



# Chapter 2

## Adhesion to Intra-Radicular Dentin

**Lorenzo Breschi**  
**Annalisa Mazzoni**  
**Marco Ferrari**

**A**dhesion is a complex of physical and chemical mechanisms that allows the attachment of one substance to another. The bonding systems allow resistance to separation between the substrate and the restorative material/cement and stress distribution along the adhesive interface.<sup>1</sup> In addition, and pivotal for all dental restorations, adhesion means the possibility to properly seal the interface between the cavity and the restorative material, thus reducing the risk of post-operative sensitivity, marginal staining and recurrent caries.<sup>2</sup>

## General Concepts

The modern concepts of adhesive dentistry began a long time ago with the pioneer studies of Dr. Buonocore, which revealed how etching with phosphoric acid can increase bond effectiveness, in terms of bond strength and sealing ability.<sup>3</sup> As the first adhesives were mainly based on bisphenol glycidyl methacrylate (Bis-GMA),<sup>4</sup> the bonding system was extremely hydrophobic (i.e. no compatibility with water) and no adhesion was possible with the dentin tissue which is an intrinsically wet substrate. Further developments and the incorporation within the adhesive systems of more hydrophilic monomers, such as 2-hydroxyethyl methacrylate (HEMA), allowed adhesives to bond to dentin.<sup>5</sup> The ability of dental adhesives to tolerate water is extremely important, particularly after the introduction of the total etch technique (i.e. the simultaneous etching of enamel and dentin that removes the smear layers and smear plugs funneling the tubule orifices)<sup>6</sup> since a relatively large amount of water permeates throughout the dentin thickness, wetting the cavity surface.<sup>7</sup>

Despite major simplifications in dental adhesion, bonding to intra-radicular dentin remains an unpredictable goal due to various clinical factors influencing the procedure. In particular, several differences can be found between bonding to coronal and to intra-radicular dentin due to the relative limited access of the post space that may lead the clinician to various errors, which could finally jeopardize the adhesion.<sup>8</sup> For this purpose a standardized step-by-step procedure that should also be applicable within the endodontic space is needed.

## Definition of dental bonding systems and classification

Dental bonding systems are resin blends possessing both hydrophilic and hydrophobic properties, thus named amphiphile. In other words, adhesives are compounds containing both hydrophilic monomers that allow bonding with the tooth structure, as well as hydrophobic monomers contributing to the coupling with restorative materials or resin based cements.

From a physical perspective, bonding is a relationship between the free energy of the tooth surface and the wetting ability of the adhesive solution.<sup>9</sup> If bonding cannot wet the substrate, no adhesion can occur. The adhesive process involves the enhancement of the free surface energy of the tooth structure with an acidic solution (i.e. etching) in order to reduce the contact angle with the bonding solution that should also contain a surfactant agent (i.e. primer) to allow

proper wetting of the substrate.<sup>10</sup>

Despite their different formulation, all adhesives systems contain three cardinal steps which are considered pivotal to establishing a durable adhesive interface: 1) etching, 2) primer, 3) bonding.<sup>2</sup> The etching is an acidic solution that demineralizes the enamel/dentin surface, thus increasing their surface-free energy. The primer is composed of a mixture of hydrophilic monomers and solvents aiming to allow the wettability of the tooth surface and to permit the substitution of the water retained within the substrate with the resin monomers. The bonding contains the hydrophobic part of the system that allows the coupling with the resin based restorative materials or the resin cements.

Adhesive systems interact with the dentin tissue following two different strategies: they can either remove the smear layer (etch-and-rinse technique) or maintain it as the substrate for the bonding (self-etch technique).<sup>2</sup> The etch-and-rinse strategy is characterized by the application of a preliminary and separate etching step (usually a gel of 35-37% phosphoric acid) that is later rinsed away. Conversely the self-etch approach refers to the application of an etching/primer solution that is only air-dried, additionally named "etch-and-dry".<sup>11</sup> As no rinsing occurs after etching, the acidic compound of the self-etch system remains entrapped within the modified smear layer and the acid is buffered by the mineral released by the substrate.<sup>12,13</sup> The other cardinal steps such as priming and bonding can be separate or combined, depending on the adhesive formulation. If the bonding is combined with the primer (for the etch-and-rinse technique) or with the self-etching/primer agent (for the self-etch technique) the adhesives are considered as "simplified".<sup>14</sup>

As all adhesives contain etching, primer and bonding within their formulation,<sup>2</sup> a classification based on the number and combination of the steps constituting the adhesive system is proposed.

Four different classes can be identified (**Table 1**):

1. **Etch-and-rinse three-step:** adhesive systems characterized by the sequential application of etching, primer and bonding as separate and individual solutions.
2. **Etch-and-rinse two-step:** simplified adhesive systems characterized by the use of a combined primer&bonding agent that is applied onto the tooth surface after the etching is rinsed away from the tooth surface (**Figures 1a and 1b**).
3. **Self-etch two-step:** adhesive systems characterized by a self-etching primer that is dried on the tooth surface,

**Table 1: Classification of contemporary dental bonding systems and commercial names of some of the most common adhesive systems.**

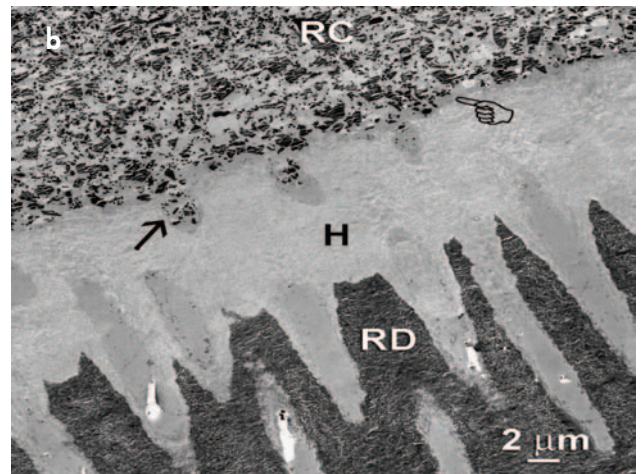
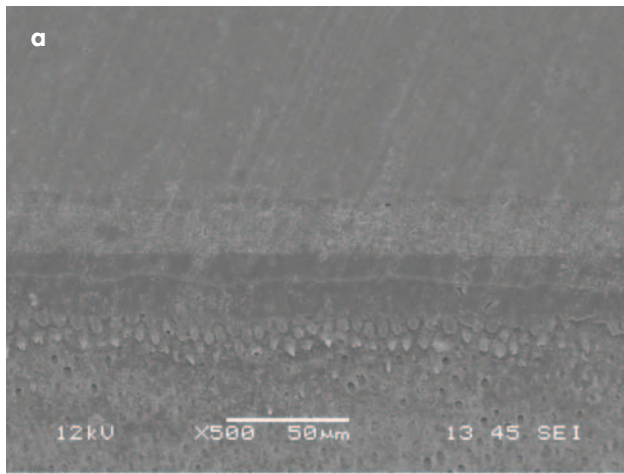
ETCH-AND-RINSE		SELF-ETCH or ETCH-AND-DRY	
3-step	2-step	2-step	1-step
4th generation	5th generation	6th generation	7th generation
<b>Etching</b> <i>Apply for 15 sec, rinse for 15 s, air-dry gently, keeping dentin moist</i>	<b>Etching</b> <i>Apply for 15 sec, rinse for 15 s, air-dry gently, keeping dentin moist</i>	<b>Etching &amp; Primer</b> <i>1 application without rinsing, air-dry gently</i>	<b>Etching &amp; Primer &amp; Bonding</b> <i>Apply 1-5 layers without rinsing, air-dry gently, light cure</i>
<b>Primer</b> <i>Apply 1 to 5 layers, air-dry gently</i>	<b>Primer &amp; Bonding</b> <i>Apply 1 to 5 layers, air-dry gently, light cure</i>		
<b>Bonding</b> <i>Apply 1 layer, air-dry gently, light cure</i>			
<b>Adper Scotchbond Multi-Purpose</b> (3M ESPE) <b>All Bond 3</b> (Bisco) <b>Optibond FL</b> (Kerr) <b>Syntac</b> (Ivoclar Vivadent) <b>Gluma Solid Bond</b> (Heraeus Kulzer)	<b>Prime &amp; Bond NT</b> (Dentsply) <b>XP-Bond</b> (Dentsply) <b>Excite</b> (Vivadent) <b>Adper Scotchbond 1XT</b> (3M ESPE) <b>One-Step Plus</b> (Bisco) <b>PQ1</b> (Ultradent) <b>Gluma Comfort Bond</b> (Heraeus Kulzer)	<b>AdheSE</b> (Ivoclar Vivadent) <b>Clearfil Protect Bond</b> (Kuraray) <b>One-Step Plus /TYRIAN</b> (Bisco) <b>Peak</b> (Ultradent)	<b>AdheSE One</b> (Ivoclar Vivadent) <b>All-Bond SE</b> (Bisco) <b>Adper Prompt L-Pop</b> (3M ESPE) <b>Clearfil S3Bond</b> (Kuraray) <b>XENO V</b> (Dentsply) <b>I-Bond</b> (Heraeus Kulzer)

followed by a separate hydrophobic bonding agent (Figure 2).

4. **Self-etch one-step:** simplified adhesive systems characterized by the combination in a single application solution of the etching&primer&bonding. These extremely simplified adhesive systems can be formulated as “one-bottle” systems or they can be in multi-bottle systems that are mixed only at the time of the clinical application.

When the dentin tissue is instrumented, a smear layer is created on top of the dentin surface.<sup>15</sup> The smear layer is removed by etch-and-rinse adhesive systems during the etching and water rinsing, and the sound dentin is demineralized.<sup>16</sup> Since the peritubular dentin is highly mineralized, the use of the etching opens the tubules, by funnelling their orifices, and removes all residual smear plugs.<sup>17</sup> The intertubular dentin is demineralized for few microns, depending on acid concentration, gel formulations, time and mode of application (i.e. a continuous brushing technique enhances the demineralization).<sup>18</sup> The removal of the mineral phase from the superficial dentin allows the

exposure of the dentin organic matrix, which is constituted by an intricate network of type I collagen fibrils (90% of the organic matrix)<sup>19</sup> and other non-collagenous proteins, such as proteoglycans, lipids and enzymes.<sup>20</sup> The resin monomers (primer and bonding of the adhesive system) should then fully infiltrate this delicate network of demineralized collagen fibrils, creating the so-called hybrid layer.<sup>21</sup> The penetration of the adhesive into the funnelled dentin tubules creates so-called resin tags,<sup>22</sup> that are particularly extended if the adhesive is applied to endodontically treated teeth, since no adverse pulpal pressure is present. Although resin tags have been morphologically described by a large number of researchers, their active role in adhesion is controversial, as bond strength values are reduced in deep dentin, where most of the substrate is represented by dentin tubules,<sup>24</sup> thus confirming that the hybridization of the intertubular dentin is pivotal for adhesion.<sup>25</sup> The bond established by etch-and-rinse adhesive systems relies only on the micromechanical retention between the demineralized dentin matrix and the polymerized adhesive system.<sup>22</sup>



**Figure 1:** 1a (SEMx500) and 1b (TEM x2000) Hybrid layer and resin tag formation of an etch-and-rinse adhesive system.

When self-etch adhesive systems are used, the smear layer is only partially demineralized, depending on the pH and pKa of the relative etching acidic solution. In relation to the etching ability of the adhesives, self-etch systems are classified as mild, intermediate and strong.<sup>2</sup> Strong self-etch adhesives are able to dissolve the smear layer completely (i.e. similar to the etch-and-rinse strategy),<sup>26</sup> while intermediate systems modify the smear layer and demineralize the dentin matrix, leaving residual hydroxyapatite crystals on the collagen fibrils. Interestingly this residual mineral on the collagen network accounted for an additional chemical bond with adhesive monomer,<sup>27</sup> which cannot be obtained with etch-and-rinse adhesives, since they fully demineralize the dentin collagen fibrils.

