

## Bonding to enamel and dentin: A brief history and state of the art, 1995

Edward J. Swift, Jr\* / Jorge Perdigão\*\* / Harald O. Heymann\*\*\*

*The acid-etch technique for bonding composite resins to enamel has revolutionized the practice of restorative dentistry. The ability of clinicians to bond restorative materials to enamel has fundamentally changed such diverse areas as cavity preparation, caries prevention, and esthetic treatment options. Although bonding of resin to dentin has proved to be a difficult challenge, ongoing advances are improving the reliability and predictability of dentinal adhesion. The purpose of this article is to provide a brief history of enamel and dentinal bonding, as well as an overview of the current state of the art. (Quintessence Int 1995;26:95-110.)*

### The acid-etch technique

The foundation for adhesive restorative and preventive dentistry was laid in 1955, when Buonocore<sup>1</sup> proposed that acids could be used to alter the surface of enamel to "render it more receptive to adhesion." His hypothesis was based on the common industrial use of phosphoric acid to improve adhesion of paints and acrylic coatings to metal surfaces. Buonocore found that acrylic resin could be bonded to human enamel that was conditioned with 85% phosphoric acid for 30 seconds. Prophetically, he proposed several potential uses for this new "bonding" technique, including Class III and Class V restorations and pit and fissure sealants.

Subsequent work by Gwinnett and Matsui<sup>2</sup> and Buonocore and others<sup>3</sup> suggested that the formation of "resin tags" was the primary attachment mechanism of resin to phosphoric acid-etched enamel. Acid etching removes about 10  $\mu\text{m}$  of the enamel surface and creates a porous layer ranging from 5 to 50  $\mu\text{m}$  deep. When a low-viscosity resin is applied, it flows into the microporosities and channels of this layer and polymerizes to form a micromechanical bond with the enamel. Etching also increases the wettability and surface area of the enamel substrate.<sup>4-6</sup>

Gwinnett<sup>6</sup> and Silverstone et al<sup>7</sup> described three patterns of etching in enamel (Figs 1a to 1c). The most common, or Type 1, etching pattern involves preferential removal of enamel prism cores: prism peripheries remain relatively intact. The Type 2 etching pattern is the reverse process; ie, the peripheries are removed, leaving the cores intact. The Type 3 etching pattern is less distinct. It includes areas resembling each of the other patterns, as well as regions in which the etching pattern appears unrelated to prism morphology.

Various concentrations of phosphoric acid have been evaluated as enamel etchants, and some form precipitates that might interfere with resin bonding.<sup>8</sup> One study showed that 60-second applications of 50% phosphoric acid produce a precipitate (monocalcium phosphate monohydrate) that can be rinsed off. However, concentrations of less than approximately 27% form a precipitate (dicalcium phosphate dihydrate) that cannot be easily removed.<sup>9</sup>

\* Associate Professor, Department of Operative Dentistry, University of North Carolina, School of Dentistry, Chapel Hill, North Carolina.

\*\* Assistant Professor, Department of Operative Dentistry, University of Coimbra, Medical and Dental School, Coimbra, Portugal.

\*\*\* Associate Professor and Chair, Department of Operative Dentistry, University of North Carolina, School of Dentistry, Chapel Hill, North Carolina.

Reprint requests: Dr Edward J. Swift, Jr, Associate Professor, Department of Operative Dentistry, CB # 7450, Brauer Hall, University of North Carolina, School of Dentistry, Chapel Hill, North Carolina 27599-7450.

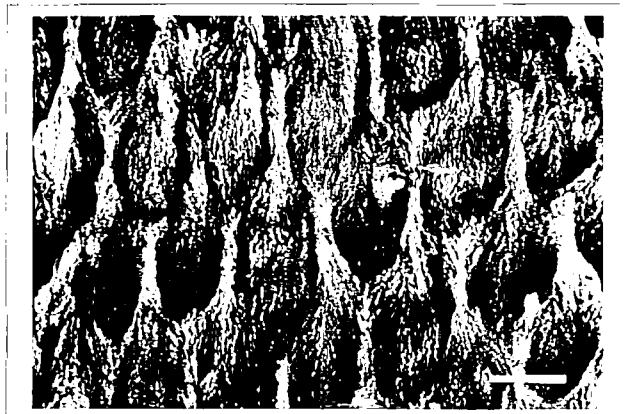


Fig 1a Scanning electron micrograph of etched enamel showing Type I etching pattern. (Bar = 5  $\mu$ m.)

