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Review article

Mathematical models of polymer-dentin physicochemical interactions and their biological effects

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A R T I C L E   I N F O

A B S T R A C T

Dental adhesion is the result of a physicochemical interaction between tooth structure and the adhesive polymeric restorative material. Adhesion involves molecular interactions at the interface between these constituents. Furthermore, mechanical interlocking is a common type of adhesion important in dental materials. This type of bonding involves the penetration of the adhesive into the dental surface and requires different energetic considerations for an optimal interface. An adequate infiltration of adhesive monomers into demineralized dentin depends on several factors that are determined by the atoms on the surface of the structures and the effects of surface energy on the thermodynamic work of adhesion. The polarity, solubility and viscosity of the adhesive system and the surface energy and moisture of dentin tissue are key factors that contribute to adhesion energy. The main goal of dental material adhesion is to produce an interface that is strong and durable. Thus, it is important to optimize the infiltration of adhesive monomers into exposed collagen fiber networks and dentinal tubules in order to increase the strength of the Resin-dentin bonds and produce adequate dentin sealing.

Abbreviations

Bis-GMA: bisphenol A diglycidyl methacrylate
BS: bond strength
DC: degree of conversion
EGDMA: ethyleneglycoldimethacrylate
HEMA: 2-hydroxyethyl methacrylate
10-MDP: 10-methacryloyloxydecyl-dihydrogen phosphate
4-META: 4-methacryloyloxyethyl trimellitate anhydride
MMPs: matrix metalloproteinases
Phenyl-P: 2-methacryloxyetyl-phenyl-hydrogen phosphate
TEGDMA: triethylene glycol dimethacrylate
UDMA: urethane ethyl dimethacrylate

1. Introduction

Scientific advances in dental materials have enabled the incorporation of polymeric technology in the direct and indirect restoration of dental structure. Composite resins have been classified as an alternative for ceramics or metal materials used in amalgam restorations. Composite resins are cheaper and have aesthetic advantages over these other materials (Kirsten et al., 2007). Over the past two decades, polymeric resin-based bonding materials for both dental cementation and dental restoration have been revolutionized by continuous technological developments in dentin bonding. These technological developments have focused on optimizing dentin-polymer interface durability (Liu et al., 2011).

Dental adhesives are polymeric composites of several chemical substances but mainly include the resin monomers HEMA and TEGDMA. These substances have low molecular weights and form a mixture capable of infiltrating dental tissue when used in combination with solvents, such as ethanol and acetone (Kirsten et al., 2007). HEMA is soluble in water, ethanol and acetone when in a non-polymerized state. This monomer is highly hydrophilic; thus, HEMA is well-matched with the relative wetness of dentin. This compatibility leads to improved adhesive penetration and dentin bond strength. However, polymerized or non-polymerized HEMA easily absorbs water. This water absorption can lead to monomer dilution and impairment of adhesive interface durability (Jacobsen and Soderholm, 1995). TEGDMA is mainly used in combination with higher molecular weight monomers, such as Bis-GMA and UEDMA. This combination of materials provides a less viscous mixture that compensates for Bis-GMA viscosity and improves adhesive manipulation (Asmussen and Peutzfeldt, 2001). Based on the "interpenetration" concept, the micro-mechanical bonding between the polymer and tooth is caused by adhesive diffusion into irregularities and acid conditioned spaces on the dental surface. This dental adhesive mechanism produces a continuous connection with dentin collagen fibers referred to as the "hybrid layer" (Carrilho et al., 2007a; Craig, 1997; Nakabayashi et al., 1991) (Figure 1).
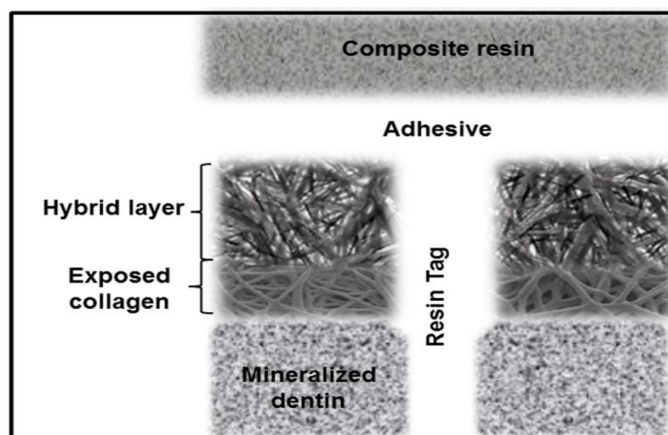