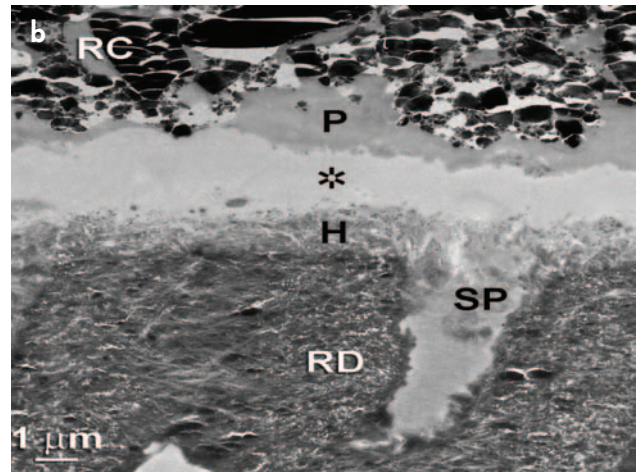
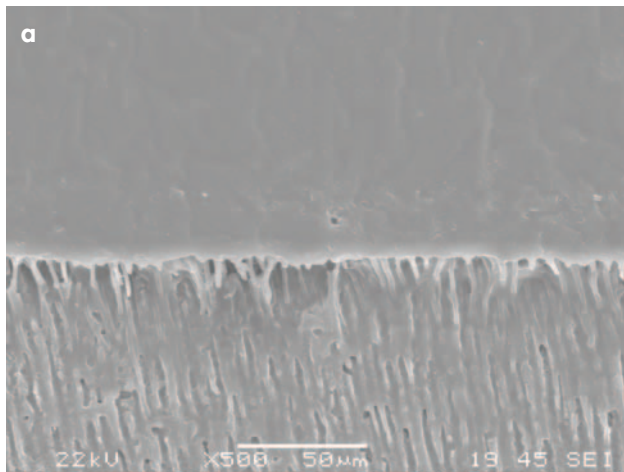
While self-etch adhesive systems are characterized by simultaneous demineralization and infiltration (since the primer is combined with the etching), etch-and-rinse monomer impregnation occurs after demineralization. For this reason, etch-and-rinse systems (mainly two-step systems as primer and bonding are combined) should be applied on wet dentin to maintain large interfibrillar spaces between the demineralized collagen fibrils, thus facilitating a proper monomer impregnation.<sup>28</sup> The solvent of the bonding agent (usually ethanol, water or acetone) acts as a carrier for the resin monomer that enhances the substitution of the residual dentin water. The air-drying that follows the primer/bonding application allows for solvent evaporation, leaving the resin materials within the collagen network. The bonding copolymerizes with the primer and creates a hydrophobic surface that can be polymerized and then coupled with the resin based material or with the resin based cement.

### Substrate: Intra-radicular dentin

The analysis of the radicular portion allows the identification of pulpal tissue, predentin and mineralized dentin surrounded by cement. Predentin is a layer of unmineralized organic matrix that lines the inner-most pulpal portion and may greatly vary in thickness, although remaining constant during aging, as the amount that calcifies is balanced by the addition of a newly-secreted organic matrix.<sup>29</sup> The synthesis of predentin begins with the production of large-diameter collagen fibrils (called von Korff's fibers) by the odontoblasts, that consist mainly of type III-collagen fibrils.<sup>30,31</sup>

Predentin and dentin are in direct and dynamic contact as the odontoblasts produce type I-collagen fibrils and proteoglycans by extending their processes into the formation of an extracellular matrix, thus starting the process of dentinogenesis. This formation structure of un-mineralized organic components constitutes the dentin organic matrix which represents approximately 30% in volume of mineralised sound dentin. The remaining dentin tissue is composed of water (approx. 20%) and minerals such as apatite.<sup>19</sup>

As the predentin is removed by the instrumentation of the pulpal tissue due to endodontic treatment (associated with sodium hypochlorite rinses), followed by the use of calibrated burs to prepare the post-space, the substrate of any adhesive luting procedure within the roots is mineralized intra-radicular dentin.<sup>32</sup> Several studies have investigated composition and structure of the intra-radicular dentin. However, despite the major differences in the bond



**Figure 2:** 2a (SEMx500) and 2b (TEM x2000) Hybrid layer and resin tag formation of a self-etching adhesive system.

strength between intraradicular and coronal dentin that were demonstrated, only minor morphological and biochemical differences were found. Similar to coronal dentin, intra-radicular dentin is a non-homogenous tissue characterized by the presence of tubules extending from the pulp to the tooth periphery.<sup>32</sup> For this reason intra-radicular dentin tissue can be classified as peritubular and intertubular tissue, in relation to the density and distribution of the tubules. Peritubular dentin is characterized by the presence a collar of hyper-mineralized tissue and low content of type I-collagen fibrils. Conversely, intertubular dentin is mainly composed of mineralized type I-collagen fibrils.<sup>17</sup> As the number of the tubules greatly diminish toward the apical region of the intra-radicular dentin, the ratio between peritubular and intertubular dentin changes substantially from the apical to the coronal third.<sup>32,33</sup>

Moving toward the apex, the substrate modification will induce changes of the impregnation pattern of the adhesive system, thus reducing peritubular dentin infiltration and resin tag formation, while increasing intertubular dentin impregnation.<sup>34</sup> Since it is well known that resin tags only minimally contribute to bond strength,<sup>25</sup> the greater amount of intertubular dentin available for hybridization should potentially lead to the formation of a higher bond strength in the apical, rather than in the coronal third.<sup>32</sup> However, the overwhelming majority of the studies reports that bond strength to intra-radicular dentin reduces from the coronal to the apical third of the root canal and it has been revealed that the thickness of the hybrid layer is significantly reduced in the apical third. The thinning of the hybrid layer observed by some authors toward the apex was accounted as

responsible for the lower bond strength due to reduced impregnation of the adhesive system.<sup>32</sup>

However, this issue is still controversial as some studies reported similar or increased bonding closer to the apical region, showing no differences in terms of thickness of the hybrid layer (**Table 2**).

As both the thickness of the hybrid layer and the morphology of the resin tags (determined by the substrate) have been recently shown to contribute minimally to bond strength, we may conclude that the reduced bond strength reported in most of the studies of the intra-radicular dentin, compared to the coronal dentin, should probably be attributed to factors other than the substrate morphology, such as the negative C-factor of the endodontic space and the difficult clinical handling due to the limited endodontic space.

### Clinical procedures - factors affecting bonding to intra-radicular dentin

A fundamental pre-requisite for adhesion to intra-radicular dentin is represented by the ability of the clinician to obtain a perfectly clean post space, as the use of sodium hypochlorite rinses, EDTA, endodontic cements, gutta-percha or other endodontic filling materials clearly modify the intra-radicular dentin<sup>35</sup> (**Figure 3**).

In addition, the difficulty to control the substrate surface as well as to correctly apply the adhesive and the cement inside the narrow endodontic space, is evident.

Several factors may affect intra-radicular dentin: the presence and thickness of the endodontic smear layer, the post space preparation method, adverse clinical factors, the

**Table 2: Studies reporting bond strength values to intra-radicular dentin**

Bond strength to intra-radicular dentin		
Coronal third > apical third	Coronal third ≥ apical third	Coronal third < apical third
Yoshiyama et al., J Dent 1998 Bouillaguet et al., Dent Mater 2003 Goracci C, et al. Eur J Oral Scien 2004 Perdigao et al., Am J Dent 2004 Bolhuis et al., Quintessence Int 2004 Mallmann et al., Oper Dent 2005 Bolhuis et al., Oper Dent 2005 Kalkan, J Prosthet Dent 2006 Perez et al., Int J Prosthodont 2006 de Durão Mauricio et al., J Biomed Mater Res 2007 Perdigao et al., Dental Mater 2007 Perdigao et al., J Prosthodont 2007 Faria Silva et al., J Endodont 2007 Boff et al, Quintessence Int 2007 Wang et al., Dent Mater 2007 Ohlmann et al., J Dent 2007	Yoshiyama et al., J Dent 1996 Burrow et al., Am J Dent 1996 Aksornmuang et al., J Dent 2004 Foxton et al., J Oral Rehabil 2005 Ngho et al., J Endod 2001 Kanno et al., Dent Mater J 2004 Foxton et al., Oper Dent 2003	Gaston et al., J Endodo 2001 Mannocci et al., Dent Mater 2004 Muniz & Matias oper Dent 2005

use of irrigants or medicaments during the endodontic treatment, the use of eugenol-based materials or bleaching agents, the influence of endodontic re-treatment, possible incompatibility between different resin based materials, and geometric factors are some of the most important aspects to be clarified.

**Endodontic smear layer**

The theoretical goals for successful endodontic therapy are the disinfection and the complete obturation of the root canal space with an inert filling material creating an optimal seal with the tooth structure. The prerequisite for a tight seal is the closed adaptation of the filling material to the canal walls, which, however, is impaired by the presence of the endodontic smear layer, invariably formed after manual and rotary instrumentation.<sup>36</sup> According to its original definition, the smear layer has been defined as “any debris, calcific in nature, produced by reduction or instrumentation of dentin, enamel or cementum”,<sup>37</sup> or as a “contaminant”<sup>38</sup> that precludes interaction with the underlying pure tooth tissue.<sup>1</sup> The burnishing action of the cutting instruments generates frictional heat and shear forces, so that the smear layer becomes attached to the underlying surface in a manner that prevents it from being rinsed off or scrubbed away.<sup>1,39</sup> The morphological features, composition and thickness of the

smear layer are determined by the type of endodontic instrument used, the method of irrigation and tooth substrate which is formed.<sup>1,40</sup>

The coronal smear layer reflects the substructure of dentin matrix composition while the endodontic smear layer contains inorganic and organic substances that also include fragments of odontoblastic process, microorganisms and necrotic material<sup>15</sup> (Figure 4).

Despite its different composition, the thickness of the smear layer ranges from 0.5 to 2 µm, in addition to a deeper layer packed into the dentin tubules to a depth of up to 40 µm, obstructing their orifices thus forming *smear plugs* (Figure 5). The smear layer can be detrimental to effective bonding: in early smear layer research, non acidic-adhesives, applied without prior etching, did not penetrate profoundly enough to establish a bond with intact dentin; such bonds were prone to cohesive failure of the smear layer.<sup>24</sup>

As previously mentioned in the description of the adhesive systems, two bonding strategies are used to overcome the low attachment strengths of the smear layer. With the etch-and-rinse approach, the use of the etching, followed by extensive rinsing, removes the smear layer prior to the bonding, while in the self-fetch approach the smear layer is only modified beforehand and is incorporated within the



**Figure 3.** A fiber post luted into a root canal. (SEM x15)

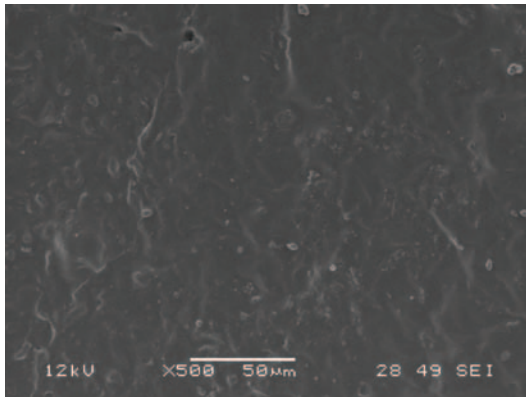
hybrid layer complex.<sup>2,26</sup> The more acidic and aggressive the conditioner, the more completely the smear layer and smear plugs are removed.<sup>41</sup>

Within the root canal, dentin surfaces covered with debris and remnants of pulp tissue are unlikely to achieve effective bonding,<sup>35,42</sup> as the endodontic smear layer acts as a barrier, significantly influencing any adhesive bond formed between the instrumented canal walls and the restorative material,<sup>2</sup> as well as the resin

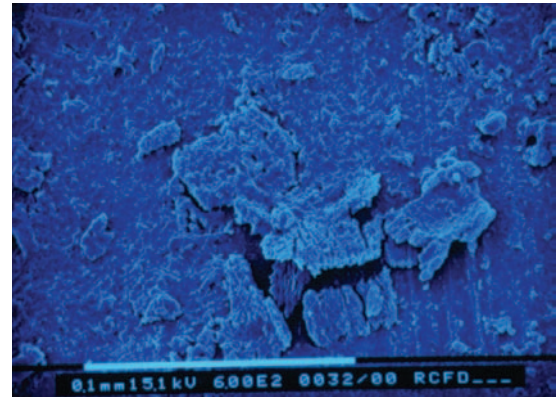
cementation of fiber posts. Although there is some controversy regarding the desirability of retaining the smear layer in adhesive dentistry, in endodontics its removal is considered to be advantageous and highly desirable.<sup>43</sup> The endodontic smear layer, in fact, may be infected and may protect the bacteria already present in the dentinal tubules; because of these concerns, one may deem it prudent to remove the initially created smear layer in infected root canals and to allow the penetration of intra-radicular medicaments into the dentinal tubules.<sup>44</sup> In addition to the reduced penetration of root canal medicaments, several studies have also reported a better adhesion of obturation materials after the removal of the smear layer.<sup>45</sup> The penetration depth within the dentinal tubules of different sealers is also consistently increased (10-80  $\mu\text{m}$ ) once the smear layer is removed.<sup>44,46</sup>

#### **Post space preparation and "Secondary" smear layer**

In addition to the "traditional" smear layer produced by



**Figure 4.** Coronal smear layer. (SEM x500)



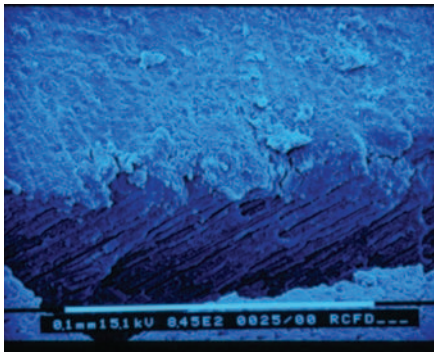
**Figure 5.** Tubules' orifices are closed by smear plugs. (SEM x85)

manually or rotary instrumentation of the root canal walls, the subsequent preparation of the post space using post drills resulted in an additional and even thicker smear layer composed of debris and sealer/gutta-percha remnants that significantly influenced the adhesion of fiber posts<sup>43</sup> (**Figure 6**).