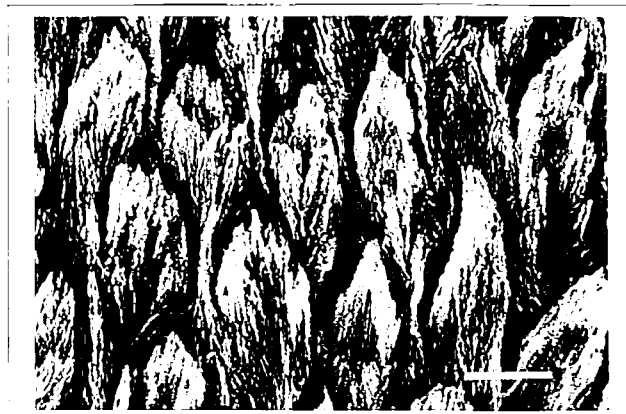


Fig 1b Scanning electron micrograph of etched enamel showing Type II etching pattern. (Bar = 5  $\mu$ m.)



Fig 1c Scanning electron micrograph of etched enamel showing Type III etching pattern. (Bar = 5  $\mu$ m.)

Silverstone<sup>5</sup> reported that phosphoric acid concentrations of between 30% and 40% provide enamel surfaces that have the most retentive appearance. Also, calcium dissolution and etching depth increase with phosphoric acid concentration until the acid concentration reaches 40%. Stronger solutions dissolve less calcium and result in smaller etching depths.<sup>10</sup>

As a result of these studies, most commercial enamel etchants are 30% to 40% (frequently 37%) concentrations of phosphoric acid. However, lower concentrations have been shown, in some studies,<sup>11-13</sup> to provide bond strengths similar to those obtained with 30% to 40% phosphoric acid.

#### Reduced enamel etching times

A 60-second application time traditionally has been

recommended for etching enamel with 30% to 40% phosphoric acid. One study concluded that shorter etching times resulted in lower tensile bond strengths.<sup>14</sup> However, subsequent studies with scanning electron microscopy (SEM) have indicated that etching times as brief as 15 seconds provide essentially the same surface roughness as a 60-second etching time.<sup>15-17</sup> Laboratory tests also have shown that shear bond strengths and marginal microleakage are similar for 15- and 60-second etching times.<sup>16-21</sup> In addition, clinical studies have shown that sealant retention is not adversely affected by reduced etching time.<sup>22,23</sup>

#### Benefits of enamel bonding

Shear bond strengths of composite resin to phosphoric acid-etched enamel are typically in the range of 20 MPa.<sup>13,17,19</sup> Such bond strengths provide routinely successful retention of resins for a variety of clinical applications, including direct anterior and posterior composite restorations, porcelain and composite resin veneers and inlays, orthodontic brackets, resin-bonded prostheses, and pit and fissure sealants.

Furthermore, etching reduces leakage around restoration margins in enamel<sup>20,21</sup> (Fig 2). Composite resins shrink as they polymerize, and contraction stresses of up to 7 MPa develop within the resin.<sup>24-27</sup> However, the magnitude of these stresses varies with cavity configuration. For example, when composite resin is bonded to a single surface, flow relaxation occurs within the composite resin as it sets, relieving some of the contraction forces. In three-dimensional cavity preparations, only the outer surface of composite resin is unbonded, so less flow is possible and much greater stresses occur

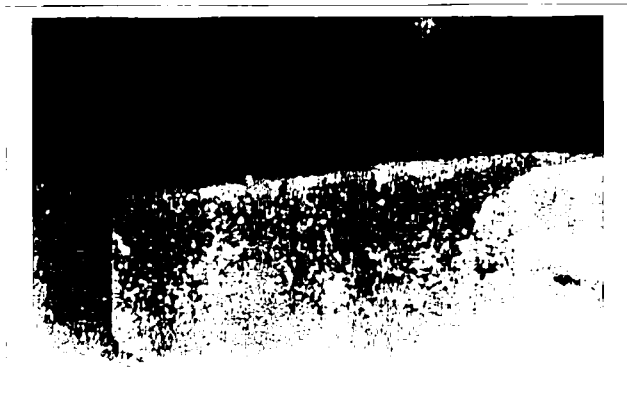


Fig 2 Section of a specimen from a microleakage study. Note the complete absence of leakage at the etched enamel margin and the extensive leakage at the gingival (dentin-cementum) margin. (Courtesy of Dr Daniel Fortin, University of Montreal.)

