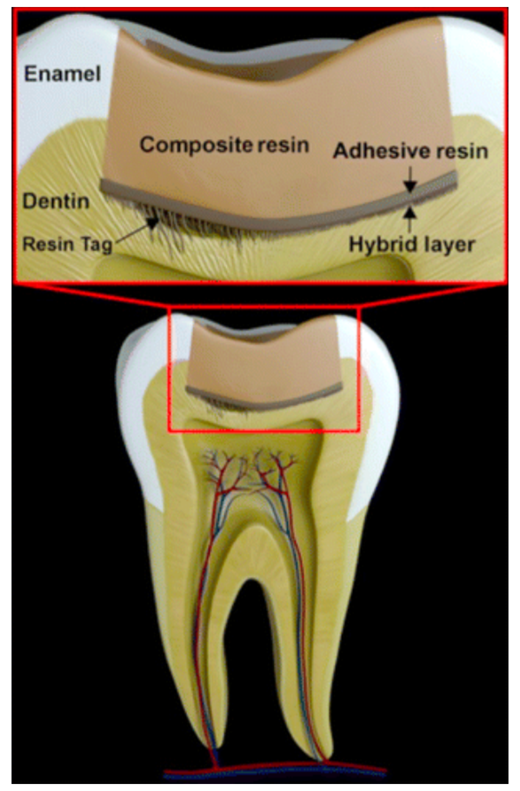
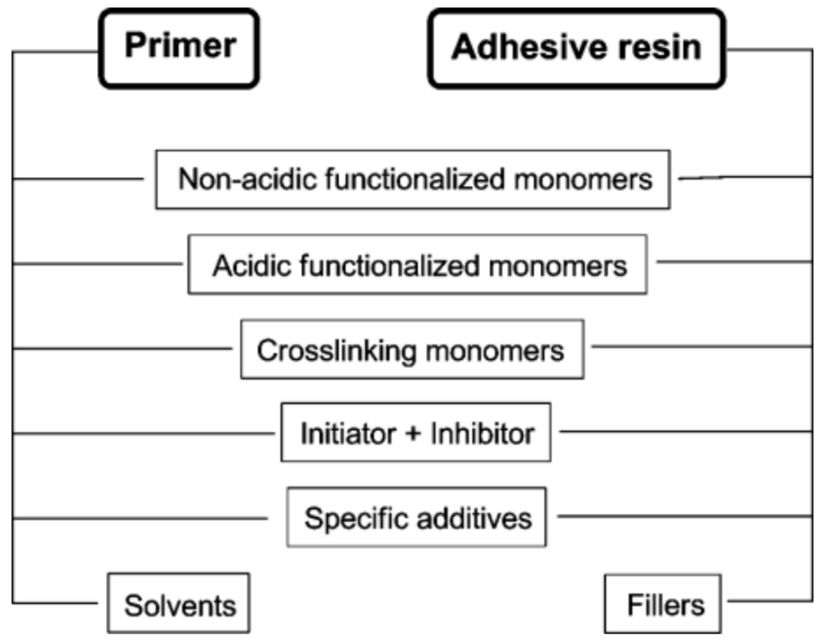


Figure 1: Cross-sectional composite resin-dentin interface [1]



Primer

Adhesive resin

Non-acidic functionalized monomers

Acidic functionalized monomers

Crosslinking monomers

Initiator + Inhibitor

Specific additives

Solvents

Fillers

Figure 2: Components of adhesive system [2]

To better understand the role of the adhesive layer, it's important to visualize the interface itself **(Fig. 1)** and the components that make up an adhesive system **(Fig. 2)**. All adhesive systems are resin-based materials that adhere enamel/dentin, the two outer layers of the tooth, to the composite material that serves as a substitution of the missing tooth material. In general, adhesive systems rely on development of resin tags reaching into the etched enamel substrate. In order to form an adhesive layer, the inorganic dentin matrix is replaced by adhesive monomers and becomes interlocked between collagen fibrils after polymerization takes place.

DENTAL ADHESIVES AND THEIR LIMITATIONS

Current literature demonstrates a focus on identifying the reasons for a restorative failure, and approaching the solution from the root of the problem. The following sections investigate these challenges:

1. HYDROLYSIS/DEGRADATION

Ideal monomers should be relatively hydrophilic for efficient infiltration into water-saturated dentin and binding to collagen fibrils [3]. However, many hydrophilic methacrylate adhesives are far more susceptible to hydrolysis in the aqueous oral environment. Enzymatic and hydrolytic degradation of dental adhesives greatly contribute to the formation of secondary caries and remains to be a challenge to overcome for polymer chemists. In the cases of cross-linking monomers like HEMA and Bis-GMA, the hydrolysis of such molecules can result in dangerous and harmful molecules as seen in **Fig's 3 and 4**. Decha et. all explored this issue and synthesized a new monomer that they called **HMTAF** [3]. After a series of tests, **HMTAF** proved to be a hydrolytically resistant monomer.