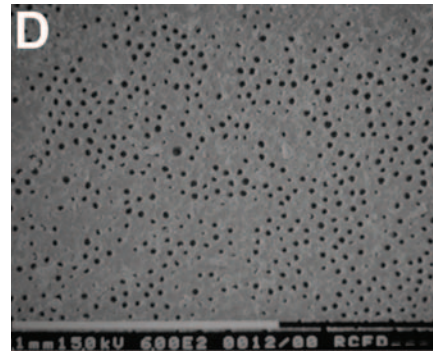
In fact, the action of the drills used to remove the root filling material to create post space, produces a new smear layer, which is rich in sealer and gutta-percha remnants that are plasticized by the frictional heat of the drill. This may diminish the penetration and chemical action of the agents used to bond fiber posts. In addition, only minimal irrigation can be performed inside the endodontic canal. Thus, achieving clean dentinal surfaces after mechanical post space preparation seems to be a critical step for optimal post retention, particularly when resin cement is used.<sup>47</sup> It has been reported that the use of phosphoric acid after post space preparation resulted in discontinuous areas of deep intertubular demineralization, alternating with areas characterized by open tubules and other areas covered by debris, smear layer and gutta-percha and/or sealer remnants as the result of an incomplete chemical dissolution during the etching procedure, due to the penetration into the dentinal tubules of the sealer and the plasticized material during the condensation procedure.<sup>48</sup>

To increase retention when resin cement is used, some authors suggested a pre-treatment with a chelating agent and sodium hypochlorite before post cementation in order to efficiently remove the large areas that are not available for bonding and resin cementation of fiber posts.<sup>49</sup>

Others authors also suggested the use of ultrasonic instrumentation in association with EDTA pretreatment prior to the bonding procedure, resulting in a decrease of debris and open tubules.<sup>48</sup>



**Figure 6:** Root canal smear layer. (SEM x600)



**Figure 7:** Root canal dentin after EDTA in combination with ultrasonics. (SEM x600)

Although the removal of this tenacious and thickness smear layer is enhanced by the suggested combination of EDTA and ultrasonic instrumentation (**Figure 7**), the effectiveness in terms of interfacial post bond strength is still related to the bonding strategy selected, i.e. the etch-and-rinse or the self-etch approach.<sup>50</sup>

#### **Negative clinical factors**

Besides the success of the root canal treatment, a successful final restoration is also mandatory for long-term clinical success. Extensive loss of tooth structure may require post core restoration of a root canal filled tooth. However, in these systems, the lack of adhesion permits apical or coronal microleakage that causes failure of root canal treatment.<sup>51</sup> For this reason effective adhesion to intra-radicular dentin is a fundamental pre-requisite to achieve the proper sealing of the endodontic space. Adhesion to intra-radicular dentin may be affected by several factors. The use of some disinfectant solutions or medication during root canal preparation may have an adverse effect on the bond strength of post to root canal dentin<sup>52</sup> as well as bleaching and re-treatment procedures.<sup>42</sup>

#### **Irrigating solutions and medicaments**

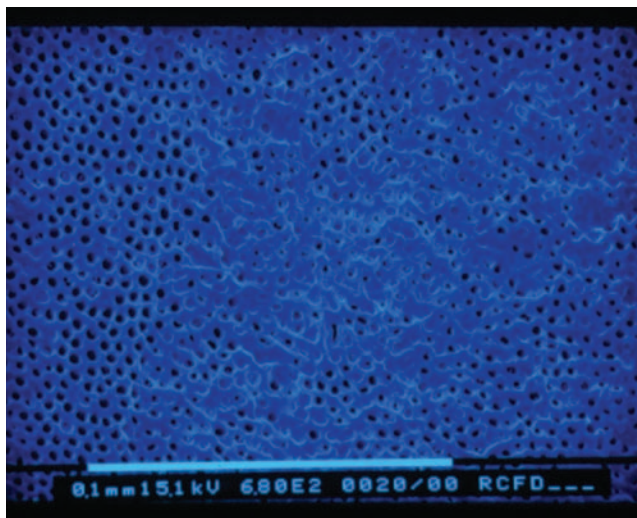
During irrigation, radicular and coronal dentin is exposed to the various solutions used to disinfect the endodontic space. This may cause alterations on the dentin surface and affect their interactions with resin based materials used either for root canal obturation or for coronal restoration.<sup>53</sup>

The effect of some medicaments, such as EDTA and NaOCl on dentin has been widely investigated.<sup>52-55</sup> Although NaOCl is theoretically an ideal endodontic irrigant, despite its positive effects, it can cause problems if used in association with resin based materials due to its strong oxidizing properties. NaOCl leaves a dentin surface

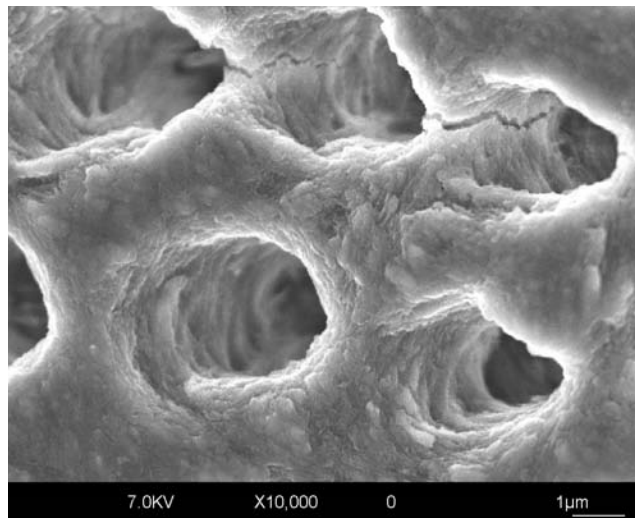
characterized by an oxygen-rich layer that can significantly reduce bond strength and increase microleakage<sup>52,54,55</sup> (**Figure 8a and 8b**). Thus, if resin cements are used to lute endodontic posts, it is important to optimize clinical procedures that result in high bond strength between adhesive and dentin and between the resin-based material and the post.

Adhesion to intra-radicular dentin can be favorably influenced with 10% ascorbic acid and 10% sodium ascorbate after NaOCl irrigation, as this additional step was shown to completely reverse the compromised bond obtained on 5% NaOCl treated dentin.<sup>54</sup> Interestingly 10% sodium ascorbate (pH 7) has been reported to be effective and even better than 10% ascorbic acid (pH 4) at restoring high bond strengths to NaOCl-treated dentin, thus suggesting that the mechanism of action of ascorbate is a reducing agent. It is likely that the oxidizing action of NaOCl leads to residual-free oxygen within the dentin matrix that may critically interfere with the initiation of the interfacial polymerization of resin cements leading to lower bond strengths.<sup>54</sup> According to Morris et al.,<sup>54</sup> by treating dentin with 10% sodium ascorbate, the intra-radicular dentin substrate is converted from an oxidized to a reduced surface, speculating that this treatment restores the redox potential of the dentin and facilitates the polymerization of the resins.

Beside NaOCl and EDTA, the use of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) during canal instrumentation effectively removes remnants of pulp tissue and dentin debris, although the use of 3% H<sub>2</sub>O<sub>2</sub> has been reported to negatively influence the bond strength of resin cement to root canal dentin.<sup>51,52,56</sup> Hydrogen peroxide breaks down to water and oxygen thus inducing liberation of oxygen by the chemical reaction of hydrogen peroxide with sodium hypochlorite. Oxygen from such chemicals causes strong inhibition of the interfacial



**Figure 8a:** Root canal dentin after NaOCl endodontic irrigant use (SEM x680)



**Figure 8b:** Root canal dentin after NaOCl endodontic irrigant use (FEI-SEM x1000)

polymerization of resin bonding material.<sup>56,57</sup> After the use of 3% H<sub>2</sub>O<sub>2</sub> alone, or in combination with NaOCl, residues of the chemical irrigants and their products are likely to diffuse into dentin along the tubules contaminating the dentin surface, which may affect the penetration of resin monomers into the dentin structure or the polymerization of the monomers within the demineralized dentin. This is believed to decrease bond strength to dentin.<sup>51,56</sup>

Reduction in resin bond strength to root dentin is also reported to be produced after the use of RC-Prep (Premier Dental Products, Plymouth, PA) as a lubricating and demineralizing agent.<sup>54</sup> This reduction has been described as the result of concomitant contributing factors. Primarily the presence of hydrogen-peroxide in RC-Prep, which, when breaking down to oxygen and water during the bonding procedure, might generate bubbles or voids, altering the resin infiltration process as reported additionally for bleaching agents and 3% H<sub>2</sub>O<sub>2</sub> alone, or if used in combination with NaOCl.<sup>56,58</sup> On the other hand, the RC-Prep formulation contains the polyethylene glycol (PG) vehicle (Carbowax®) to provide lubricating properties which might be difficult to rinse off completely, thus interfering with the polymerization process and preventing complete polymerization of the resin. However, a plausible restoration of the bond strength to control values can be achieved with a post RC-Prep treatment with 10% ascorbic acid.<sup>54</sup>

An additional side effect of these intra-radicular irrigating solutions is the significant reduction in the microhardness of the root canal dentin. Sodium hypochlorite, hydrogen

peroxide and EDTA decreased the microhardness value of root dentin.<sup>53,59</sup> This reduction after irrigation indicates direct effects of the chemical solutions on the components of the dentin structure. Although the relative softening effect exerted by chemical irrigants on the dentinal walls could be of clinical benefit as it permits rapid preparation and facilitates access to small and tight root canals, these alterations affect the adhesion and sealing ability of sealers to the softened chemical treated dentin surfaces.<sup>53,59</sup> According to these observations, the use of 0.2% chlorhexidine gluconate as an irrigating solution to provide optimal obturation due to its harmless effect on the microhardness and roughness of root canal dentin has been suggested.<sup>59</sup> Additional positive effects are attributed to chlorhexidine supporting its use as a widely effective irrigating solution during endodontic procedures: highest bond strength compared with other irrigants;<sup>51</sup> more effectiveness; more residual antibacterial effect and lower toxicity compared to 5.25% NaOCl with similar clinical timing required to eliminate all microorganisms.<sup>60,61</sup> Moreover chlorhexidine absorption by dentin and subsequent release from dentin lasts for 48 to 72 h after instrumentation.<sup>62</sup>

Calcium hydroxide paste is sometimes placed in the root canal for its antimicrobial properties and other desirable effects between endodontic appointments. Furthermore, as the complete removal of calcium hydroxide before obturation is almost impossible, residual particles might interfere with bonding in some areas by acting as a physical barrier.<sup>63,64</sup> In addition, due to its high pH, calcium

hydroxide may also neutralize the self-etching/primer solutions of self-etch adhesives, significantly reducing its etching effect and resulting in lower bond strength.

### **Eugenol**

It is well known that eugenol negatively affects the resin polymerization process, thus altering the bonding effectiveness. Sealers and temporary restorative material such as zinc oxide eugenol may contain eugenol in its formulation. The eugenol released from these products can permeate dentin<sup>65</sup> and further interact with resin-based restorative materials. As with other phenolic compounds, eugenol is a radical scavenger that inhibits the polymerization of resin based materials.<sup>66</sup> The negative chemical reaction involves the hydroxyl group of the eugenol that tends to protonize the free radicals formed during the polymerization of resin-based materials, thereby blocking their reactivity and reducing the degree of the conversion of these materials.<sup>67,68</sup>

In order to avoid the sub-optimal polymerization and the related reduced bond strength due to the use of an eugenol-based sealer (or temporary material), a mechanical cleaning of the canal walls associated with scrubbing with a detergent or alcohol to remove all visible signs of residual material has been proposed.<sup>69,70</sup> This procedure may help to remove an oily layer of debris before performing the bonding procedure.<sup>42</sup>

The use of 37% phosphoric acid as the etching agent of most of the etch-and-rinse adhesives has only been reported to remove remnants of the temporary restoration incompletely.<sup>71</sup> However, the phosphoric acid pre-treatment eliminates the contaminated smear layer and results in the demineralization of dentin to a depth of 9-10  $\mu\text{m}$ .<sup>72</sup> This depth of demineralization and the water rinsing after etching reduces the amount of free eugenol and temporary restoration remnants on the dentin surface.<sup>66</sup> Studies have, in fact, demonstrated that the etch-and-rinse, three-step adhesive systems allow better and more effective bonding to eugenol contaminated dentin surfaces, compared to the self-etch approach due to the non-removal of the eugenol debris entrapped within the smear layer.<sup>66,73</sup>

Therefore, in daily clinical practice, when posts are placed after the use of eugenol-based sealers or eugenol-based temporary materials, clinicians should prefer the use of an etch-and-rinse adhesive system, as self-etch systems incorporate the eugenol-rich smear layer into the hybrid layer, rather than removing it.<sup>42</sup>

### **Bleaching**

With the increased interest in aesthetic dentistry, tooth discoloration due to endodontic treatment is a severe problem.<sup>74</sup> Although aesthetics can be improved using a variety of techniques, tooth bleaching is the most conservative and cost-effective alternative to enhance the appearance of non-vital teeth.<sup>75</sup> However, despite the satisfactory results, side effects of this therapy have been reported,<sup>76,77</sup> which include a decrease of the bond strength of resin-based restorative materials.<sup>74</sup> It has been reported that the lower bond strength after bleaching is due to the oxygen rich surface leaving behind hydrogen-based peroxide products, which significantly inhibits the polymerization of the adhesive systems.<sup>56,76,77</sup> Thus, the bond strength may be improved by replacing the final restoration several days after bleaching to allow the release of the residual oxygen. If an immediate bond is needed, extending the length of polymerization time may reverse part of the polymerization inhibition.<sup>57</sup>