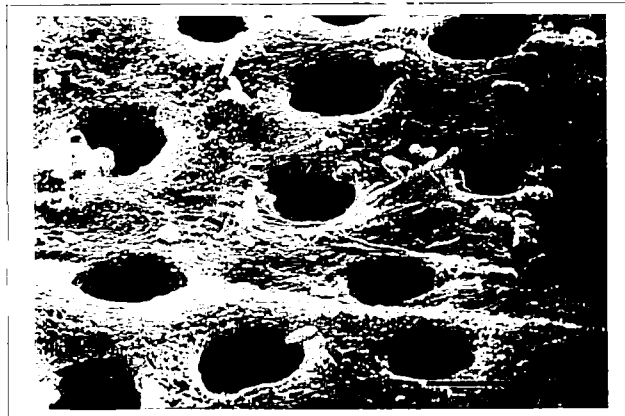


Fig 3 Scanning electron micrograph of dentinal tubules. (Bar = 5  $\mu$ m.)

within the material.<sup>26-28</sup> It has been estimated that shear bond strengths of 17 to 20 MPa are required to resist contraction forces sufficiently to produce gap-free restoration margins.<sup>27,29</sup> Enamel bond strengths are generally adequate to prevent opening of margins by polymerization shrinkage.

Composite resin restorations bonded to etched enamel provide another important benefit—reinforcement of cusps. Cavity preparations weaken teeth and increase the risk of cuspal fracture, and conventional restorative materials provide little or no reinforcement of the weakened tooth structure. In contrast, laboratory and clinical data suggest that bonded composite resin restorations provide substantial cuspal reinforcement.<sup>30-35</sup>

The benefits of enamel bonding are enhanced by the use of proper isolation techniques. In a recent clinical study, composite resin posts were bonded to teeth that were treatment planned for extraction.<sup>36</sup> The teeth were isolated with either rubber dam or cotton rolls for the bonding procedures. Shear bond strengths were determined after the teeth were removed and were found to be significantly higher for specimens that had been isolated with rubber dam.

#### Alternative acids for etching enamel

Several new adhesive systems rely on simultaneous etching of dentin and enamel with weaker acids than the traditional 30% to 40% phosphoric acid etchants.

Some studies indicate that acids such as 10% phosphoric acid, 10% maleic acid, and 2.5% nitric acid etch enamel as effectively as 37% phosphoric acid.<sup>13,37-40</sup> However, data from other studies indicate that the weaker acids provide significantly lower shear bond strengths when the manufacturers' recommended application times are used to etch enamel.<sup>41,42</sup> The clinical consequences of etching enamel with weaker acids are not yet fully known.

#### Problems in bonding to dentin

Adhesion of restorative materials to enamel has become a routine and reliable aspect of modern restorative dentistry, but dentinal adhesion has proved to be more difficult and less predictable. Much of the difficulty in bonding to dentin is the result of the complex histologic structure and variable composition of dentin itself. Whereas enamel is 92% inorganic hydroxyapatite by volume, dentin is (on average) only 45% inorganic. Also, in contrast to the regular arrangement of hydroxyapatite crystals in enamel, dentinal hydroxyapatite is randomly arranged in an organic matrix that consists primarily of collagen.<sup>43</sup>

Dentin is intimately connected with the pulpal tissues, and numerous fluid-filled channels or tubules (Fig 3) traverse through dentin from the pulp to the dentinoenamel junction (DEJ). An odontoblastic process extends from the pulp into the inner portion of each tubule.<sup>44</sup> The fluid in the tubules is under a slight, but con-

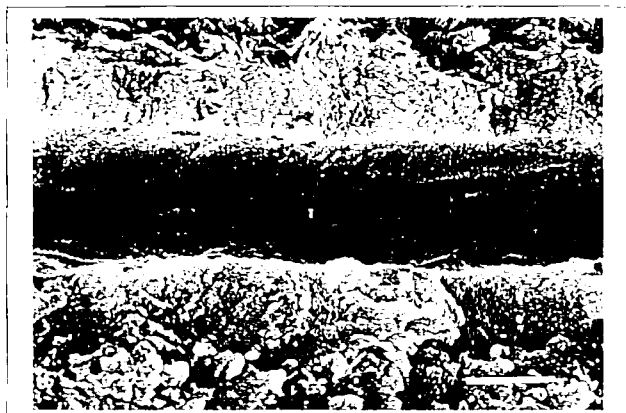


Fig 4 Scanning electron micrograph showing intertubular and peritubular dentin. Lumen of dentinal tubule (T); peritubular dentin (P); intertubular dentin (I). (Bar = 1  $\mu$ m.)