Fig. 1. Hybrid layer created by an etch-and-rinse adhesive.

The mechanism of bonding to dentin is based on diffusion. Minerals are removed from the dental hard tissues with phosphoric acid and replaced by resin monomers. Note the depth of the hybrid layer and the incomplete infiltration of resin into water-filled collagen fibrillar matrices. The resin tags seal the dentinal tubules and decrease dentin permeability. Dentin is a highly organic tissue with a high relative wetness associated with a constant dentinal fluid, which causes difficulty in the adhesive penetration of hydrophobic materials in dentin structures (Pashley et al., 2011; Spencer, 2010; Hashimoto et al., 2004).

Dentin permeability depends on the pulp-dentin complex. This complex functions as a suction-impeller pump and behaves as a permeable, diffusible and penetrable solid. Additionally, this system functions as a dynamic substrate that varies morphologically under certain clinical situations (Pashley et al., 2011). Adhesive inter diffusion into the collagen fiber network and adhesive polymerized monomer stability in the hybrid layer are key micro-mechanical events within the interface co structure that contribute to stress distribution, high sealability and decreased dentin permeability (Frassetto et al., 2016; Ferracane, 2006). The interfacial physicochemical relationship between the adhesive polymer and dental structure depends on surface characteristics. Thus, the interaction between a liquid (adhesive polymer) and a solid (dentin) is based on atom binding and not the shape or size of the structure. This is an important feature for mechanical property analyses (Craig, 1997).

Hence, a thorough review of the factors related to polymer-dentin interface behavior can lead to a better understanding of interfacial interactions and the development of novel materials and techniques.

2. Factors influencing the dental bonding structure

Resin monomer diffusion into collagen fiber networks is directly related to the wettability characteristics of the liquid (adhesive) and solid (dentin). This relationship depends on multiple factors, including surface free energy, contact degree, solubility parameters, polarity, viscosity and capillarity.

2.1. The relationship between energy, surface tension and thermodynamic work of adhesion

Energy and surface tension are phenomena of work that occur as a result of the sum of intermolecular forces within the solid (surface energy) or liquid surface (surface tension). This force is expressed as free energy per unit of area (Toledano et al., 2003). The phenomenon occurs because the surface molecules have a higher energy than the inner molecules and experience less intermolecular attraction. This energy difference occurs because of the change in cohesive forces between atoms at the surface. Work is necessary to attract molecules to generate a surface. This work is produced by the attraction of liquid inner molecules to the surface molecules (Craig, 1997; Bayne et al., 1992). (Figure 2).
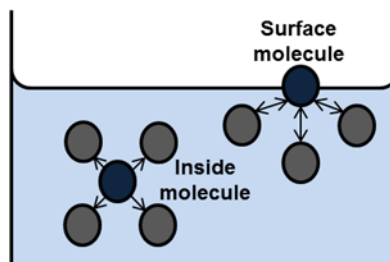

Fig. 2. Surface tension.

The internal atoms are in equilibrium, and interatomic forces are balanced. However, there are fewer interatomic interactions between the atoms on the outer most layer of the surface. The surface free energy represents the difference between an atom on the surface and an atom in the interior. Systems in nature tend to have an energetic equilibrium with low energy consumption. To achieve this, liquid must diminish its surface area to create higher stability. Therefore, there is a force from the exterior area to the inner area. This force makes the liquid resistant to extension or penetration (Toledano et al., 2003; Baier, 1992).