In addition, it has been reported that a high concentration of hydrogen peroxide causes a substantial decrease in dentin microhardness.<sup>78,79</sup> This is an indirect evidence of mineral loss in the dental hard tissue, which may affect the adhesion and sealing ability of sealers to the bleached dentin surfaces.<sup>53,59</sup>

### **Retreatment**

During endodontic retreatment procedures, radicular and coronal dentins are sometimes exposed to gutta-percha solvents deposited in the root canal. Chloroform and, more recently, halothane are the most commonly used gutta-percha solvents employed for this.<sup>51</sup> These agents are strong lipid solvents that may alter the chemical composition of the dentin surface and of the dentin organic matrix, thus affecting its interaction with resin based materials used for restorations. The solvents may redeposit on the root canal surface as a waxy film interfering with the resin-dentin bonds,<sup>51,80</sup> causing significant loss of bond strength.<sup>51</sup>

### **Incompatibility between simplified adhesives and chemical/dual-cured composites**

In response to the increasing demand for procedural simplification in the formulation of adhesives, the classical multi-step dentin adhesives have been replaced by simplified-step systems that are simpler, faster and more user-friendly.<sup>14</sup> However, incompatibility between simplified adhesives (i.e. two-step etch-and-rinse and one-step self etch



**Figure 9:** A post luted with all-in-one adhesive system in combination with a dual-cure resin cement: the material combination cannot cure.

adhesives) and chemical/dual-cured composites has been reported.<sup>81-84</sup> The decrease in bond strength was inversely proportional to the acidity of the adhesives<sup>83-85</sup> and adverse chemical interaction between sub-optimally polymerized acidic adhesive resin monomers and the basic tertiary amine catalyst in the composite was thought to be responsible for the observed incompatibility.<sup>83</sup> In the etch-and-rinse strategy, only the two-step were claimed to show incompatibility, while the conventional three-step total etch involving the use of intermediate resin layer were unaffected.<sup>83,84</sup> Similarly, within the self-etch bonding strategy, only one-step self-etch adhesives are incompatible with chemical/dual-cured composites,<sup>82</sup> due to their more acidic content by virtue of the increased concentration of lower pKa acidic resin monomers,<sup>86</sup> which is responsible for the additional increased permeability showed by one-step self-etch adhesives.<sup>82</sup> These acidic resin monomers can both react with the basic components (aromatic tertiary amine) of the composite, and/or create a hypertonic environment that osmotically draws fluid from the bonded hydrated dentin through the permeable adhesive layer.<sup>85,87,88</sup> Tay et al. also reported that the increased permeability that characterized these adhesives, due to the higher concentration of the ionic resin monomers, is responsible for the aforementioned incompatibility.<sup>82</sup>

Thus, according to these observations, three-step etch-and-rinse and two-step self-etch do not show incompatibility with chemical/dual-cure resin composites due to the use of intermediate bonding resin layer: this additional coat of less acidic and less hydrophilic resin layer prevents the negative acid-base reaction since the composite layer does not come into direct contact with the acidic monomer components in the primer layer, and reduces permeability of the resin-tooth

interfaces.<sup>83,84</sup>

Most clinicians generally use dual-cure adhesives for bonding to root canal dentine because of their ability to self-polymerise in the absence of light in the deeper regions of post cavity. However, clinically, the incompatibility of one-step self-etch adhesives with chemical/dual-cured composites precludes their use for indirect bonding procedures in such areas that are inaccessible for light-activation.<sup>83</sup>

For the aforementioned reasons, the use of self-etch one-step adhesives should be avoided, although the use of a ternary catalyst has been proposed to overcome the acid-base reaction.<sup>88</sup> This solution has been formulated in most etch-and-rinse two-step adhesives with the addition of a separate bottle of activator solution containing a ternary catalyst, and in some self-etch one-step adhesives by the incorporation of ternary catalysts as adhesive components.<sup>88</sup> Nevertheless it has been reported that adhesive permeability still occurs when these activated adhesives are employed for bonding to hydrated dentin.<sup>82,88,89</sup>

In conclusion, the use of one-step self-etch adhesives within the root canal is not recommended (**Figure 9**) while the two-step etch-and-rinse should be used only in conjunction with a chemical activator in order to circumvent the adverse acid-base reaction. Light-curing still remains mandatory to obtain complete adhesive polymerization, overcoming the chemical interaction with cements and finally avoiding low bond strength and resin leaching.

### Geometric factors

The use of methacrylate-based resin materials in endodontics also focuses attention to the shrinkage stresses associated with their polymerization. During polymerization process, the intermolecular spaces between the monomers are reduced, generating sufficient shrinkage stresses to debond the material from dentin, thereby decreasing retention and increasing leakage.<sup>90</sup> In clinical practice, the polymerization phenomenon leads to stress development, gap formation and potential bacterial presence at the tooth/resin material interface. However, in addition to polymerization shrinkage, several other factors may influence shrinkage stress and gap formation.

Feilzer et al., reported that shrinkage stress is related to the cavity configuration factor, (C-factor), defined as the ratio of bonded to unbonded surfaces area of the restoration,<sup>91</sup> and when the so-called "C-factor" of a restoration, is above a certain limit, the stress development

**Table 3. Median push-out bond strength values\* (SD) expressed in MPa, number of specimens (N), and percentage of failure mode distribution recorded in the experimental groups<sup>104</sup>.**

Experimental groups	Bond Strength (SD)	Number of Slices	Failure mode (%) A/M/PA/C
1. All Bond 2+ DuoLink	3.98 (2.2) <sup>d</sup>	30	0/38/11/50
2. One-Step + DuoLink	6.06 (4.4) <sup>c,e,d</sup>	28	0/0/22/77
3. All Bond 2 + Unfilled Resin	7.99 (3.8) <sup>a,e</sup>	33	0/50/38/11
4. One-Step + Unfilled Resin	11.95 (3.9) <sup>a</sup>	30	0/32/64/4
5. DuoLink	0.37 (0.94) <sup>b</sup>	32	14/57/28/0
6. Unfilled Resin	3.59 (2.3) <sup>c,d</sup>	35	0/13/25/61

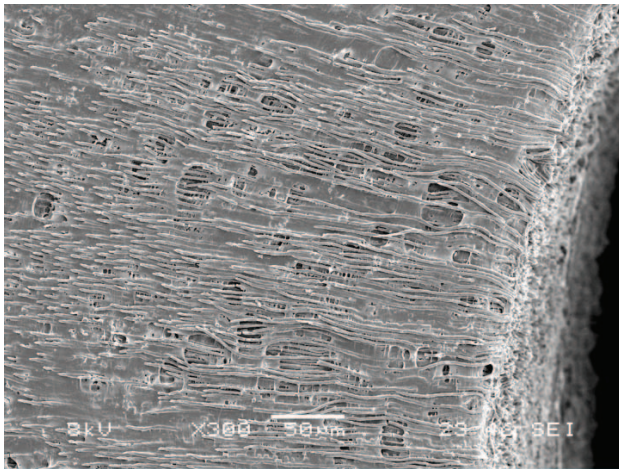
\*Values identified by same superscript letter are not significantly different ( $p > 0.05$ ) by the Dunn's test. Failure mode (in percentage): A=adhesive between dentin and cementing agent; M=mixed; PA=adhesive between post and cementing agent; C=cohesive in cementing agent

exceeds the bond strength of the present bonding agents.<sup>92</sup> The extent of shrinkage stress is, however, also dependent on the viscoelastic properties of the resin material: at a given polymerization shrinkage, the most rigid resin material will produce the highest shrinkage stress, and consequently increase gap formation at the tooth-resin interface.<sup>93,94</sup> Only if the shrinkage stress caused by the wall-to-wall contraction of the resin material can be relieved by sufficient elastic yielding of the surrounding materials, may the bond survive,<sup>95</sup> revealing that a major problem associated with endodontic bonding is the lack of relief of shrinkage stresses created in deep root canals<sup>96,97</sup> which is strictly dependent upon the cavity geometry and the resin film thickness.<sup>92</sup> Within the root canal the cavity geometry is unfavourable, since the unbonded surface area decreases with the consequence of insufficient stress relief, in conjunction with the high probability that one or more bonded areas will pull off or debond.<sup>90</sup> Braga et al.,<sup>98</sup> analyzing the influence of cavity dimensions on shrinkage stress in composite restorations, showed that the cavity depth had a stronger influence than the diameter. Thus, if we relate these data to the endodontic cavity configuration, the influence on shrinkage stress is even worse.

As with bonding to root canals, the cementation of endodontic posts to prepared root post spaces is critical for

the negative geometric factors, and was described by Feilzer et al. as the worst scenario in achieving void-free interfaces.<sup>92</sup> According to Bouillaguet et al.,<sup>99</sup> the estimated C-factor in post spaces may, in fact, even exceed 200, compared to the coronal restoration values that range between 1 and 5. More recently, Tay et al.,<sup>90</sup> using a modelling approach, investigated the geometric variables influencing bonding adhesive root-filling materials to canal walls, revealing a negative correlation between C-factors in bonded root canals with sealer thickness. In addition to the C-factor, the contribution of the other geometric attributes, i.e. the "S-factor", was taken into consideration. As the thickness of the adhesive is reduced, the volumetric shrinkage decreases, which results in the final reduction in shrinkage stress (S-factor). However, it was concluded that the interaction of these two factors (C- and S-factor) predicts that bonding of adhesive root filling material is highly unfavourable when compared with indirect intracoronal restorations with similar resin film thickness.<sup>90</sup>

All the above-mentioned problems limit bond strength to intraradicular dentin. Recently, some authors hypothesized that the retention of fiber posts in the root canal is mainly due to friction of the post itself along the cavity walls through the interposition of luting material.<sup>100,101</sup> However, as friction occurs after bonding failure, it should not play a significant



**Figure 10:** Resin tags, more than 500 microns in length, formed after using the ethanol wet bonding technique for luting a fiber post. (SEM x300)

role for post retention until the adhesive interface is effective. Friction will improve post luting in the event that no bonding occurs at the coronal part of the abutment. Otherwise, even in the presence of low bond strength, the post will continue to be luted to the dentinal structure on account of the bonding interface with coronal dentin, until debonding of the radicular part of the post occurs. Friction is additionally influenced by the granulometry of the luting material,<sup>102</sup> although it is still unclear whether or not a macrofilled cement can develop a higher 'bond strength due to friction'.

Goracci et al.,<sup>103</sup> investigating the effect of post luting with and without the employ of adhesive systems, reported no statistical differences between the groups, and the results were mainly attributed to the limited number of samples and, in particular, to the low value recorded in the study.

In addition, the standard deviation of the two tested groups was very high, thus the authors do not believe that it can be assumed that 'retention of fiber posts is mainly due to friction'. More recently, a paper by Carvalho et al.,<sup>104</sup> showed that the application of the adhesive system is mandatory for obtaining higher bond strength to root dentin and that the use of unfilled bonding resins as luting material consistently increases the bond strength to intra-radicular dentin. The important role of unfilled resin for luting fiber posts was further supported by recent findings<sup>105</sup> (**Table 3**). Considering the main type of failures reported in clinical practice (i.e. debonding), another important issue related to the geometric factors can be related to the circular shape of the posts which do not correspond to the root shape, notably in oval root canals. In addition, the post diameter should also be taken into account, fitting properly in only the most

apical part of the root canals, while usually remaining too thin in the most coronal compartment. These two aspects determine a wide thickness of luting cement, which become the weakest part of the system under occlusal loading.

Thus, for minimizing the cement's thickness, the use of 'anatomic posts',<sup>106</sup> 'oval posts', indirect luting procedures,<sup>107,108</sup> and/or additional smaller sizes of posts may be useful in clinical practice.<sup>109</sup>



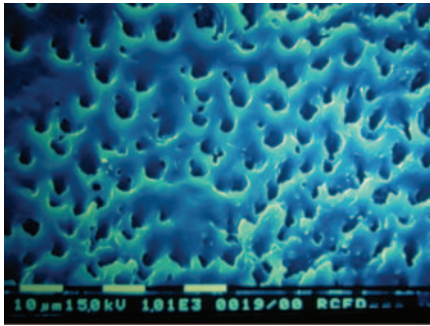
**Figure 11:** Half a root with a post luted inside after being directly exposed to water for 6 months. Direct exposition of the bonding interface to water determined degradation of the hybrid layer.