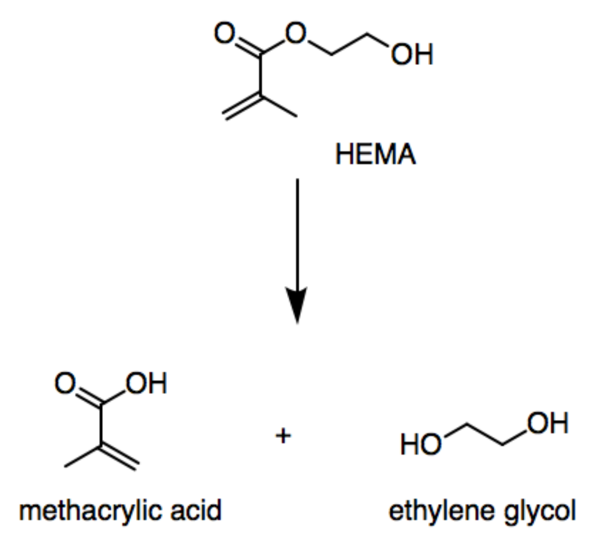


Figure 3: Hydrolysis of HEMA resulting in methacrylic acid and ethylene glycol

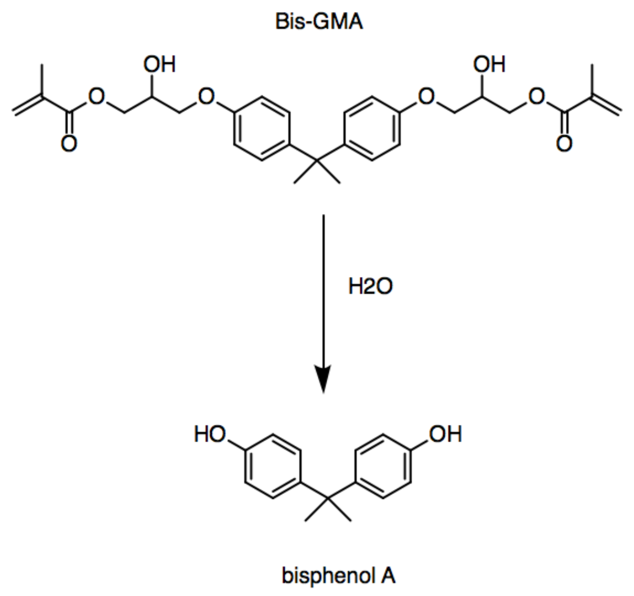


Figure 4: Hydrolysis of Bis-GMA resulting in BPA

2. INADEQUATE POLYMERIZATION

There are numerous factors that have the potential to affect the extent of polymerization in an adhesive system. Although there are several important considerations for monomer selection, one of the most important is dependent on which technique is used - self-etch or etch & rinse [4]. Since SE adhesives simultaneously demineralize and infiltrate dental tissues, this technique has become increasingly popular in the field.

With that in mind, Catel et. all carried out a series of synthetic experiments to find synthetic monomers that exhibit strong chelating properties in SE adhesives [4]. Ultimately, they reported the synthesis of four new polymerizable α-phosphonooxy phosphonic acids. In comparison to other adhesives based on MDPA and MDP, these four new adhesives exhibited a significant improvement in both reactivity and bond strength [4].

3. CONTAMINATION

Due to the natural wetness of the oral environment, oral fluid contamination is a common problem during clinical restorative procedures [5]. Lee et. all report the synthesis of a new polymer functionalized with catechol groups as a solution to this problem [5]. The catechol groups of proteins work by displacing the water molecules that are tightly bound to the substrates, to form hydrogen bonding with surfaces. The catechol groups exhibit strong chelation with metal oxides and ions, which allow it to provide strong cross-links or polymerization [5]. As seen in **Figure 5 part c)**, a new polymer was synthesized and proved to be resistant to contamination by oral fluids.

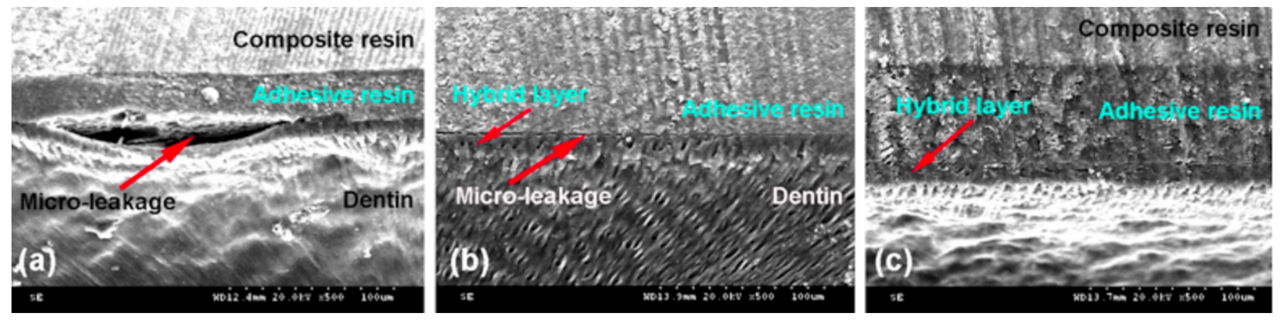


Figure 4. SEM micrographs of dentin bonded with adhesives [5].

CONCLUSION

Adhesive systems will continue to rapidly revolutionize operative dentistry. The stability of the adhesive layers is strongly influenced by numerous factors and must be optimized to ensure adequate bonding and lasting restorations. In order to deliver quality and ethical patient care, further clinical studies must be conducted to evaluate the in-vitro findings with the goal to develop more effective and long-lasting adhesive systems.

ACKNOWLEDGEMENTS

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POLYMER CHEMISTRY OF DENTAL ADHESIVES

Abstract

Dental adhesives are water soluble, non-toxic materials that bind composite resins to dentin and enamel. Adhesive systems are dependent on a polymerization process at the interface and require different moieties to prepare the substrate to effectively interact with the tooth surface. Due to their critical role in restorative procedures, many chemists are interested in strengthening the adhesive bond strength at the interface. This review paper covers the evolution of dental adhesive systems over time and provides an extensive overview of what components make up a dental adhesive system. Additionally, this article explores the common issues found in adhesive systems, and how current researchers are working to approach these complications to increase the success rate of dental restorations.

Keywords

polymer chemistry, dental materials, adhesive systems

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INTRODUCTION

For decades, dental researchers have extensively studied biomaterials and their interface with dental hard tissue. Although dental metals, cements, and ceramic materials have been used for many years, none of these materials have the ideal mechanical, physical, biological, and surface characteristics that are required for successful everlasting restoration [1-3]. For these reasons, researchers have been searching for a biocompatible material that allows for strong interfacial interactions, while maintaining the durability and longevity that materials such as metals and cements offer [4]. Due to their desired biological and mechanical properties, the use of polymeric materials in dentistry and medicine has been on the rise. Polymeric materials can be tailored to a wide range of biomedical applications in dentistry such as drug delivery, antimicrobials, prosthetics, and restorative dentistry [1-3,5].