If the dentin surface energy and the attraction of adhesive molecules for tissue exceed the surface tension of the adhesive, the work between the adhesive and dentin can be spread to achieve balance. Conversely, if the adhesive surface tension exceeds the tooth surface energy, there is no interaction between molecules at the interface, the work does not spread and the wettability is minimal (Henestroza, 2010). Thus, the attraction or

repulsion degree is determined by the interfacial strain between material surfaces, which determines the adsorption, wettability and adhesion at the interface (Toledano et al., 2003). Fowkes (1990) and Asmussen and Peutzfeldt (1998) have determined that there is a thermodynamic work of adhesion through the adhesive interface with the substratum, (W_A), expressed as:

$$W_A = \gamma_l(1+\cos\theta) = 2\,(\gamma_s^d \cdot \gamma_l^d)^{1/2} + 2(\gamma_s^+ \cdot \gamma_l^-)^{1/2} + 2(\gamma_s^- \cdot \gamma_l^+)^{1/2}$$

Where γ is the surface free energy present on solids (γ_s) and in liquids (γ_l); d represents disperse energy; and (+) and (-) represents the polar components (acid or basic) of the solid and liquid (Asmussen and Peutzfeldt, 1998). W_A is expressed in units of mJ/m^2. In the determination of $W_A = \gamma_1\,(1+\cos\vartheta)$, θ is an important factor. θ is defined as the contact angle, which is the angle connecting the solid-gas interface and the solid-liquid interface. The contact angle is defined as the "wettability measure"(Henestroza, 2010; Toledano et al., 2003).(Figure 3).
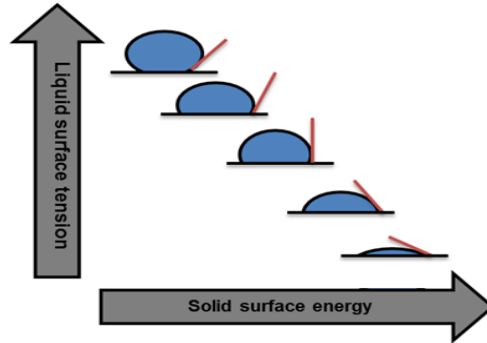

Fig. 3. Contact angle.

The angle is formed by the solid surface and the tangent from the contact with the drop of liquid from the equator. According to the Wenzel equation (Asmussen et al., 1995), the measure of the contact angle as related to the true contact angle is expressed as:

$$\theta = \cos\theta = r \cdot \cos\theta$$
Where r is the average surface roughness.

The interactions between the solid's surface energy, the liquid's surface tension and air contact can be summarized in the concept by calculating the interfacial energy. The interfacial energy incorporates the three phases that constitute the interface: solid, liquid and vapor. (Figure 4).
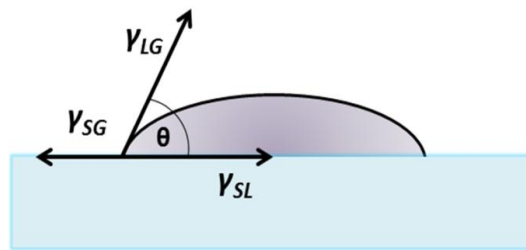

Fig. 4. Interfacial energy.

If the solid–vapor interfacial energy or surface energy of the solid is denoted by γ_{SG}, the solid–liquid interfacial energy or surface tension of the liquid is denoted by γ_{SL}, and the liquid–vapor interfacial energy by γ_{LG}, then the equilibrium contact angle ϑ can be determined by Young's Equation:

$$\gamma_{SG} - \gamma_{SL} - \gamma_{LG}\cos\theta = 0$$

Thus, wettability can be quantified as non-wetting (>90∘), wetting (<90∘) and spreading (∼0∘) according to the liquid spread on the solid (Krawczyk et al., 2013; Toledano et al., 2003). Ideal conditions should be selected to promote spreading without reaching a liquid surface tension that is low enough to adversely decrease the liquid's cohesive strength (Marshall et al., 2010). For optimal wettability and penetration, near zero contact angle values

should be achieved in adhesive-dental structure interactions. Additionally, it is necessary to increase the free energy of solid surface molecules that are available to interact with the wetting liquid (Toledano et al., 2003).