### Ethanol wet bonding technique

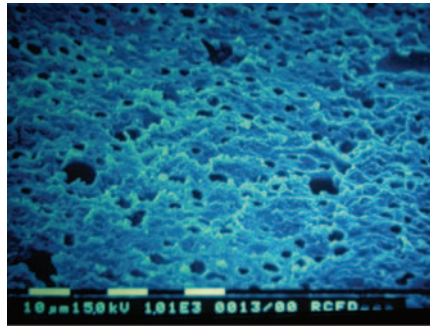
An ethanol wet bonding technique has been recently proposed to improve bonding to dentin.<sup>110</sup> The original wet bonding technique of etch-and-rinse adhesives requires water that is originally present within the interfibrillar spaces of the collagen network, to be displaced by the polar solvents contained in these adhesives and ultimately replaced by pure resins.<sup>110</sup> It has been reported that by replacing water in the demineralized collagen matrix with ethanol, phase separation of the hydrophobic dimethacrylates can be prevented as they are applied to ethanol-saturated instead of water-saturated dentin.<sup>110,111</sup> Using a macromodel of the hybrid layer to predict how well adhesives can bond to dentin, Pashley et al.<sup>110</sup> indicated that ethanol wet bonding may be superior to water wet bonding and several studies evaluated the effectiveness of this technique.<sup>111-113</sup>

Certain investigations evaluated the effects of the "ethanol wet bonding technique" on luting fiber posts, revealing that this procedure does not improve bond strength with the fiber posts surface.<sup>114</sup> However it can improve bond strength to intra-radicular dentin (**Figure 10**).

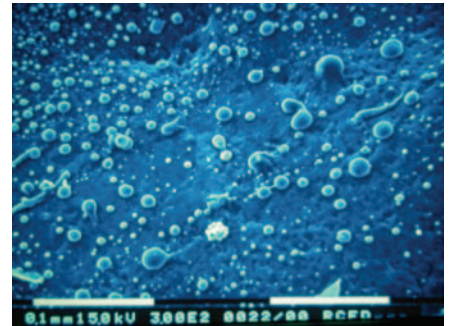
The main problem in using this technique is due to the complex clinical procedure based on several steps, the instability of its component (shelf life), as well as to the fact that the system is not yet available on the market. In vital



**Figure 12:** Root canal dentin *in vivo* after etching and proper drying. The dentin surface is completely free of water.



**Figure 13:** The same root canal dentin of Figure 12 after being treated with pure ethanol for 1 min; the surface is completely dehydrated.



**Figure 14:** (same surface of Figs. 12 and 13). After applying primer of a one-bottle adhesive system and not completely air drying it, the dentin surface is covered by blisters due to incomplete evaporation of the solvent of the primer.

teeth, possible pulp damage due to the application of pure ethanol on vital dentin for fixing the collagen fibers is theoretically reasonable. Several *in vivo* studies are thus currently ongoing to challenge the pulp effect of this technique. Although the concept of ethanol wet bonding may sound radical to a clinician who may have doubts on the potential effects on vital pulp, Pashley et al. remarked that such a procedure is not that different from the application of acetone-based or ethanol-based primers, as most of these primers may contain up to 85% ethanol or acetone.<sup>110</sup> According to these observations, further laboratory and clinical studies are needed to test this procedure.

### Failure of the adhesive interface

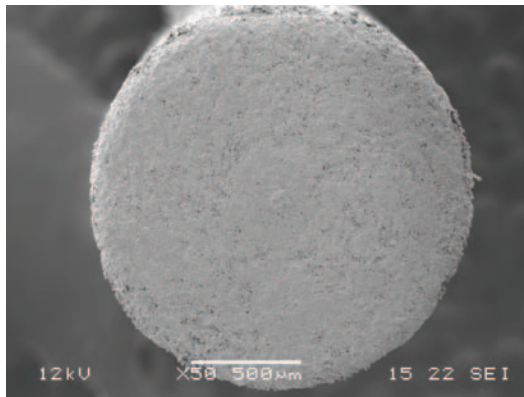
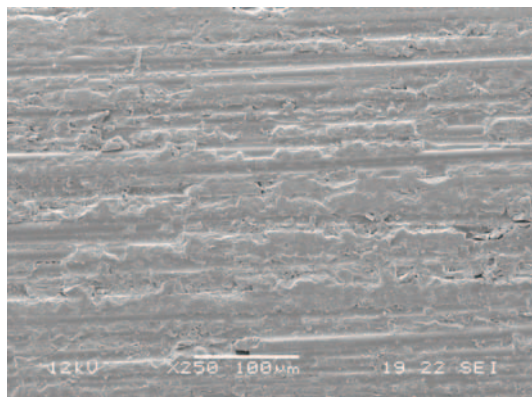
As clinical investigations revealed that bond failure occurs after time, researchers recently focused their attention on the chemical phenomena that occur during aging. Since the hybrid layer is a complex mixture of collagen and adhesive monomers, each of the two components may be affected by aging.

Two degradation patterns were morphologically described within the hybrid layer thickness after storage in water for 1 year: 1) hydrolysis of the resin from interfibrillar spaces and 2) disorganization of collagen fibrils.<sup>115</sup> These phenomena clearly weaken the strength of resin–dentin bond allowing leakage, marginal stain and finally failure of the adhesive interface (**Figure 11**).

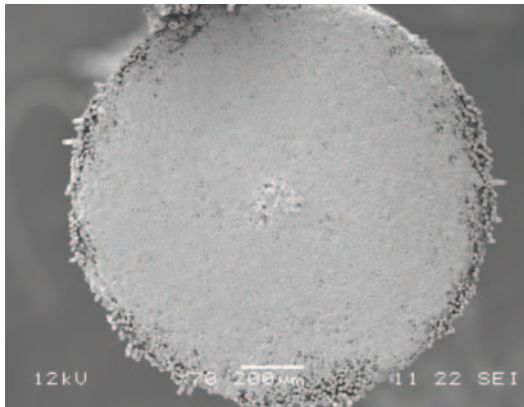
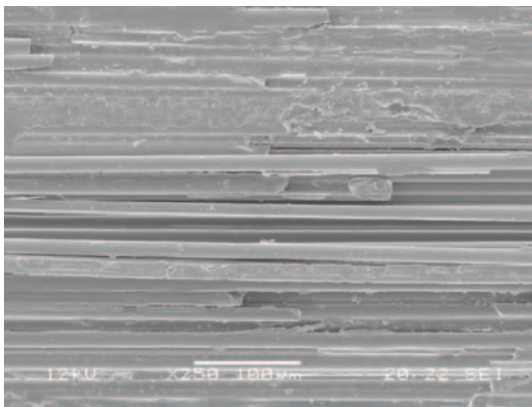
Since resin degradation is related to water sorption within the hybrid layer,<sup>116</sup> resin blends characterized by low water sorption result in the formation of bonds that are more stable than hydrophilic adhesive systems, which are prone to water sorption. In addition as the hydrolytic degradation of the resin monomers occurs only in the presence of water, adhesive hydrophilicity, water sorption and subsequent

hydrolytic degradation are correlated.<sup>116-118</sup> This allowed the researchers to hypothesize that simplified adhesives (i.e. etch-and-rinse two-step and self-etch one-step that are characterized by the combination of hydrophilic and ionic resin monomers into the bonding agent) are less stable than ‘non-simplified’ adhesives (etch-and-rinse three-step and self-etch two-step) which are characterized by the presence of a non-solvated hydrophobic resin coating.<sup>11,119</sup> The lack of hydrophobic characteristics exhibited by simplified adhesives has also been revealed by morphological evidence that their hybrid layer behaves as a semi-permeable membrane after polymerization, allowing movements of water throughout the interface.<sup>82</sup> Recent studies also correlated adhesive permeability with their polymerization kinetic.<sup>120</sup> Interestingly, all simplified adhesives exhibited sub-optimal polymerization that correlated with their high permeability to fluid movement, due to the presence of high concentrations of hydrophilic monomers, while unsimplified adhesives showed higher extents of polymerization and were correlated with less permeability to water.<sup>121</sup> As polymerization within the endodontic space may be reduced due to limited access of the curing light tip, extending the curing time could be one of the important clinical tips to be suggested during the luting of the post, in conjunction with the use of translucent fiber posts. It is important that the posts used are made with translucent components, and are thus able to permit to the light to pass through themselves.

Similar to resin monomers, the collagen fibrils constituting the hybrid layer can also degrade after time, contributing to the weakening of the hybrid layer structure.<sup>122</sup> In fact, these extrinsic degradation mechanisms of the resin-dentin interface that originate in the adhesive above the hybrid layers are accompanied by intrinsic degradation mechanisms that originate from beneath dentin hybrid



**Figures 15a and 15b** A fiber post after being stored in a root canal kept in water for 6 months: no degradation of the post is noted (SEM x250, x50)



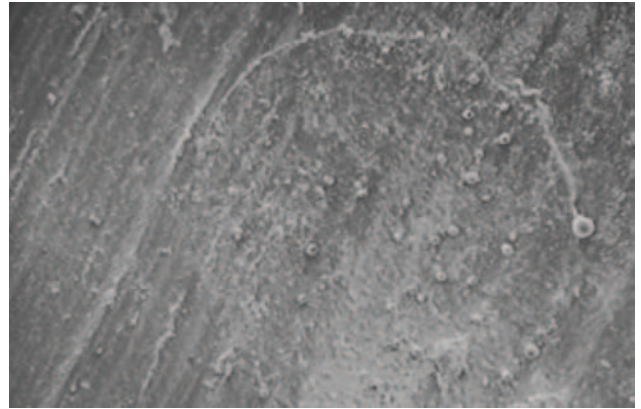
**Figures 16a and 16b**: A fiber post after being stored directly in water for 6 months: degradation of the post is evident (SEM x250, x50)

layers.<sup>7</sup> The recent reports of collagenolytic and gelatinolytic activities in partially demineralised dentin collagen matrices<sup>122-124</sup> are indirect proof of the existence of matrix metalloproteinases (MMPs) in human dentin. MMPs are a class of zinc- and calcium-dependent endopeptidases<sup>125</sup> that are trapped within the mineralised dentin matrix during tooth development.<sup>125-128</sup> The release and activation of these endogenous enzymes during dentin bonding<sup>122</sup> are thought to be responsible for the *in vitro* manifestation of the thinning and disappearance of collagen fibrils from incompletely infiltrated hybrid layers in aged, bonded dentin.<sup>119,123,124,129</sup>

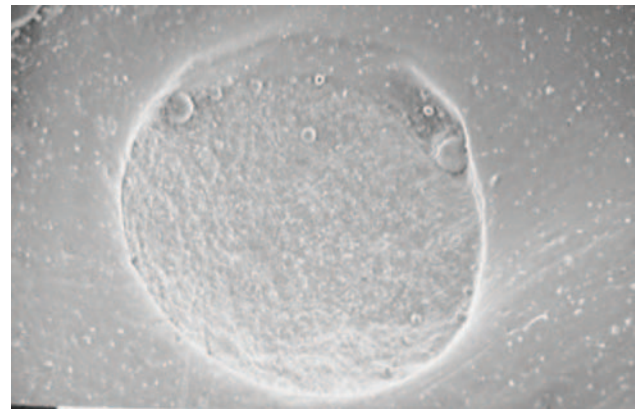
Collagen degradation at the bottom of hybrid layers has subsequently been confirmed *in vivo* in both primate<sup>130</sup> and human studies.<sup>131</sup> The involvement of host-derived MMPs in this degradation process has also been indirectly confirmed, since the application of chlorhexidine, an inhibitor of MMPs,<sup>132</sup> to acid-etched human primary dentin resulted in the preservation of collagen integrity within the hybrid layers

after the application of a simplified etch-and-rinse adhesive.<sup>131</sup>

Unfortunately, a definitive cause and effect relationship between the different procedures employed in the etch-and-rinse technique and the degradation of the dentin hybrid layers has not been yet established. Presumably, phosphoric acid demineralization could have activated the MMPs, trapped within the mineralized dentin,<sup>122</sup> resulting in the collagenolytic and gelatinolytic activities identified within the hybridized dentin. However, using a fluorescein-labeled collagen enzymatic assay, it was found that treatment of mineralized dentin powder with 37% phosphoric acid gel for 15 s actually reduced the inherent collagenolytic activity of mineralized dentin, probably due to its low acidity (pH 0.7), that partially denatures the MMPs<sup>122</sup> leaving confusion of how dentin hybrid layers could be degraded over time. In a recent study, Mazzonei et al.<sup>133</sup> revealed the potential roles of adhesives on dentin proteolytic activities using a modeling



**Figures 17a and 17b:** Fiber post exposed on the occlusal surface of an abutment. After 5 years of clinical service no sign of degradation is noted. (SEM x50)



**Figures 18a and 18b :** A upper premolar showing posts on the occlusal surface. No sign of degradation of the post is noted, but signs of wear are detected (SEM x50)

approach in which the relative proteolytic activities derived from dentin has been quantified, before and after the sequential applications of the phosphoric acid-etchant and an etch-and-rinse adhesive. Within the limits of the study, it was concluded that simplified etch-and-rinse adhesives can activate new endogenous enzymes present in dentin that counteract the MMPs which were previously inactivated by phosphoric acid-etching, providing a plausible explanation for the *in vitro* and *in vivo* observations of the degradation of dentin hybrid layers.<sup>133</sup> Similarly, the less aggressive (i.e. less acidic) versions of self-etch adhesives were also tested, highlighting the same effect of activation of endogenous MMPs present in crown dentin.<sup>134</sup>