The complexity of both the tooth structure and dental adhesive have made it challenging to achieve the optimal interaction between the dental hard tissue and selected biomaterial [6]. These adhesive systems are complex mixtures of hydrophilic and hydrophobic monomers, solvents, photo initiators and additives that help strengthen the adhesive bond [2]. Each of these components could be attributed to the failure of an adhesive layer, which ultimately influences the success of the restorative procedure. For this reason, investigators have spent many years optimizing dental adhesive systems.

To better understand the role of the adhesive layer, it’s important to visualize the interface itself. **Fig. 1** demonstrates a cross sectional image of an anatomical tooth [7]. All adhesive systems are resin-based materials that adhere enamel/dentin, the two outer layers of the tooth, to the composite material that serves as a substitution of the missing tooth material. In general, adhesive systems rely on development of resin tags reaching into the etched enamel substrate. For dentin, the formation of resin tags in the dentin tubules is the major retention formation of the dentin/composite interface [7,8]. In order to form an adhesive layer, the inorganic dentin matrix is replaced by adhesive monomers and becomes interlocked between collagen fibrils after polymerization takes place.

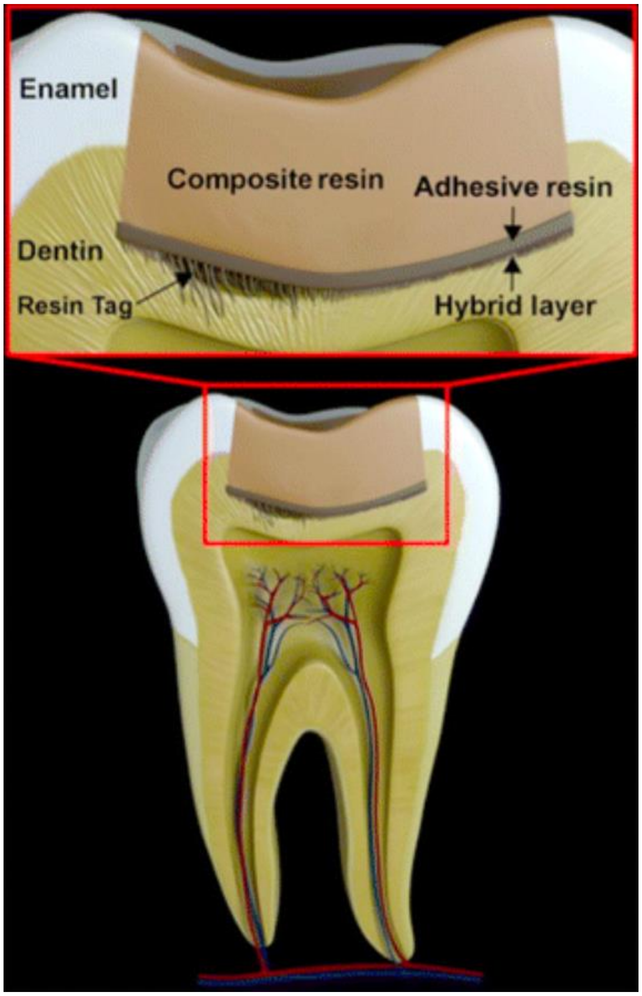


Figure 1: Cross-sectional composite resin-dentin interface [7]. Adhesive resin, resin tags and the hybrid layer are represented in the dentin and adhesive resin interface.

This review paper will provide an overview of the current literature for dental adhesive systems, and discuss the synthetic approaches to improve bond strength. By improving bonding interface strength, researchers hope to develop techniques that will provide successful, long-term restorations and ultimately improve dental care for patients. Current literature demonstrates a focus on identifying the reasons for a restorative failure, and approaching the solution from the root of the problem. Some of the complications in restorative dentistry that are addressed in this review paper are hydrolysis/degradation, inadequate polymerization, and cross-contamination at the dentin surface.

ETCH-AND-RINSE VERSUS SELF-ETCH TECHNIQUE DEVELOPMENTS

Dating back to 1955, Buonocore introduced the idea of an acid etching technique to dental enamel that revolutionized adhesive dentistry [9-11]. At the time, one of his students, John Gwinnett, reported that adhesive resins have the ability to penetrate acid-etched enamel and form apatite crystallites [12]. In this experiment, Gwinnett discovered a new hybridized surface composed of both enamel and resin, [8,9,12]. Since that discovery, researchers have focused on improving adhesive technology which has extensively advanced the clinical performance of dental restoratives.

Nowadays, adhesive systems follow either an “etch-and-rinse” or “self-etch” technique that interact at the tooth surface differently (**Fig. 2)** [4,9,10]. Etch-and-rinse systems pretreat the dental tissue with phosphoric acid before applying an adhesive. The left side of **Fig. 2** demonstrates the differences between the three and two step approach to the Etch-and-rinse strategy. The two step strategy eliminates the need for a second and third step by combining the primer and adhesive resin in one bottle. On the right side of **Fig. 2**, Self-etch technique utilizes an acidic monomer that can condition and prime dentin and enamel simultaneously and eliminate the need for a third step[2]. One-step self-etch techniques are known as “all-in-one” adhesives that combine all three parts into one bottle. Regardless of the approach, both systems ultimately form a hybrid layer between the resin and dentin [10]. Oftentimes, the choice of technique used is at the discretion of the dentist and is depending on the location of the restoration.