The acid conditioning of dental surfaces increases cleanliness and roughness. Importantly, this conditioning increases surface energy and provides a proper micro mechanical anchoring that increases surface contact area and improves bonding effectiveness. This vital feature creates porosities that improve adhesive polymer penetration into dental enamel (Henestroza, 2010; Kanca, 1992). In dentin, the conditioning effect of etch-rinse adhesives is related to smear layer removal and the creation of spaces for hybridization. This effect occurs at both the intertubular dentin surface and in the peritubular dentin (Nakabayashi et al., 1991). Another important factor is polarity (Asmussen and Peutzfeldt, 1998) (Figure 5).
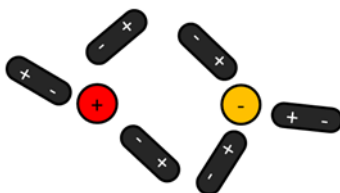

Fig. 5. Polarity.

Polarity is defined as a molecule with permanent dipoles created by a separation of negative and positive charges. The dipoles interact with other molecules through electrostatic forces. These forces occur due to the attraction between electrons of covalent molecules and other molecules with higher electronegativity. Dental monomer adhesives differ in their polar components of free surface energy (γ^{ab}). This polarity of free surface energy can be estimated with the following equation:

$$\gamma^{ab} = 2(\gamma_s^+ . \gamma_l^-)^{1/2}$$

Monomer polarity is based on the refraction index and the dielectric constant of the components. There is a linear variation in polarity based on the weight percentage (%) composition of monomers with positive (+) and negative (-) charges in the system. The charges determine the surface energy (Krawczyk et al., 2013; Asmussen and Peutzfeldt, 1998; Asmussen and Uno, 1993; Asmussen et al., 1995; Fowkes, 1990). Asmussen and Peutzfeldt (1998) found that altering the acidity of substances to increase γ_l+ also increases W_A. (Figure 6).
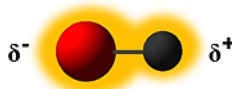

Fig. 6. Dipole-dipole interactions.

Dipole-dipole interactions are electrostatic interactions between permanent dipoles in molecules. These interactions typically align molecules and increase attraction. A physical, but weak, bond is always present. Thus, while van der Waals forces occur at the interface, they are often supplemented by significant contributions from stronger bonds, such as permanent dipoles. Methacrylate monomers that comprise adhesive systems, such as Bis-GMA, UEDMA and TEGDMA, are characterized by their hydrophobic behavior. To improve adhesive wettability, it is necessary to add HEMA as a bi-functional monomer because of its hydrophilic properties. This mixture of hydrophobic and hydrophilic compounds becomes thinner and avoids adhesive segregation of nano-phases when polymerized, which improves the composite stability (Kirsten et al., 2007).

In addition to HEMA, maleic acid and 4-META can be utilized. These compounds typically contain functional groups that contain a carboxylic acid (-COOH) or its anhydride, phosphoric acid [-OP (=O) (OH)$_2$], or phosphonic acid [-P (=O)(OH)$_2$] (Ikemura and Endo, 2010).Hydrophilic functional monomers that enhance dentin bond strength are referred to as adhesion promoters (Van Landuyt et al., 2007).

A solid surface typically has a high value of $\gamma s-$, which can increase the interaction between adhesive materials that dissociate in aqueous solutions to release protons for acid–base reactions. Thus, high values of γ_l^+ are a mechanism to increase monomer adhesion. Apart from 'adhesion-promoting' and wetting effects, the proton-releasing functional groups of monomers may also lead to surface demineralization when applied to a solid surface (Nishiyama et al., 2004). However, this demineralization could lead to undesirable consequences related to

material biocompatibility, the activation of collagenolytic enzymes in subjacent tissue and polymeric hydrolysis (Mazzoni et al., 2007; Nishitani et al., 2006).