With the increasing popularity in bonding to root canals, it was not known if intraradicular dentin possesses similar intrinsic degradation mechanisms that may adversely affect the longevity of resin-dentin bonds. Thus, with the same modelling approach, Tay et al.<sup>135</sup> demonstrated that intraradicular dentin possesses latent collagenolytic activity

which can be activated by mild self-etching adhesives. In fact, in this study the decrease in fluorescence associated with the calcium chelator, EDTA, and the classic MMPs inhibitor, chlorhexidine, indirectly showed that latent MMPs are present in the instrumented intraradicular dentin and can be further activated by mild self-etch adhesives, resulting in an increase of the collagenolytic activity up to 15-fold.<sup>135</sup> This is an important finding with potential clinical implications, since MMPs are zinc-activated, calcium-dependent enzymes. Hence, the use of 17% EDTA as an endodontic irrigant may result in chelation of the calcium ions that are required for functioning of these enzymes. Similarly, the use of chlorhexidine as an endodontic irrigant has potential merits, apart from its well-documented antimicrobial benefits, in inactivating MMPs activities. However, as reported by Tay et al., 2% chlorhexidine and 17% EDTA only partially inhibited the MMPs activated by the self-etch adhesives, concluding that time, concentration and method of delivery to be used for maximal MMPs



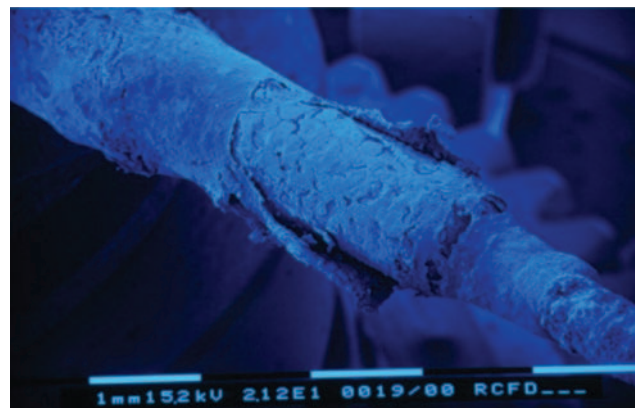
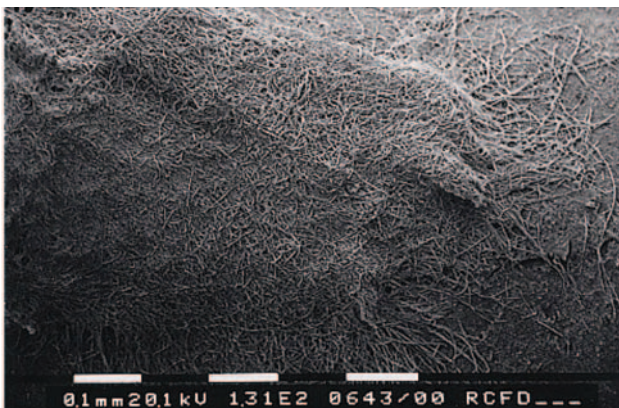
Figures 19a, 19b and 19c : Three types of posts show different penetration of light through them.

inactivation have to be optimized in future studies.<sup>135</sup>

In conclusion, as several studies stressed the effectiveness of the aging process on bonding interfaces and some of them considered the possible detrimental effect of water on the bonding interface of luted posts, the role of water inside the root canal should be considered. The main hypothesis of water contact along the interface of root dentin/luted post is based on the study by Chersoni et al.,<sup>136</sup> demonstrating that permeability of simplified adhesives results in water movement, even in root-treated dentin. However, more recently, a similar protocol<sup>137</sup> was repeated demonstrating that under *in vivo* conditions, water is not in direct contact with the bonding/luting/post system (Figures 12-14), as further confirmed by several other clinical and laboratory studies<sup>138</sup> (Figures 15 and 16). According to these findings, we can assay that the presence of water blisters detected by Chersoni et al.,<sup>136</sup> may probably be attributed to the experimental procedure, or to the incomplete solvent

evaporation of the tested adhesives<sup>138,139</sup> in place of the presence of water.

It should be considered that the aging process occurring at the adhesive interface was studied mainly in coronal dentin in simulated laboratory conditions, whilst almost no data are available on the aging process affecting bonding to root dentin. As the vitality of the tooth determines the movement of fluids through the dentinal tubules, because of the presence of the pulpal fluid, aging of the adhesive interface in intra-radicular dentin can not be related to water mediated phenomena. At the same time, other reasons such as degradation caused *via* the activity of endogenous enzymes such as matrix metalloproteinases can be hypothesized.<sup>122,124</sup> In fact, a restoration placed at the coronal dentin level has a bonding interface exposed to the oral environment and consequently subjected to 'water aging process', whilst the bonding interface created within the root canal is not in direct contact with water, unless a



Figures 20a and 20b: Figure 20a shows proper resin tag polymerization, whilst Fig 20b shows an uncomplete setting of adhesive and resin cements.

**Table 4**

Manufacturer	Type of Post Name	Size	Length	Counts at Apical (2mm)	Middle (5mm)	Cervical (8mm)	Tip
3M ESPE	RelyX Fiberpost	1	20mm	100	200	710	110
		2	20mm	120	300	900	180
		3	20mm	170	620	1900	180
Ivoclar Vivadent	FRC Postec Plus	1	20mm	200	480	1160	1410
		3	20mm	240	620	1590	2820
GC		0,8	22mm	180	270	815	4096
		1.2	22mm	230	380	750	2500
		1.4	22mm	700	770	1230	4096
		1.6	22mm	200	1130	1130	4096
RTD	DT Light Post Illusion	0.5	20mm	100	90	470	450
		1	20mm	115	470	1040	820
		2	20mm	140	190	720	250
		3	20mm	230	580	1600	435
	Fiber Cone	1	16mm	100	130	160	260
		2	16mm	130	150	180	4096
	Macro Lock	1	17,5mm	210	300	410	4096
3		17,5mm	310	500	680	4096	
Jeneric Pentron	Fiberkor		18mm	0	0	0	0
Dentsply	Radix fiber post	1	20mm	390	400	600	4096
		2	20mm	200	460	500	4096
VDW		0.5	20mm	200	380	880	1680
		3	20mm	620	820	900	4096
Komet	Dentin Post X		16,5mm	300	580	1460	2300
Angelus	Reforpost	1	20mm	0	0	110	0
		2	20mm	0	0	110	0

**Legend:** The spectrophotometer was completely saturated by the light passing through the post at 4096 pixel, 0 pixel corresponded to no light passed through. **Size:** size of the post. **Counts at:** 4 different levels along post surface: 2 mm, 5 mm, 8 mm from the tip and at the tip of the post. **Length:** length of the post

very small amount of intrinsic dentin is made by water.<sup>32</sup> Moreover it was recently reported that under *in vivo* conditions (after 5 years of clinical function) post's surfaces that remained exposed to oral environment, showed only a minimum amount of wear because of occlusion, while no degradation occurred due to water uptake<sup>140</sup> (**Figures 17 and 18**).

**The role of light during luting procedures**

Many posts available on the market are claimed to be 'translucent', or in other words, permit light to pass through the post and irradiate the luting/bonding materials. Because it is well accepted that light-cure resin cements are not indicated for luting fiber posts, the role of light can be important when dual-cure cements are used. Theoretically,

light should start the setting reaction of the cement by activating the light-curing catalyzers, after which the reaction should continue in self-cure mode. Several manufacturers now propose light-curing both dual cement and bonding adhesives through the translucent post. This creates higher expectations in the efficacy of light, although the thickness of the resin cement can be another factor limiting it.

Unfortunately there is no complete information concerning which posts available on the market allow light to pass through and also how light (its intensity) can be transmitted by the posts. Furthermore, it must be ascertained whether light mostly irradiates the tip of the posts apically or in the lateral walls, along the post surfaces.

A recent investigation<sup>141</sup> that evaluated certain fiber posts

available in the market using the spectrophotometer, (Table 4) pointed out that there are essentially three families:

1. Fiber posts that permit light to pass in a consistent entity, and theoretically should allow the curing of a dual-cure cement (Figure 19a)

2. Fiber posts that permit light to only pass through partially and, in particular, do not transmit light at the most apical part of the post (Figure 19b)

3. Fiber posts that cannot permit light to irradiate at all (Figure 19c).

When a luting procedure is selected, the type of post and the quantity of light which can pass through it, must be considered in order to use the proper luting/bonding material combination (Figure 20).

## Conclusions

Although in the last 15 years fiber posts were widely investigated with different technologies and in many aspects, there has been rapid progress in materials and techniques. Many new horizons will be developed in the near future before reaching the most ideal procedure for luting posts into root canals of endodontically treated teeth. Some of the new materials and techniques already available and/or soon available on the market are included in the following chapters of this book.

## References

1. Van Meerbeek B, Van Landuyt K, De Munk J, Inoue S, Yoshida Y, Perdigao J, Lambrechts P, Peumans M. in Summitt et al. *Fundamentals of Operative Dentistry* ed. Quintessence Books 2006:183-260.
2. Van Meerbeek B, De Munck J, Yoshida Y, Inoue S, Vargas M, Vijay P, Van Landuyt K, Lambrechts P, Vanherle G. Buonocore memorial lecture. Adhesion to enamel and dentin: current status and future challenges. *Oper Dent* 2003;28:215-235.
3. Buonocore MG. A simple method of increasing the adhesion of acrylic filling materials to enamel surface. *J Dent Res* 1955;34:849.
4. Bowen RL. Dental filling material comprising the reaction product of bis-phenol and glycidyl acrylate, U.S. Patent No. 3,066,112, 1962.
5. Bowen RL. Adhesive bonding of various materials to hard tooth tissues. 3. Bonding to dentin improved by pre-treatment and the use of surface-active comonomer. *J Dent Res* 1965;44: 903-905.
6. Fusayama T, Nakamura M, Kurosaki N, Iwaku M. Non-pressure adhesion of a new adhesive restorative resin. *J Dent Res* 1979;58:1364-1370.
7. Tay FR, Pashley DH. Have Dentin Adhesives Become Too Hydrophilic? *J Can Dent Assoc* 2003;69:726-731.
8. Simonetti M, Radovic I, Vano M, Chieffi N, Goracci C, Tognini F, Ferrari M. The influence of operator variability on adhesive cementation of fiber posts. *J Adhes Dent*. 2006;8:421-425.
9. Baier RE. Principles of adhesion. *Oper Dent Suppl* 1992;5:1.
10. Padday JF. Contact angle measurement. 1992. In: Packham DE (ed): *Handbook of adhesion* ed 1. Essex. England: Longman, 88.
11. Breschi L, Mazzoni A, Ruggeri A Jr, Cadenaro M, Di Lenarda R, Dorigo E. Dental adhesion review: aging and stability of the bonded interface. *Dental Mater* 2008; 24:90-101.
12. Perdigao J, Lopes L, Lambrechts P, Leitao J, Van Meerbeek B, Vanherle G. Effects of a self-etching primer on enamel shear bond strengths and SEM morphology. *Am J Dent*. 1997;10:141-146.
13. Salz U, Mucke A, Zimmermann J, Tay FR, Pashley DH. pKa value and buffering capacity of acidic monomers commonly used in self-etching primers. *J Adhes Dent* 2006;8:143-150.
14. Tay FR, Pashley DH. Dental adhesives of the future. *J Adhes Dent*. 2002;4:91-103.
15. Pashley DH. Smear layer: an overview of structure and function. *Proc Finn Dent Soc* 1992;88(suppl I):215-224.
16. Pashley DH, Horner JA, Brewer PD. Interaction of conditioners on the dentin surface. *Oper Dent* 1992; suppl 5:137.
17. Perdigão J. An ultramorphological study of human dentine exposed to adhesive systems. PhD thesis, Catholic University of Leuven. Ed Van der Poorten, Leuven, 1995.
18. Perdigão J, Lambrechts P, Van Meerbeek B, Tomé AR, Vanherle G, Lopes AB. Morphological field emission-SEM study of the effect of six phosphoric acid etching agents on human dentin. *Dent Mater* 1996;12:262-271.
19. Marshall GW, Marshall SJ, Kinney JH, Balooch M. The dentin substrate: structure and properties related to bonding. *J Dent* 1997;25:441-458.
20. Linde A. Dentin matrix proteins: Composition and possible functions in calcification. *Anat Rec* 1989;224:154-166.
21. Van Meerbeek B, Dhem A, Gorel-Nicaise M, Braem M, Lambrechts P, Vanherle G. Comparative SEM and TEM examination of the ultrastructure of the resin-dentin interdiffusion zone. *J Dent Res* 1993;72:495-501.
22. Nakabayashi N, Kojima K, Mashuara E. The promotion of adhesion by the infiltration of monomers into tooth substrates. *J Biomed Mater Res* 1982;16:1240-1243.
23. Pashley DH. Interactions of dental materials with dentin. *Trans Acad Dent Mater* 1990;3:55.
24. Tao L, Pashley DH. Shear bond strengths to dentin: effects of surface treatments, depth and position. *Dent Mater* 1988;4:371-378.
25. Gwinnett AJ, Tay FR, Pang KM, Wei SH. Quantitative contribution of the collagen network in dentin hybridization. *Am J Dent* 1996;9:140-144.
26. Tay FR, Pashley DH. Aggressiveness of contemporary self-etching systems. I: Depth of penetration beyond dentin smear layers. *Dent Mater* 2001;17:296-308.
27. Yoshida Y, Van Meerbeek B, Nakayama Y, Snauwaert J, Hellemans L, Lambrechts P, Vanherle G, Wakasa K. Evidence of chemical bonding at biomaterial-hard tissue interfaces. *J Dent Res* 2000;79:709-714.
28. Kanca J III. Resin bonding to wet substrate. I. Bonding to dentin. *Quintessence Int* 1992;23:39-41.
29. Nanci A. Dentin-pulp complex. In: Nanci A ed. *Ten Cate's oral histology: development, structure and function*, 6th ed. St Louis, Missouri, Mosby. 2003;pp.192-239.
30. Ohsaki Y, Nagata K Type III collagen is a major component of

interodontoblastic fibers of the developing mouse molar root. *The Anatomical Record* 1994;240:308-313.