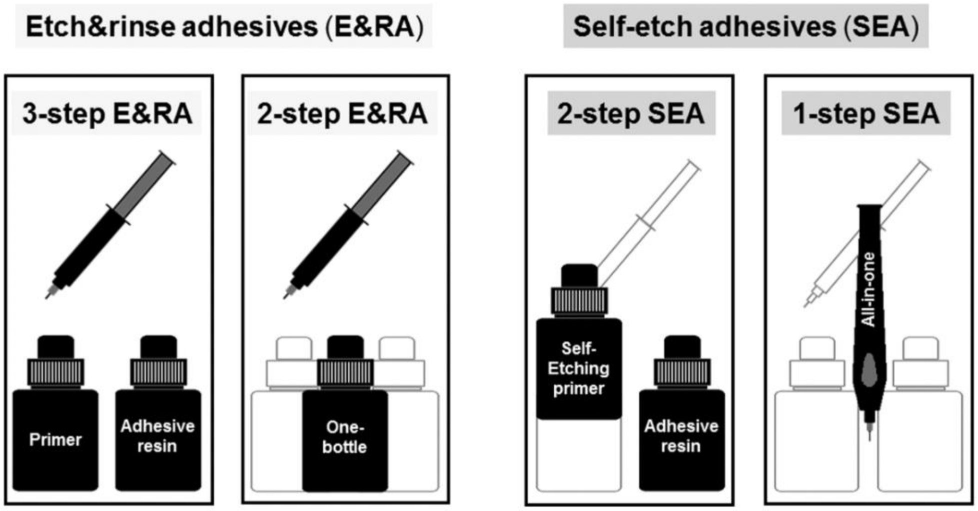


Figure 2: Self-etch vs. Etch and Rinse adhesives [2]. Etch-and-rinse adhesive (E&RA) involves two or three steps whereas the simplified Self Etch Adhesive (SEA) approach can be done in one or two steps.

A. ETCH-AND-RINSE TECHNIQUE

The Etch-and-Rinse (E&R) technique offers an effective method to achieve strong interfacial bonds between adhesive materials and dental hard tissue. It is solely used on enamel. On dentin, this approach is offered as a two or three step system, depending on whether the primer and bonding agent are combined or separated **(Fig. 2)**. After using phosphoric acid etchant in acid-etching, this step results in a selective dissolution of hydroxyapatite crystals [2,9,10]. Once the acid etching step is complete, the exposed network of collagen is rinsed out with water. Next, adhesive resin and primers incorporate monomers into the collagen network by replacing the water between the collagen fibrils. In this step, it is important to select a hydrophilic monomer like 2-hydroxyethyl methacrylate (HEMA), to ensure the coating of wet collagen fibrils expands the collagen network. This results in the formation of polymerized resin tags and a hybrid layer that helps seal the dentin tubules. By separating the etching, priming and bonding processes, this approach can be advantageous and allows for multiple goals to be achieved.

B. SELF-ETCH TECHNIQUE

Unlike E&R's, Self-etching techniques (SE) rely on acidic monomers that simultaneously condition and prime the dentin [10]. This eliminates the need for a separate etching step and makes it possible to demineralize and infiltrate the dentin at the same time [2,9,10].

COMPONENTS OF DENTAL ADHESIVE SYSTEMS:

Enamel-dentin-adhesive systems are composed of a variety of monomers, photo polymerization initiators, inhibitors, solvents, and further additives (**Fig. 3) [2].** Each of these components will be discussed in the section below.

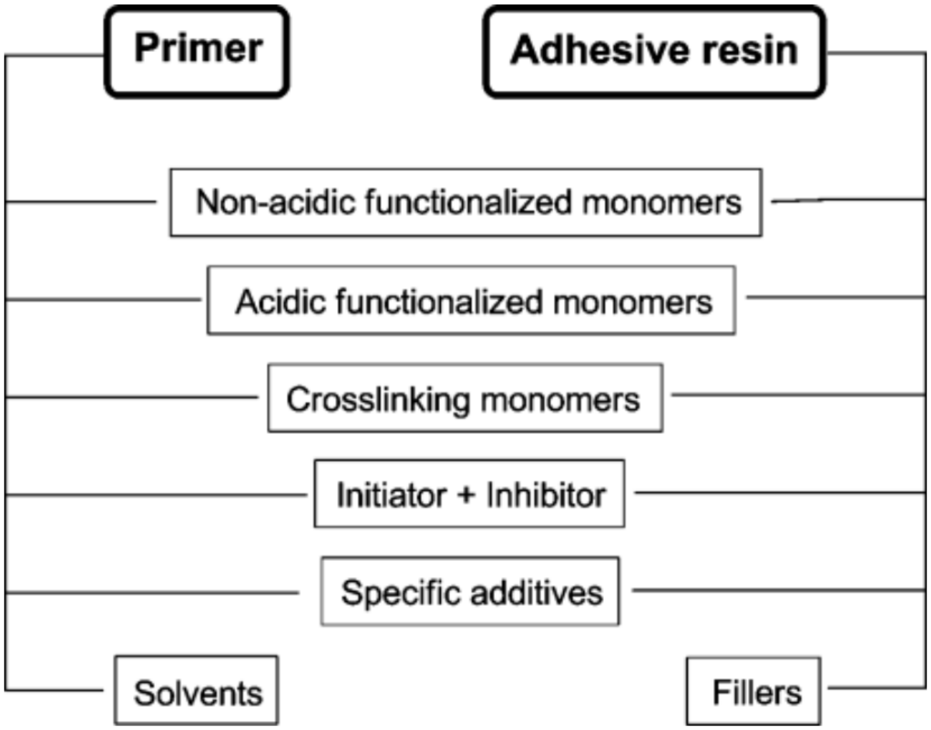


Figure 3: Components of adhesive system [2]. Contemporary adhesive systems consist of a mixture of monomers, polymerization initiators, inhibitors and solvent additives.

MONOMERS

The main components of dental adhesive systems are the monomers that ensure a strong bond between the resin composite and the adhesive layer. In addition to the general requirements for dental monomers, enamel-dental adhesives require specific characteristics for a long-lasting, successful bond. Some of these special requirements are as follows:

1) Optimal wetting/film-forming characteristics
2) Rapid and strong interaction with dentin and enamel
3) Hydrolytic stability in water-based adhesives