HEMA has a higher fractional polarity (0.093) than other hydrophobic monomers, such as Bis-GMA (0.005), TEGDMA (0.030) and UEDMA (0.040) (Asmussen and Uno, 1993). Increasing UEDMA in a mixture produces an increase in the contact angle and surface tension. This phenomenon is due to the molecular weight, polarity and hydrophobicity of UEDMA. The addition of polar substances, such as propionic aldehyde and maleic acid, reduces the contact angle and surface tension due to an increase in γ_l^+. A proper balance between the dispersed energy and surface free energy of the acid-base components that determine material polarity is required to maximize the thermodynamic work of adhesion. These characteristics determine the compatibility of different adhesives with adherent surfaces (Asmussen and Peutzfeldt, 1998; Krawczyk et al., 2013).

2.2. Molecular interactions between adhesives molecules and dentinal collagen

There are other functional monomers, such as 10-MDP, 4-META and phenyl-P. These monomers can chemically interact with dentinal residual hydroxyapatite and collagen fibers (Vaidyanathan et al., 2007). Non-covalent intermolecular interactions, including electrostatic attractions, result from an attraction between oppositely charged atoms. Vander Waals forces are responsible for the penetration of adhesive primers into the exposed type I collagen net of dentin (Vaidyanathan et al., 2007).

Self-etching adhesives do not require acid conditioning. Thus, the surface minerals remain intact. This advantage allows for an array of secondary interactions with the calcium salts of the hydroxyapatite (Van Meerbeek et al., 2011). The mechanism of "decalcification-adhesion" (Yoshida et al., 2001) is based on the precept of acid chemical bonding with the calcium of hydroxyapatite. This bonding is accompanied by a release of phosphate (PO_4^{3-}) and hydroxide (OH-) ions from the hydroxyapatite. Bond stability depends on the stability of the calcium salts formed (Van Meerbeek, 2011).

Feitosa et al. (2014) found that the interaction between calcium salts and monomers and the initial bond strength are influenced by the spacer chain length of functional monomers, i.e., the number of carbons within the molecule. The authors recommended a formulation of functional monomers with long hydrophobic spacer chains to achieve a more stable chemical interaction and increase adhesive-dentin interface durability (Feitosa et al., 2014). Another major factor that influences intermolecular interactions is the variability in the structural composition of collagen residues. The polarity and amino acid type strongly influence the chemical bonding of adhesive primers. However, this bonding effectiveness minimally contributes to resin-dentin bond strength (Vaidyanathan et al., 2007; Yoshida et al., 2004).

Vaidyanathan et al. (2007) concluded that "adhesion to biological molecules is a highly complex process based on interaction on a nano or atomic level, which can vary with the estimated parameters as molecular composition, charges differences, surface morphology and favorable 3D conformation of monomer functional groups to interact with bonding molecule". The development of functional monomers that can interact at a molecular level with dentin can improve technique sensitivity and decrease the use of phosphoric acid. The use of acid is controversial. Some authors consider this procedure to be an aggressive treatment for tissue because collagen is vulnerable to degradation by an incomplete infiltration of demineralized dentin (Van Meerbeek et al., 2011).