31. Kitasako Y, Shibata S, Cox CF, Tagami J. Location, arrangement and possible function of interodontoblastic collagen fibers in association with calcium hydroxide-induced hard tissue bridges. *Int Endod J* 2002;35:996-1004.

32. Ferrari M, Mannocci F, Vichi A, Cagidiaco MC, Mjor IA. Bonding to root canal: structural characteristic of the substrate. *Am J Dent* 2000;13:255-260.

33. Mjor IA, Smith MR, Ferrari M, Mannocci F. The structure of dentine in the apical region of human teeth. *Int Endod J* 2001;34:346-353.

34. Mannocci F, Pilecki P, Bertelli E, Watson TF. Density of dentinal tubules affects the tensile strength of root dentin. *Dent Mater* 2004;20:293-296.

35. Schwartz RS. Adhesive dentistry and endodontics. Part 2: bonding in the root canal system the promise and the problems: a review. *J Endod* 2006;32:1125-1134.

36. Prabhu SG, Rhaim N, Bhat KS, Mathew J. Comparison of removal of endodontic smear layer using NaOCl, EDTA, and different concentrations of maleic acid – A SEM study. *Endodontology*, 2003;15:20-25.

37. Ishioka S, Caputo AA. Interaction between the dentinal smear layer and composite bond strengths. *J Prosthet Dent* 1989;61:180-185.

38. Gwinnett AJ. Quantitative contribution of resin infiltration/hybridization to dentin bonding. *Am J Dent* 1993;6:7-9.

39. Pashley DH, Tao L, Boyd L, King GE, Horner JA. Scanning electron microscopy of the substructure of smear layers in human dentine. *Arch Oral Biol* 1988;33:265-270.

40. Pashley DH. Smear layer: physiological considerations. *Oper Dent Suppl.* 1984;3:13-29.

41. Meryon SD, Tobias RS, Jakeman KJ. Smear removal agents: a quantitative study in vivo and in vitro. *J Prosthet Dent* 1987;57:174-179.

42. Schwartz RS, Fransman R. Adhesive dentistry and endodontics: materials, clinical strategies and procedures for restoration of access cavities: a review. *J Endod* 2005;31:151-165.

43. Goracci C, Sadek FT, Fabianelli A, Tay FR, Ferrari M. Evaluation of the adhesion of fiber posts to intraradicular dentin. *Oper Dent* 2005;30:627-635.

44. Torabinejad M, Handysides R, Khademi AA, Bakland LK. Clinical implications of the smear layer in endodontics: a review. *Oral Surg Oral Med Oral Pathol Oral Radiol Endod* 2002;94:658-666.

45. White RR, Goldman M, Lin PS. The influence of the smeared layer upon dentinal tubule penetration by plastic filling materials. *J Endod* 1984;10:558-562.

46. Pallares A, Faus V, Glickman GN. The adaptation of mechanically softened gutta-percha to the canal walls in the presence or absence of smear layer: a scanning electron microscopic study. *Int Endod J* 1995;28:266-269.

47. Boone KJ, Murchison DF, Schindler WG, Walker WA 3rd. Post retention: the effect of sequence of post-space preparation, cementation time, and different sealers. *J Endod* 2001;27:768-771.

48. Serafino C, Gallina G, Cumbo E, Ferrari M. Surface debris of canal walls after post space preparation in endodontically treated teeth: a scanning electron microscopic study. *Oral Surg Oral Med Oral Pathol Oral Radiol Endod* 2004;97:381-387.

49. Standlee JP, Caputo AA. Endodontic dowel retention with resinous cements. *J Prosthet Dent* 1992;68:913-917.

50. Coniglio I, Magni E, Goracci C, Radovic I, Carvalho CA, Grandini S, Ferrari M. Post space cleaning using a new nickel titanium endodontic drill combined with different cleaning regimes. *J Endodont* 2008 In press.

51. Erdemir A, Eldeniz AU, Belli S, Pashley DH. Effect of solvents on bonding to root canal dentin. *J Endod* 2004;30:589-592.

52. Ari H, Yasar E, Belli S. Effects of NaOCl on bond strengths of resin cements to root canal dentin. *J Endod* 2003;29:248-251.

53. Saleh AA, Ettman WM. Effect of endodontic irrigation solutions on microhardness of root canal dentine. *J Dent* 1999;27:43-46.

54. Morris MD, Lee KW, Agee KA, Bouillaguet S, Pashley DH. Effects of sodium hypochlorite and RC-prep on bond strengths of resin cement to endodontic surfaces. *J Endod* 2001;27:753-757.

55. Ozturk B, Ozer F. Effect of NaOCl on bond strengths of bonding agents to pulp chamber lateral walls. *J Endod* 2004;30:362-365.

56. Nikaido T, Takano Y, Sasafuchi Y, Burrow MF, Tagami J. Bond strengths to endodontically-treated teeth. *Am J Dent* 1999;12:177-180.

57. Cadenaro M, Breschi L, Antonioli A, Mazzoni A, Di Lenarda R. Influence of whitening on the degree of conversion of dental adhesives on dentin. *Eur J Oral Sci* 2006;114:257-262.

58. Titley KC, Torneck CD, Smith DC, Applebaum NB. Adhesion of a glass ionomer cement to bleached and unbleached bovine dentin. *Endod Dent Traumatol* 1989;5:132-138.

59. Ari H, Erdemir A, Belli S. Evaluation of the effect of endodontic irrigation solutions on the microhardness and the roughness of root canal dentin. *J Endod* 2004;30:792-795.

60. Oncag O, Hosgor M, Hilmioglu S, Zekioglu O, Eronat C, Burhanoglu D. Comparison of antibacterial and toxic effects of various root canal irrigants. *Int Endod J* 2003;36:423-432.

61. Vianna ME, Gomes BP, Berber VB, Zaia AA, Ferraz CC, de Souza-Filho FJ. In vitro evaluation of the antimicrobial activity of chlorhexidine and sodium hypochlorite. *Oral Surg Oral Med Oral Pathol Oral Radiol Endod* 2004;97:79-84.

62. Leonardo MR, Tanomaru Filho M, Silva LA, Nelson Filho P, Bonifacio KC, Ito IY. In vivo antimicrobial activity of 2% chlorhexidine used as a root canal irrigating solution. *Endod* 1999;25:167-171.

63. Lambrianidis T, Margelos J, Beltes P. Removal efficiency of calcium hydroxide dressing from the root canal. *J Endod* 1999;25:85-88.

64. Kim SK, Kim YO. Influence of calcium hydroxide intracanal medication on apical seal. *Int Endod J* 2002;35:623-628.

65. Kielbassa AM, Attin T, Hellwig E. Diffusion behavior of eugenol from zinc oxide-eugenol mixtures through human and bovine dentin in vitro. *Oper Dent* 1997;22:15-20.

66. Carvalho CN, de Oliveira Bauer JR, Loguercio AD, Reis A. Effect of ZOE temporary restoration on resin-dentin bond strength using different adhesive strategies. *J Esthet Restor Dent* 2007;19:144-152.

67. Fujisawa S, Kadoma Y. Action of eugenol as a retarder against polymerization of methyl methacrylate by benzoyl peroxide. *Biomaterials* 1997;18:701-703.

68. Bayindir F, Akyil MS, Bayindir YZ. Effect of eugenol and non-eugenol containing temporary cement on permanent cement retention and microhardness of cured composite resin. *Dent Mater* 2003;22:592-

599.

69. Woody TL, Davis RD. The effect of eugenol-containing and eugenol-free temporary cements on microleakage in resin bonded restorations. *Oper Dent* 1992;17:175-180.

70. Watanabe EK, Yamashita A, Imai M, Yatani H, Suzuki K. Temporary cement remnants as an adhesion inhibiting factor in the interface between resin cements and bovine dentin. *Int J Prosthodont* 1997;10:440-452.

71. Terata R, Yoshinaka S, Nakashima K, Kubota M. Effect of resinous temporary material on tensile bond strength of resin luting cement to tooth substrate. *Dent Mater* 1996;15:45-50.

72. Pashley DH, Carvalho RM. Dentine permeability and dentine adhesion. *J Dent* 1997;25:355-372.

73. Mayer T, Pioch T, Duschner H, Staehle HJ. Dentinal adhesion and histomorphology of two dentinal bonding agents under the influence of eugenol. *Quintessence Int* 1997;28:57-62.

74. Arcari GM, Araujo E, Baratieri LN, Lopes GC. Microtensile bond strength of a nanofilled composite resin to human dentin after nonvital tooth bleaching. *J Adhes Dent* 2007;9:333-340.

75. Baratieri LN, Ritter AV, Monteiro S Jr, Caldeira de Andrada MA, Cardoso Vieira LC. Nonvital tooth bleaching: guidelines for the clinician. *Quintessence Int* 1995;26:597-608.

76. Heller D, Skriber J, Lin LM. Effect of intracoronal bleaching on external cervical root resorption. *J Endod* 1992;18:145-148.

77. Elkhatab H, Nakajima M, Hiraishi N, Kitasako Y, Tagami J, Nomura S. Surface pH and bond strength of a self-etching primer/adhesive system to intracoronal dentin after application of hydrogen peroxide bleach with sodium perborate. *Oper Dent* 2003;28:591-597.

78. Pecora JD, Cruzfilho AM, Sousesano MD, Silva RG. In vitro action of various bleaching agents on the microhardness of human dentin. *Braz Dent J* 1994;5:129-134.

79. Chng HK, Palamara JE, Messer HH. Effect of hydrogen peroxide and sodium perborate on biomechanical properties of human dentin. *J Endod* 2002;28:62-67.

80. Kaufman D, Mor C, Stabholz A, Rotstein I. Effect of gutta-percha solvents on calcium and phosphorus levels of cut human dentin. *J Endod* 1997;23:614-615.

81. Swift EJ Jr, Perdigao J, Combe EC, Simpson CH 3rd, Nunes MF. Effects of restorative and adhesive curing methods on dentin bond strengths. *Am J Dent* 2001;14:137-140.

82. Tay FR, Pashley DH, Suh BI, Carvalho RM, Itthagarun A. Single-step adhesives are permeable membranes. *J Dent* 2002;30:371-382.

83. Cheong C, King NM, Pashley DH, Ferrari M, Toledano M, Tay FR. Incompatibility of selfetch adhesives with chemical/dual-cured composites: two-step vs one-step systems. *Operative Dentistry* 2003;28:747-755.

84. Tay FR, Suh BI, Pashley DH, Prati C, Chuang SF, Li F. Factors contributing to the incompatibility between simplified-step adhesives and self-cured or dual-cured composites. Part II. Single-bottle, total-etch adhesive. *J Adhes Dent* 2003;5:91-105.

85. Sanares AM, Itthagarun A, King NM, Tay FR, Pashley DH. Adverse surface interactions between one-bottle light-cured adhesives and chemical-cured composites. *Dent Mater* 2001;17:542-556.

86. Inoue S, Vargas MA, Abe Y, Yoshida Y, Lambrechts P, Vanherle

G, Sano H, VanMeerbeek B. Microtensile bond strength of eleven contemporary adhesives to dentin. *J Adhes Dent* 2001;3:237-245.

87. Tay FR, Pashley DH, Yiu CK, Sanares AM, Wei SH. Factors contributing to the incompatibility between simplified-step adhesives and chemically-cured or dual-cured composites. Part I. Single-step self-etching adhesive. *J Adhes Dent* 2003;5:27-40.

88. Suh BI, Feng L, Pashley DH, Tay FR. Factors contributing to the incompatibility between simplified-step adhesives and chemically-cured or dual-cured composites. Part III. Effect of acidic resin monomers. *J Adhes Dent* 2003;5:267-282.

89. Tay FR, King NM, Suh BI, Pashley DH. Effect of delayed activation of light-cured resin composites on bonding of all-in-one adhesives. *J Adhes Dent* 2001;3:207-225.

90. Tay FR, Loushine RJ, Lambrechts P, Wellar RN, Pashley DH. Geometric factors affecting dentin bonding in root canals: a theoretical modelling approach. *J Endod* 2006;31:584-588.

91. Feilzer AJ, Dauvillier BS. Effect of TEGDMA/BisGMA ratio on stress development and viscoelastic properties of experimental two-paste composites. *J Dent Res* 2003;82:824-828.

92. Feilzer AJ, De Gee AJ, Davidson CL. Setting stress in composite resin in relation to configuration of the restoration. *J Dent Res* 1987;66:1636-1639.