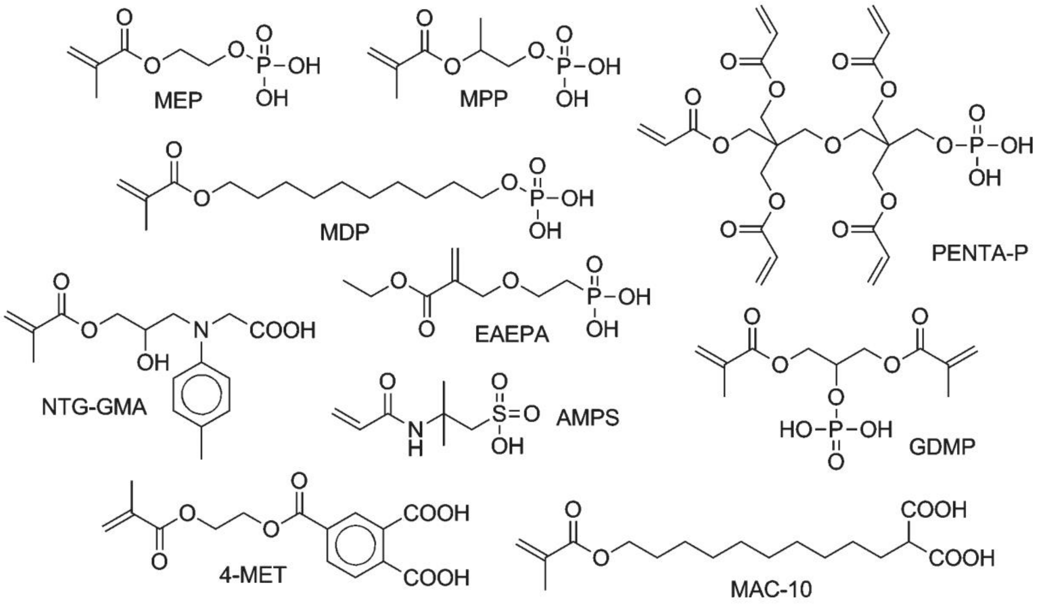
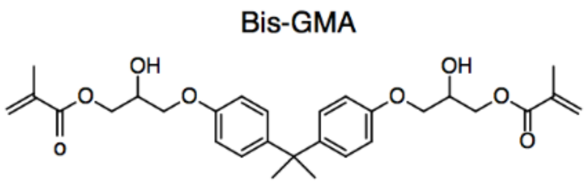


Figure 4: Acidic monomers used in adhesive systems [2]

Acidic monomers are used to etch and interact with the dental hard tissues. Although there are many possible monomers that are available for use as seen in **Fig. 4**, cross-linking dimethacrylates are commonly used to adhesive systems to effectively form a polymer network [2]. The two most commonly used cross-linking dimethacrylates are bisphenol-glycidyl methacrylate (bis-GMA) and hydroxylethyl methacrylate (HEMA) **(Fig. 5)** [2, 3,5]. Each of these dimethacrylates exhibit different properties such as polarity, polymerization shrinkage, water solubility, and reactivity in radical polymerization [2]. While bis-GMA used to be the most popular choice among dentists as a bonding agent, advances in adhesive systems have shown that hydrophobic monomers like bis-GMA are not as effective in infiltrating the hydrophilic dentin substrate [13].



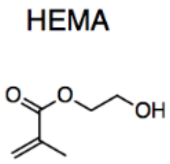


Figure 5: Most popular cross-linking monomers: Bis-GMA and HEMA chemical structures

For this reason, more hydrophilic monomers are usually used as primers in dental adhesives to enhance wetting properties, one of the necessary requirements for optimal adhesion. An example of that type of monomer is hydroxyethyl methacrylate (HEMA) which is completely miscible in water [2,7].

For the best results, adhesive systems are oftentimes composed of monomers with both hydrophilic and hydrophobic groups. One technique that has been employed is incorporating HEMA into hydrophobic mixtures to enhance miscibility in the dentin substrate [14]. On one hand, a hydrophilic, water-loving part enables the connection and infiltration of the dentin. On the other hand, the hydrophobic part, such as bis-GMA cross links the adhesive monomer to the composite materials [7].

Another approach is modifying the polymers by incorporating groups such as ethyl, methyl, or hydrogen to replace phosphate, amide, hydroxyl and carboxyl groups [15]. Introducing these groups can help achieve a chemical interaction with the hydroxyapatite and dentine collagen, ultimately increasing the hydrophilic nature of the bond [15-17].

One of the downfalls to the addition of hydrophilic groups, such as hydroxyl, phosphate, ester, and carboxyl moieties is the susceptibility to water sorption in the adhesive layer, leading to hydrolysis in the oral environment [8,12,18,19] The issue of hydrolysis and degradation will further be discussed. After air drying and evaporating the solvents from the interface, the adhesive layer is ready to begin polymerization via light curing [12,19].

PHOTOINITIATORS

Adhesive systems reach their final mechanical properties through a light-cured, free-radical polymerization process. When an adhesive monomer is exposed to photocuring light, polymerization can be achieved [5]. The curing exposure time, resin chemistry, photo initiator type and orientation of the restoration are all factors that can influence the success of polymerization. Studies have shown that the degree of polymerization of dental adhesives is greatly influenced by the functional monomers and photo-initiator selected specifically [2,3,5].

One of the most common photo-absorbing initiators used is camphorquinone(CQ)[2]. The main benefits of CQ are the low toxicity of the initiator and its photodegradation products[2,4]. CQ can absorb light in the blue region of the visible light spectrum (400-500 nm), with an absorption maximum at 465 nm.

Fig. 6 demonstrates the mechanism behind the photoinitiation step. After a rapid electron transfer from the amine to CQ, a radical is formed. Once the active CQ radical is formed, it is transferred to the tertiary amine compound via hydrogen abstraction. After these steps, radical polymerization will continue and the adhesive layer will harden [2].

Polymerization can be characterized by the formation of long and interchain cross links of carbon-carbon single bonds, marking the conversion of monomer into a polymer. During this photopolymerization process, hydrophobic and hydrophilic molecules cross-link to form a hardened adhesive bond. The extent of conversion for adhesive monomers to polymers determines the ultimate strength of the polymer [2,3].