2.3. Adherence energy at the adhesive interface

Adherence energy is related to the dissipation capacity of the adhesive energy (ɸ) and the thermodynamic work of the adhesion (W_A) (Asmussen et al., 1995). The adherence energy (W_R) is expressed in J/m^2 and represented by the following equation:

$$W_R = \phi \cdot W_A$$

The ability to dissipate energy (ɸ) is associated with the polymer degree of conversion (DC), which is defined as the monomer percentage converted into a polymer during the polymerization process. The DC never reaches 100% and depends on the monomer type, photo-polymerization light intensity, exposure time, layer thickness and primers added to the mixture. A higher degree of conversion results in a lower energy dissipation capacity (Asmussen et al., 1995). The conversion rate results in a polymer with less cytotoxic effects and better mechanical properties. Previous studies reported a low degree of conversion in adhesive-dentin systems. As a result there is

low mechanical strength, residual solvent and increased permeability at the adhesive interface (Pashley et al., 2011; Kirsten et al., 2007; Asmussen and Peutzfeldt, 2001; Craig, 1997).

The DC is calculated by Raman spectroscopy. This analysis provides chemical information about the material and high resolution images of compositional variations (Marshall et al., 2010). The calculations are based on a decrease in the band intensity of double aliphatic bond peaks at 1.640 cm^{-1} and aromatic bond peaks at 1.610 cm^{-1} before and after photo-polymerization using the following equation:

$$DC\% = [1 - \frac{R \; polymerized}{R \; non \; polymerized}] \times 100$$

Where R is the height of the band (Hass et al., 2013).

The DC for a mixture of BisGMA/TEGDMA decreases as the percentage of BisGMA increases. A UDMA/HEMA mixture results in a relatively higher DC. The DC is increased in this type of mixture by adding a photo initiator, such as diketones, to accelerate the reaction (Peutzfeldt, 1994). Thus, the energetics of the adhesive interface can be determined based on the relationship between adherence energy W_R, the DC (associated with dissipation energy) and adhesive wettability (conditions that promote spreading by decreasing the contact angle). The contact angle depends on the energy and surface tension of materials at the interface (Asmussen and Peutzfeldt, 1998; Asmussen et al., 1995; Fowkes, 1990; Asmussen and Uno, 1993).

2.4. Solubility parameters

From a physical perspective, the adhesive interpenetration into dentin describes the resin's ability to spread across and through the dentin (Asmussen et al., 1991). The solubility parameter δ is estimated using the Small method (Asmussen and Uno, 1993). An F value (reported in the literature) is attributed to each functional group of a molecule (e.g., amide, anhydride, urethane, aldehyde, etc.), and the sum of the values for all component groups (ΣF) is calculated. Using the molar volume (V) of the substance (monomer concentration in a given volume), the solubility is determined with the following equation:

$$δ = ΣF/V$$

Hydrophilic monomer solubility is higher than hydrophobic monomers; however, monomer ratios influence the overall solubility of the mixture (Asmussen and Uno, 1993). Asmussen and Uno (1993) showed that HEMA has higher solubility (23.3 MJ$^{l/2}$/m$^{3/2}$) than Bis-GMA (21.5 MJ$^{l/2}$/m$^{3/2}$), TEGDMA (18.4 MJ$^{l/2}$/m$^{3/2}$) and UEDMA (21.4 MJ$^{l/2}$/m$^{3/2}$).

2.5. Viscosity and capillarity

Viscosity (η) is defined as the resistance to fluid deformation, and it is expressed by the viscosity coefficient:

$$\eta = \frac{\tau}{D}$$

Where τ is the shear strength represented as strength/surface and D is the sliding rate, which indicates the velocity gradient of the fluid volume movement. The sliding rate is expressed using the following equation:

$$D = \frac{dv}{dn} = \frac{v}{d}$$

Viscosity depends on the molecular weight of dental adhesives monomers; therefore, the surface tension also varies. Viscosity is used to analyze the relationship between material fluidity and penetration over time.

Bis-GMA is a cross-linked polymer with a high molecular weight, and thus, a high viscosity in the non-polymerized phase. Accordingly, diluted monomers, such as EGDMA and TEGDMA, must be added to Bis-GMA mixtures to compensate for the high viscosity (Kirsten et al., 2007).