93. Davidson CL, Feilzer AJ. Polymerization shrinkage and polymerization shrinkage stress in polymer-based restoratives. *J Dent* 1997;25:435-440.

94. Moreira da Silva E, dos Santos GO, Guimaraes JG, Barcellos Ade A, Sampaio EM. The influence of C-factor, flexural modulus and viscous flow on gap formation in resin composite restorations. *Oper Dent* 2007;32:356-362.

95. Kemp-Scholte CM, Davidson CL. Marginal sealing of curing contraction gaps in Class V composite resin restorations. *J Dent Res* 1988;67:841-845.

96. Davidson CL, Van Zeghbroeck L, Feilzer AJ. Destructive stresses in adhesive luting cements. *J Dent Res* 1991;70:880-882.

97. Davidson CL, de Gee AJ. Relaxation of polymerization contraction stresses by flow in dental composites. *J Dent Res* 1984;63:146-148.

98. Braga RR, Boaro LC, Kuroe T, Azevedo CL, Singer JM. Influence of cavity dimensions and their derivatives (volume and 'C' factor) on shrinkage stress development and microleakage of composite restorations. *Dent Mater* 2006;22:818-823.

99. Bouillaguet S, Troesch S, Wataha JC, Krejci I, Meyer JM, Pashley DH. Microtensile bond strength between adhesive cements and root canal dentin. *Dent Mater* 2003;19:199-205.

100. Pirani C, Chersoni S, Foschi F, Piana G, Loushine RJ, Tay FR, Prati C. Does hybridization of intraradicular dentin really improve fiber post retention in endodontically treated teeth? *J Endod* 2005;31:891-894.

101. Bonfante EA, Pegoraro LF, de Gôes MF, RM Carvalho. SEM observation of the bond integrity of fiber-reinforced composite posts cemented into root canals. *Dent Mater* 2007, doi:10.1016/j.2007.04.010

102. Van Noort R. *Introduction to Dental Materials*. Elsevier Health Sciences, London 2002.

103. Goracci C, Fabianielli A, Sadek FT, Papacchini F, Tay FR, Ferrari

- M. The contribution of friction to the dislocation resistance of bonded fiber posts. *J Endodont* 2005; 31: 608-612.
104. Carvalho CA, Monticelli F, Cantoro A, Breschi L, Ferrari M. Push-out bond strength of fiber posts luted with unfilled resin cement. *J Adhes Dent* 2008, in press.
105. Silva ALF, Casselli DSM, Ambrosiano GMB, Martins LRM. Effect of the adhesive application mode and fiber post translucency on the push-out bond strength to dentin. *J Endodont* 2007; 33: 1078-1081.
106. Grandini S, Goracci C, Monticelli F, Borracchini A, Ferrari M. SEM evaluation of the cement layer thickness after luting two different posts. *J Adhes Dent* 2005;7:235-240.
107. Bouillaguet S, Shaw L, Barthelemy J, Krejci I, Wataha JC. Long-term sealing ability of Pulp Canal Sealer, AH-Plus, GuttaFlow and Epiphany. *Int Endod J* 2008; 41:219-226.
108. Jongsma LA, Bolhuis PB, Pallav P, Kleverlaan CJ, Feilzer AJ. Benefits of a two-step cementation procedure for prefabricated fiber posts. IADR-CED and Israel Divisions Annual Meeting, Thessaloniki, Greece, Sept. 2007, abstract #0424.
109. Porciani PF, Vano M, Goracci C, Grandini S, Ferrari M. Fracture resistance of multiple combinations of new endodontic fiber posts. *Am J Dent* 2008, in press.
110. Pashley DH, Tay FR, Carvalho RM, Rueggeberg FA, Agee KA, Carrilho M, Donnelly A, Garcia-Godoy F. From dry bonding to water-wet bonding to ethanol-wet bonding. A review of the interactions between dentin matrix and solvated resins using a macromodel of the hybrid layer. *Am J Dent* 2007;20:7-20.
111. Tay FR, Pashley DH, Kapur RR, Carrilho MR, Hur YB, Garrett LV, Tay KC. Bonding BisGMA to dentin—a proof of concept for hydrophobic dentin bonding. *J Dent Res* 2007;86:1034-1039.
112. Sadek FT, Pashley DH, Nishitani Y, Carrilho MR, Donnelly A, Ferrari M, Tay FR. Application of hydrophobic resin adhesives to acid-etched dentin with an alternative wet bonding technique. *J Biomed Mater Res A*. 2007, in press.
113. Wang Y, Spencer P, Yao X, Brenda B. Effect of solvent content on resin hybridization in wet dentin bonding. *J Biomed Mater Res A*. 2007;82:975-983.
114. Ouns H, Salameh Z, Carvalho CA, Cantoro A, Grandini S, Ferrari M. Bond strength to fiber-reinforced posts: a comparison between conventional and wet-ethanol bonding systems. *J Adhes Dent* 2008, in press.
115. Hashimoto M, Ohno H, Sano H, Kaga M, Oguchi H. In vitro degradation of resin dentin bonds analyzed by microtensile bond test, scanning and transmission electron microscopy. *Biomaterials* 2003;24:3795-3803.
116. Malacarne J, Carvalho RM, de Goes MF, Svizzerd V, Pashley DH, Tay FR, Yin CK, Carrilho MR. Water sorption/solubility of dental adhesives resins. *Dent Mater* 2006;22:973-980.
117. Tay FR, Hashimoto M, Pashley DH, Peters MC, Lai SC, Yiu CK, Cheong C. Aging affects two modes of nanoleakage expression in bonded dentin. *J Dent Res* 2003;82:537-541.
118. Ito S, Hashimoto M, Wadgaonkar B, Svizero N, Carvalho RM, Yiu C, Rueggeberg FA, Foulger S, Saito T, Nishitani Y, Yoshiyama M, Tay FR, Pashley DH. Effects of resin hydrophilicity on water sorption and changes in modulus of elasticity. *Biomaterials* 2005;26:6449-6459.
119. De Munck J, Van Landuyt K, Peumans M, Poitevin A, Lambrechts P, Braem M, Van Meerbeek B. A critical review of the durability of adhesion to tooth tissue: methods and results. *J Dent Res* 2005;84:118-132.
120. Cadenaro M, Antonioli F, Sauro S, Tay FR, Di Lenarda R, Prati C, Biasotto M, Contardo L, Breschi L. Degree of conversion and permeability of dental adhesives. *Eur J Oral Sci*, 2005;113:525-530.
121. Breschi L, Cadenaro M, Antonioli F, Sauro S, Biasotto M, Prati C, Tay FR, Di Lenarda R. Polymerization kinetics of dental adhesives cured with LED: correlation between extent of conversion and permeability. *Dental Materials* 2007;23:1066-1072.
122. Pashley DH, Tay FR, Yiu C, Hashimoto M, Breschi L, Carvalho RM, Ito S. Collagen degradation by host-derived enzymes during aging. *J Dent Res* 2004;83:216-221.
123. Hashimoto M, Tay FR, Ohno H, Sano H, Kaga M, Yiu C, Kumagai H, Kudou Y, Kubota M, Oguchi H. SEM and TEM analysis of water degradation of human dentinal collagen. *J Biomed Mater Res B Appl Biomater* 2003;66:287-298.
124. Ferrari M, Mason PN, Goracci C, Pashley DH, Tay FR. Collagen degradation in endodontically treated teeth after clinical function. *J Dent Res* 2004;83:414-419.
125. Sorsa T, Tjäderhane L, Salo T. Matrix metalloproteinases (MMPs) in oral diseases. *Oral Disease* 2004;10:311-318.
126. Tjäderhane L, Larjava H, Sorsa T, Uitto VJ, Larmas M, Salo T. The activation and function of host matrix metalloproteinase in dentin matrix during breakdown in carious lesions. *J Dent Res* 1998;77:1622-1629.
127. van Strijp AJ, Jansen DC, DeGroot J, ten Cate JM, Everts V. Host-derived proteinases and degradation of dentine collagen in situ. *Caries Res*. 2003;37:58-65.
128. Martin-De Las Heras S, Valenzuela A, Overall CM. The matrix metalloproteinase gelatinase A in human dentine. *Arch Oral Biol* 2000;45:757-765.
129. Armstrong SR, Vargas MA, Chung I, Pashley DH, Campbell JA, Laffoon JE, Qian F. Resin-dentin interfacial ultrastructure and microtensile dentin bond strength after five year water storage. *Oper Dent* 2004;29:705-712.
130. Koshiro K, Inoue S, Sano H, De Munck J, Van Meerbeek B. In vivo degradation of resin-dentin bonds produced by a self-etch and an etch-and-rinse adhesive. *Eur J Oral Sci* 2005;113:341-348.
131. Hebling J, Pashley DH, Tjäderhane L, Tay FR. Chlorhexidine arrests subclinical degradation of dentin hybrid layers in vivo. *J Dent Res* 2005;84:741-746.
132. Gendron R, Greiner D, Sorsa T, Mayrand D. Inhibition of the activities of matrix metalloproteinases 2, 8, and 9 by chlorhexidine. *Clin Diagn Lab Immunol* 1999;6:437-439.
133. Mazzoni A, Pashley DH, Nishitani Y, Breschi L, Mannello F, Tjäderhane L, Toledano M, Pashley EL, Tay FR. Reactivation of inactivated endogenous proteolytic activities in phosphoric acid-etched dentine by etch-and-rinse adhesives. *Biomaterials* 2006;27:4470-4476.
134. Nishitani Y, Yoshiyama M, Wadgaonkar B, Breschi L, Mannello F, Mazzoni A, Carvalho RM, Tjäderhane L, Tay FR, Pashley DH. Activation of gelatinolytic/collagenolytic activity in dentin by self-etching adhesives. *Eur J Oral Sci* 2006;114:160-166.
135. Tay FR, Pashley DH, Loushine RJ, Weller RN, Monticelli F, Osorio R. Self-etching adhesives increase collagenolytic activity in radicular dentin. *J Endod* 2006;32:862-868.
136. Chersoni S, Acquaviva GL, Prati C, Ferrari M, Grandini S,

Pashley DH, Tay FR. In vivo fluid movement through dentin adhesives in endodontically treated teeth. *J Dent Res* 2005;84:223-227.

137. Ferrari M, Coniglio I, Magni E, Cagidiaco MC, Prati C, Breschi L. How can droplets formation occur in endodontically treated teeth during bonding procedures? *J Adhes Dent* 2008. In press.

138. Vano M, Vichi A, Goracci C, Ferrari M. The effect of storage time, media and reproduced clinical conditions on fiber posts. *Dent Mater* 2008, in press.

139. Van Landuyt KL, Snauwaert J, De Munck J, Coutinho E, Poitevin A, Yoshida Y, Suzuki K, Lambrechts P, Van Meerbeek B. Origin of interfacial droplets with one-step adhesives. *J Dent Res* 2007;86:739-744.

140. Vano M, Garcia-Godoy F, Goracci C, Vichi A, Ferrari M. Effects of oral environment and occlusal wear on FRC-posts integrity in clinical service for 5 years. *J Adhes Dent* 2008, in press.

141. Goracci C, Corciolani G, Vichi A, Ferrari M. Entity of light passing through fiber posts: a study with a spectrophotometer; Submitted for publication, 2008.

142. Faria e Silva AL, Casselli DS, Ambrosano GM, Martins LR. Effect of the adhesive application mode and fiber post translucency on the push-out bond strength to dentin. *J Endod* 2007;33:1078-1081.

143. Boff LL, Grossi ML, Prates LH, Burnett LH Jr, Shinkai RS. Effect of the activation mode of post adhesive cementation on push-out bond strength to root canal dentin. *Quintessence Int* 2007;38:387-394.

144. Wang VJJ, Chen Y, Yip KHK, Smales RJ, Meng QF, Chen L. Effect of two fiber post types and two luting cement systems on regional post retention using the push-out test. *Dent Mater* 2007, in press.

145. Ohlmann B, Fickenscher F, Dreyhaupt J, Rammelsberg P, Gabbert O, Schmitter M. The effect of two luting agents, pretreatment of the post, and pretreatment of the canal dentin on the retention of fiber-reinforced composite posts. *J Dent* 2008;36: 87-92

146. Perdigão J, Geraldeli S, Lee IK. Push-out bond strengths of tooth-colored posts bonded with different adhesive systems. *Am J Dent* 2004;17:422-426.

147. Goracci C, Tavares AU, Fabianelli A, Monticelli A, Raffaelli O, Cardoso PEC, Tay FR, Ferrari M. The adhesion between fiber posts and root canal walls: comparison between microtensile and push-out bond strength measurements. *Eur J Oral Sci* 2004;112:353-361.

148. Perez BE, Barbosa SH, Melo RM, Zamboni SC, Ozcan M, Valandro LF, Bottino MA. Does the thickness of the resin cement affect the bond strength of a fiber post to the root dentin? *Int J Prosthodont* 2006;19:606-609.

149. Bolhuis P, de Gee A, Feilzer A. Influence of fatigue loading on four post-core systems in maxillary premolars. *Quintessence Int* 2004;35:657-667.

150. Bolhuis P, de Gee A, Feilzer A. The influence of fatigue loading on the quality of the cement layer and retention strength of carbon fiber post-resin composite core restorations. *Oper Dent* 2005;30:220-227.