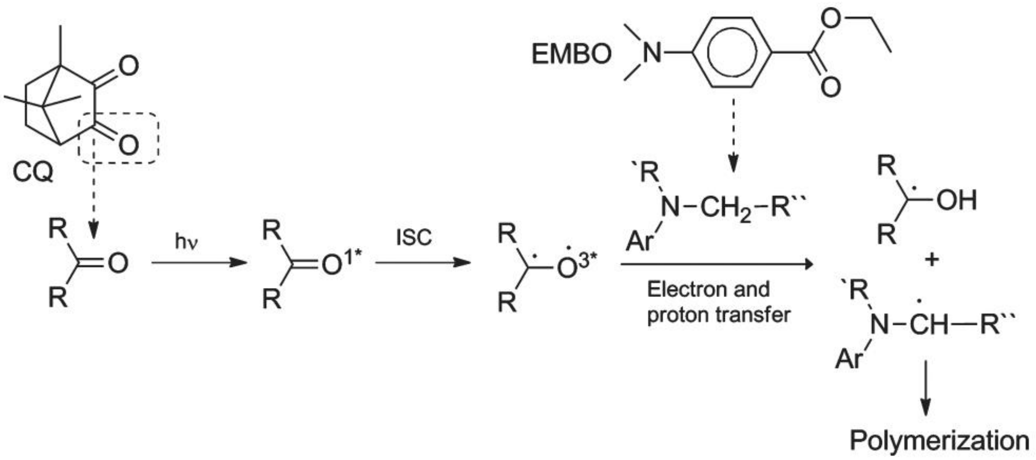


Figure 6: Radical polymerization and photoinitiation of CQ [2]. Mixture of camphorquinone (CQ) and tertiary amine (EMBO) are used to initiate free radical polymerization.

SOLVENTS AND AND INHIBITORS ADDITIVES

In order to increase the solubility and infiltration of adhesive resins into dentin, adhesive systems contain organic solvents. Solvents like water and ethanol promote interactions between monomers and dentinal water, and work to dilute the resin mixture due to their hydrophilic nature [11]. Conversely, solvents like acetone remove water from dentin. It is critical that all residual solvents be properly evaporated before polymerization, as these solvents are not polymerizable molecules and will inhibit polymer network formation. If this occurs, the physical properties of the adhesive resin are reduced, weakening the overall polymer structure [11].

Additionally, there have been numerous studies and reports demonstrating the beneficial effects of protease inhibitors on the longevity of the hybrid layer. Oftentimes, the inhibitor chlorhexidine (CHX) is added to prevent matrix metalloproteases (MMPs) from hydrolyzing and degrading the collagen fibers necessary for bonding [2]. Another example of inhibiting agents are quaternary ammonium methacrylates (QAMs), which are antimicrobial molecules that also work to inhibit MMP. Some QAMs such as methacryloyloxy dodecylpyridinium bromide

(MDPB) are very advantageous because of their ability to copolymerize with methacrylates in the adhesive resin. Although these additives show promise, further research still needs to be done to minimize the loss of tensile strength that has been observed in this study [2].

SYNTHETIC APPROACHES TO IMPROVE ADHESIVE SYSTEMS:

In recent years, resin-based composites have been increasingly used as the ideal restorative material as clinicians stray away from using amalgam. However, it has been shown that composite material is nearly twice as likely to fail and far more costly to replace [7]. With the minimal use of amalgam, it is imperative that investigators look into improving the longevity of adhesive systems [7].

Although there are numerous reasons why a composite restoration can fail, the three most common issues are as follows:

1. Hydrolysis/degradation [18]
2. Inadequate polymerization [16]
3. Contamination [7]

The following sections will address these three issues.

SYNTHESIS AND CHARACTERIZATION OF NEW HYDROLYTIC-RESISTANT DENTAL RESIN ADHESIVE MONOMER

As mentioned previously, ideal monomers in primers should be relatively hydrophilic for efficient infiltration into water-saturated dentin and can bind to collagen fibrils [18]. However, many hydrophilic methacrylate adhesives are far more susceptible to hydrolysis in the aqueous environment of the oral cavity. Enzymatic and hydrolytic degradation of dental adhesives greatly contribute to the formation of secondary caries and remains to be a challenge to overcome for polymer chemists. To address this limitation, researchers have investigated ways to synthesize a new hydrolytic resistant monomer [18].

It has been suspected that the hydrolytic degradation of ester bonds and lack of antibacterial properties in resin adhesives have greatly contributed to the short lifetime of resin-based composites. Currently, 12-methacryloyloxydecyl pyridinium bromide (MDPB) is the only commercially available antibacterial monomer. However, like other methacrylate derivative monomers, MDPB is very susceptible to hydrolysis. In the cases of HEMA and Bis-GMA, the hydrolysis of such molecules can result in dangerous and harmful molecules [2,18].

Fig. 7 and Fig. 8 illustrate the mechanisms behind this problem. The hydrolysis of HEMA as seen in **Fig. 7** provides methacrylic acid and ethylene glycol. Researchers have made note of allergic reactions to residual unpolymerized HEMA and hyper-sensitivity [18]. **Fig. 8** demonstrates the hydrolysis of Bis-GMA resulting in bisphenol A, or BPA. BPA is an endocrine disruptor that imitates the body’s hormones and interferes with the transport, function and production of natural hormones. As a result, both these commonly used monomers have the potential for dangerous physiological damage to the human body [18].