A parameter derived from capillarity and viscosity is the diffusion or penetration coefficient (PC). The PC indicates the rate at which a liquid penetrates a capillary tube and is defined by the following equation:

$$PC = \frac{\gamma \cos \theta}{2\eta}$$

This factor includes variables, such as adherence energy and contact angle, that clearly influence penetration. A liquid with a low internal resistance to flow, i.e., a low PC, requires more time to achieve adequate spreading and adaption to the adherent surface (Marshall et al., 2010). The forces that influence the penetration of a liquid into a

capillary tube include surface tension, gravity and viscosity. Within the dentinal tubules, additional factors related to opposing forces and internal moisture conditions must be considered (Leforestier et al., 2010). Positive intra-pulpal pressure generates fluid movement toward the dentin surface through the tubule (Leforestier et al., 2010); therefore, hydrophilic monomers and solvents with compatible wetness are required to improve adhesive penetration, produce resin tags and reduce dentin permeability (Kirsten et al., 2007).

According to Leforestier et al. (2010), adhesive viscosity does not significantly influence the application time recommended by manufacturers (20 seconds), and the adhesive penetration time based on surface characteristics is relatively short. However, other factors, such as continuous fluid flow through the dentinal tubules and its lateral branches, impede the formation of resin tags (Pashley et al., 2011). A saturation technique with ethanol was proposed that showed improved tag formation when compared with dentin saturated with water (Carrilho et al., 2007b).

3. Influence of surface phenomena on bond strength

The adhesive bond strength (BS) to the dental structure measures the proficiency of the interface to resist strain without breaking. From a mechanical perspective, the BS is calculated as the force per area unit (F/A) and is expressed as MPa (Craig, 1997). Dentin BS is related to surface phenomena because it mainly depends on proper hybrid layer formation. This interpenetration also depends on mentioned factors and is represented by the following equation:

$$BS = e^{a+bx}$$

Where $x = (\delta + cp + d)^2$ and (a, b, c and d) are dependent constants of conditioned dentin, such as moisture or other factors related to structure mechanical properties and adhesive composition. This equation defines an interrelationship of BS in a tridimensional space as a dependent factor of adhesive solubility δ and polarity p. All of these variables influence the adherence energy (Asmussen and Uno, 1993).

The incomplete infiltration of adhesive into the demineralized dentin matrix has a direct implication on micro-mechanical behavior at the interface (Misra et al., 2004). Defects, that act as stress concentrators, such as leaching of non-polymerized monomer, phase separation of the adhesive into hydrophobic BisGMA and hydrophilic HEMA, and non-infiltrated spaces within the hybrid layer, dominate interface failures (Van Noort et al., 1991). The conventional opinion that a low elastic modulus, e.g., resulting from a phase separation in the hybrid layer, may provide a mechanical advantage to the system has been reevaluated. A finite elements analysis showed that regions of a low elastic modulus lead to a concentration of stress in high elastic modulus regions, such as the peritubular dentin (Misra et al., 2004).

This behavior could be explained by the viscoelastic response of the demineralized dentin. Pashley et al. (2003) reported that the deformation of collagen fibers was not recovered when the load (tension or compression) was eliminated, thus demonstrating that creep causes a permanent deformation of the demineralized dentin matrix. The molecular events that occur when the collagen matrix is under load include molecular elongation of the collagen fibrils. This elongation extends the hydrogen bonds and increases the longitudinal size across the fiber axis. Third, there is a sideslip of adjacent molecules across the axis. These first two events allow for elastic recovery if the elongation is not excessive; however, the molecular sideslip can be permanent (Pashley et al., 2003).

4. Biological consequences of an incomplete adhesive infiltration

Several authors (Mazzoni et al., 2013; Breschi et al., 2008; Carrilho et al., 2007a; Pashley et al., 2004) reported that the hybrid layer is unstable in aqueous environments because of the hydrolytic degradation of the collagen fiber net after adhesive infiltration. The fibers are exposed due to inadequate monomers impregnation in the inter-fibrillar spaces (Mazzoni et al., 2007; Nishitani et al., 2006; Mazzoni et al., 2013). Dentin metalloproteinases (MMPs) are proteolytic enzymes found in the mineralized matrix of dentin and saliva that travel through the dentinal tubules (Frassetto et al., 2016; Tjäderhane et al., 2013; Moon et al., 2010; Boushell et al., 2008; Malemud, 2006; Sulkala et al., 2002). MMPs induce degradation of exposed collagen proteins, which reduces dentin-resin bond strength (Pashley et al., 2011).