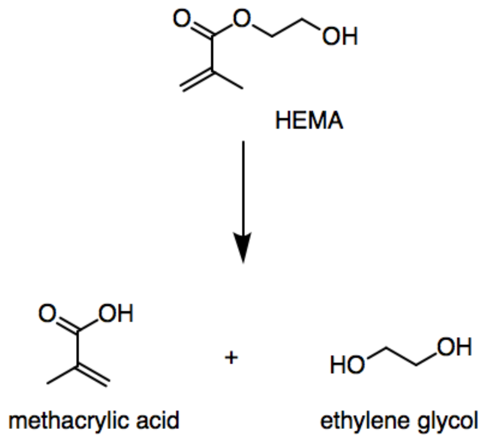


Figure 7: Hydrolysis of HEMA resulting in methacrylic acid and ethylene glycol

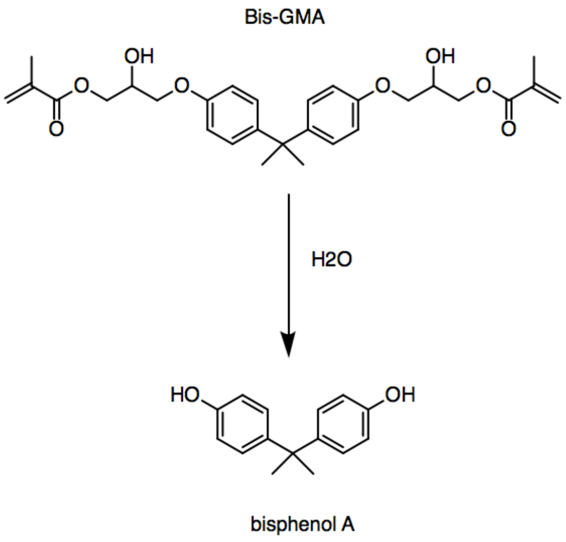


Figure 8: Hydrolysis of Bis-GMA resulting in BPA

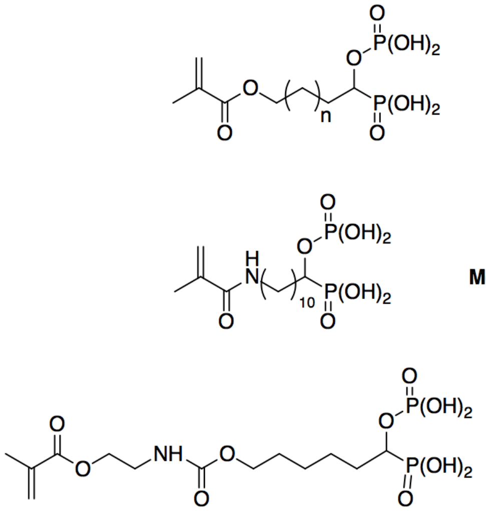
Decha et. all explored this issue and ultimately synthesized a new quaternary ammonium fluoride methacrylamide-based monomer that they called **HMTAF** [18]. HMTAF was synthesized in 7 steps with an overall yield of 30%. In order to study the hydrolytic resistance of synthesized monomers, **HMTAF** was subjected to an acidic aqueous solution of hydrochloric acid. The proton NMR spectra of **HMTAF** before and after treatment with the acid were identical indicating the high stability of monomer **HMTAF** in an acidic environment. In other words, **HMTAF** proved to be a hydrolytically resistant monomer.

SYNTHESIS, PHOTOPOLYMERIZATION AND ADHESIVE PROPERTIES OF POLYMERIZABLE α-PHOSPHONOOXY PHOSPHONIC ACIDS

There are numerous factors that have the potential to affect the extent of polymerization in an adhesive system. As mentioned previously, the selection of monomers is a critical component to the success of polymerization. Although there are several important considerations for monomer selection, one of the most important is dependent on which technique is used - self-etch or etch & rinse [16].

Since SE adhesives simultaneously demineralize and infiltrate dental tissues, this technique has become increasingly popular in the field. With this method, the acidic monomer selected is responsible for etching the tooth and must show a high rate of polymerization. It has been found that the ability of the acidic monomer to interact strongly with the calcium hydroxyapatite (HAP) significantly affects the success of an adhesive [2,16]

With that in mind, Catel et. all carried out a series of synthetic experiments to find synthetic monomers that exhibit strong chelating properties in SE adhesives [16]. It has been shown that polymerizable diphosphonic acids, β-ketophosphonic acids or phosphonic acids bearing urea groups can improve the adhesion of SE adhesives [15-17]. With the presence of both a dihydrogen phosphate group and phosphonic acids, the authors suspected that polymerizable gem-phosphonate phosphates held promising potential to increase polymerization.



Monomer
7a: n=3
7b: n=7

Monomer 16

Monomer 9

Figure 9. Structure of four synthetic monomers

Ultimately, they reported the synthesis of four new polymerizable α-phosphonooxy phosphonic acids as seen in **Fig 9**. All four monomers were characterized by ^{1}H-NMR, ^{31}P-NMR, and ^{13}C-NMR spectroscopy. As seen in **Fig. 10**, the ^{1}H-NMR spectrum of monomer 7b is shown. From 1.26-1.73 ppm, 1.75-1.96 ppm and 4.13 ppm nine methylene groups can be identified. From 4.35-4.46 ppm, the signal for the proton of the CH bearing both acidic groups can be seen. Lastly, the protons of the methacrylate groups are confirmed by the signals at 1.92 (methyl group), 5.60 and 6.07 ppm [16].

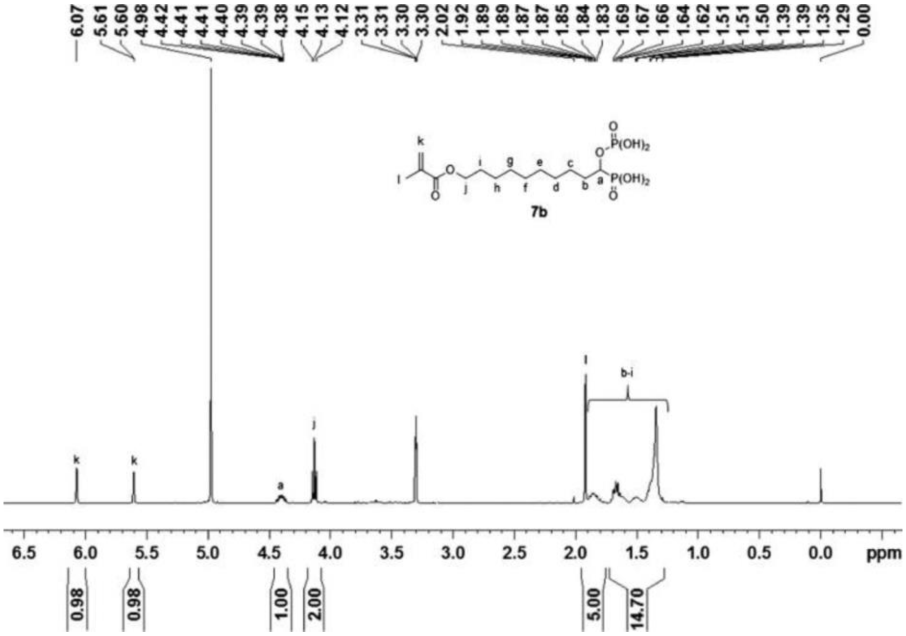


Figure 10: ^{1}H-NMR spectrum of monomer 7b [16].