The synthesis and degradation of matrix proteins physiologically requires a strict regulation of MMP activity. This process must be controlled at multiple levels, including gene expression, post-translational activation, and the activity of tissue inhibitors of the metalloproteinases (TIMMPs) (Ma, 2010).

Many MMPs are synthesized and released as pro-enzymes or zymogens from connective tissue cells including fibroblasts, osteoblasts and odontoblasts (Mazzoni et al., 2007). This process requires the activation of molecular signal pathways related to oxidative stress and inflammation (Ma, 2010; Schweikl et al., 2006). This phenomenon can be triggered with self-etch adhesives and etch-rinse adhesives (Lehman et al., 2009; Zhang and Kern, 2009). MMPs identified in demineralized dentin include MMP-2,-3,-8,-9,-20 and cathepsins (Pashley et al., 2011; Tersariol et al., 2010; Kotra et al., 2001; Moon et al., 2010). Several authors, including Mazonni et al. (2007), Mazonni et al. (2013) and Nishitani et al. (2006), established that monomeric systems incorporated in etch-rinse and self-etch adhesives increase the collagenolytic and gelatinolytic activity within the demineralized collagen matrix due to a decrease in pH.

Phosphoric acid has a low pH (0.7-1); however, it has the ability to denature MMPs and reduce enzyme activity (Breshi et al., 2008; Pashley et al., 2003; Pashley et al., 2004). Tezvergil-Mutluay et al. (2013) and Manzonni et al. (2013) reported that MMP-2 and -9 activity is increased after conditioning with phosphoric acid, and this acid does not denatured the endogenous MMPs or inhibit cathepsins activity in the dentin matrix.

A thorough understanding of adhesive infiltration mechanisms into highly organic and permeable tissue is vital because these processes directly relate to dental pulp function. The response to the adhesive materials involves transcription factor activation and protein expression, which can in turn induce MMP activity (Sbardella et al., 2012). Consequently, there is a degradation of the collagen matrix in the hybrid layer, leading to a significant decrease in dentin-resin bond durability (Mazzoni et al., 2013; Mazzoni et al., 2006; Pashley et al., 2004). The development of strategies to protect the pulp-dentin complex requires better interpenetration and stability of the adhesive monomers into the dentin. An increased durability of adhesive restorations could ameliorate a variety of problems, such as micro-leakage, recurrent caries, postoperative sensitivity and restoration loss (Tjäderhane et al., 2013a, 2013b).

5. Conclusion

The interfacial physicochemical phenomena between adhesive polymers and dental structures depend on the surface characteristics and compositional changes of both materials. Adhesion energy strongly influences the contact angle and thermodynamic work of adhesion. The effects of solubility and polarity of a substance on the adhesive wettability are important for the formation of an interpenetrating hybrid layer into collagen fibers. This layer determines the micro-mechanical behavior success at the polymer-dentin interface.

Achieving adequate infiltration by hydrophilic adhesives into a highly organic and wet tissue, such as dentin, remains a critical problem. Despite advances in adhesive composition and molecular behavior, problems related to dentin demineralization depth and adhesive monomer diffusion can impair the formation of a stable hybrid layer. In addition, the hydrolysis of resin–dentin bonds causes degradation of hybridized dentin, resin and collagen fibers.

Research into the phenomena related to the dentin bonding system has enhanced the understanding of factors affecting the long-term molecular behavior at the bonding interface and provides a rationale for the modification of current materials or development of novel materials for improved adhesive techniques.

Conflicts of interest – No competing financial interests exist.

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