In order to assess the reactivity of the four acidic monomers, they proceeded to polymerize each monomer under the same conditions. In comparison to other adhesives based on 10-methacryloyloxydecyl phosphonic acid (MDPA) and 10-methacryloyloxydecyl dihydrogen phosphate (MDP), these four new adhesives exhibited a significant improvement in both reactivity and bond strength [16].

They attributed this increase in reactivity to the presence of two additional acidic groups that allow for hydrogen bonding. Contrary to MDP and MDPA, the hydrogen bonding in the four new monomers resulted in an increase of propagation reaction rate constant [16]. Additionally, they found the hydrogen bonding to restrict mobility, thus decreasing the rate of termination and increasing the rate of polymerization.

In order to evaluate the adhesive properties and bond strength of these four monomers, they formulated SE adhesives with a mixture of the new acidic monomers, crosslinking monomers, photo initiators, solvents and additives. Ultimately, their results confirmed that the presence of two acidic groups considerably improved the adhesive properties of SEAs. In comparison to adhesives containing only phosphonic acid MDPA or dihydrogen phosphate MDP, the α-phosphonooxy phosphonic acids significantly strengthen the dentin enamel shear bond strength. All in all, these newly synthesized monomers proved to be excellent and promising candidates for high performance adhesive systems [16].

CATECHOL-FUNCTIONALIZED SYNTHETIC POLYMER AS A DENTAL ADHESIVE TO CONTAMINATED DENTIN SURFACE FOR A COMPOSITE RESTORATION

Due to the natural wetness of the oral environment, oral fluid contamination is a common problem during clinical restorative procedures [7,12,19]. In the bonding procedure, excessive water and fluids can prevent the adhesive resin from infiltrating into the dentin surface, thus reducing the strength of the bond. Additionally, salivary components may also decrease polymerization by inhibiting monomer and dentin interactions. For that reason, researchers have sought out the development of dental adhesives that can effectively adhere to contaminated, wet, dentin surfaces, while also providing adequate bond strength [7,12].

Lee et. all report the synthesis of a new polymer functionalized with catechol groups as a solution to this problem [7]. The catechol groups of proteins work by displacing the water molecules that are tightly bound to the substrates, to form hydrogen bonding with surfaces. The catechol groups exhibit strong chelation with metal oxides and ions, which allow it to provide strong cross-links or polymerization [7].

Previously, catechol groups have been used to prepare coating materials and functional adhesives such as bone adhesives, hydrogel-based adhesives, and coatings on yeast cells. Unlike alcohols, amines, and carboxylic acids, catechol groups can absorb onto hydroxyapatite more readily [7]. To test their theory, the authors prepared the catechol-functionalized polymer by free radical copolymerization of the TBDMS-protected dopamine methacrylate (TBDMS-DMA) with methoxyethyl acrylate (MEA).

After synthesizing poly(DMA-MEA), the authors investigated how salivary components would affect the adhesive resin to dentin. In order to mimic the tooth interface, they characterized a bonding region consisting of four layers: composite resin, adhesive resin, hybrid layer and dentin. Although the adhesive resin alone showed no indication of structural leakage at the interface, a leakage pattern appeared in the presence of artificial saliva. This indicated that the region between the hybrid layer and the adhesive resin layer was the weakest structure, and most susceptible to crack formation. The authors suspected that the addition of water caused the resin polymers to precipitate on the dentin surface and reduce the formation of collagen in the hybrid layer.

Previous studies have reported the potential for catechol groups to form Fe^{3+} complexes in the presence of water and polymerized cross-linked chains [17]. In an attempt to minimize any leakage patterns, the authors pretreated the poly(DMA-MEA) with Fe^{3+}. As a result, the addition of poly(DMA-MEA) with Fe^{3+} in artificial saliva showed no leakage patterns in the bonding interface [21]

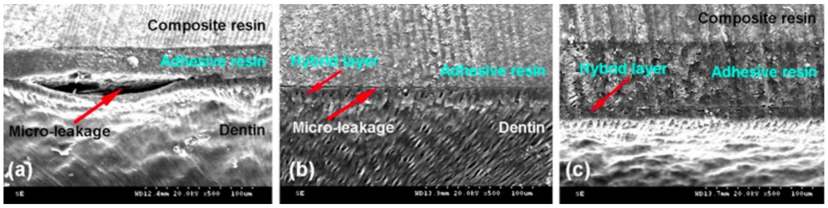


Figure 11. SEM micrographs of dentin bonded with adhesives [7]. (a) only adhesive resin, (b) adhesive resin after artificial saliva contamination and (c) adhesive resin and poly(DMA_ME) with Fe^{3+} in artificial saliva

In summary, a new catechol-functionalized polymer was synthesized and proved to be resistant to contamination by oral fluids as seen in **Fig. 11.** With the addition of Fe^{3+}, no leakage patterns were visualized and the bond strength of commercial adhesive resin to the dentin surface was improved. After a series of cytotoxic tests, the polymer did not inhibit gingival fibroblast proliferation [7]. Despite the potential of the catechol-functionalized polymer as a contamination resistant dental adhesive, the authors note that further chemical modifications must be done to maximize the bonding.

CONCLUSION

Adhesive systems will continue to rapidly revolutionize operative dentistry. The stability of the adhesive layers is strongly influenced by numerous factors and must be optimized to ensure adequate bonding and lasting restorations. In-Vitro research studies as discussed in this manuscript show promising results for better adhesion. In order to deliver quality and ethical patient care, further clinical studies must be conducted to evaluate the in-vitro findings with the goal to develop more effective and long-lasting adhesive systems.

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