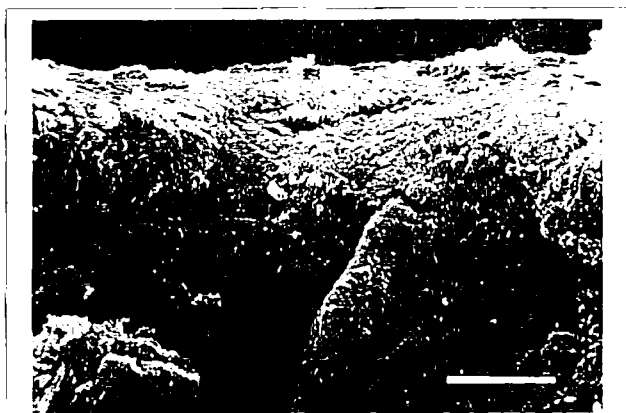


Fig 6 Smear layer on dentin that was instrumented with a diamond rotary instrument. The dentinal tubule is obstructed by a smear plug (P). (Bar = 1  $\mu$ m.)

stant, outward, pressure from the pulp. The intrapulpal pressure is estimated to be 25 to 30 mm Hg (or 34 to 40 cm H<sub>2</sub>O).<sup>45,46</sup>

Each tubule is surrounded by a collar of hypermineralized dentin called *peritubular dentin*. The less mineralized dentin between tubules is called *intertubular dentin*<sup>47</sup> (Fig 4). The relative area of dentin occupied by tubules decreases as they diverge from the pulp. The number of tubules decreases from about 45,000 per mm<sup>2</sup> at the pulp to about 20,000 per mm<sup>2</sup> at the DEJ in coronal dentin.<sup>48</sup> Pashley<sup>49</sup> has calculated that tubules occupy 22% of the cross-sectional area near the pulp and only 1% near the enamel. Heymann and Bayne<sup>50</sup> recently calculated values of 28% and 4% for tubule volumes in these areas, respectively (Fig 5).

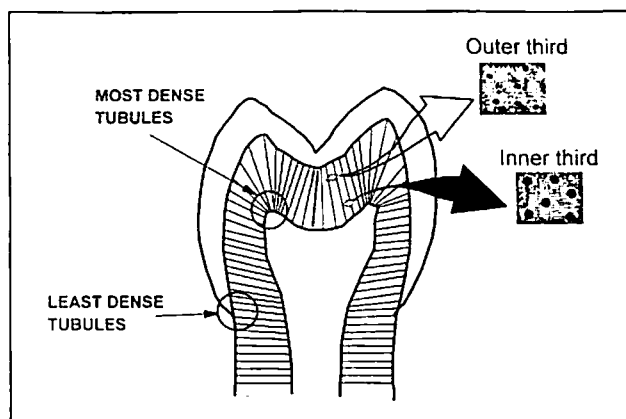


Fig 5 Diagram of tubule volume near the pulp and near the DEJ. From Heymann and Bayne.<sup>50</sup> Reprinted by permission.

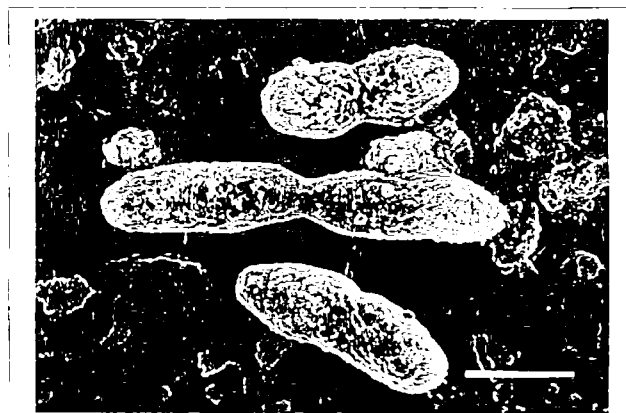


Fig 7 Scanning electron micrograph showing bacteria in the smear layer. (Bar = 1  $\mu$ m.)

Regional variations in dentinal structure and composition are related to other factors besides depth. Regional variation is reflected in the permeability characteristics (or hydraulic conductance) at different locations within a tooth. For example, the permeability of occlusal dentin is higher over the pulp horns than at the center of the occlusal surface.<sup>51</sup> Similarly, proximal dentin is more permeable than occlusal dentin, and coronal dentin is more permeable than root dentin.<sup>52</sup>

Dentinal bonding is further complicated by the formation of a *smear layer* as debris is burnished onto the dentinal surface while the dentin is cut or ground (Fig 6). The smear layer, which is 0.5 to 5.0  $\mu$ m thick, occludes the orifices of the dentinal tubules. Its thickness and appearance vary with the specific substrate and the

type of cutting instrument used.<sup>53,54</sup> Although smear layers act as "diffusion barriers" that decrease the permeability of dentin,<sup>55</sup> they can also be considered an impediment that must be removed so that resin can be bonded to the underlying dentinal substrate. Furthermore, bacteria entrapped in smear layers can survive and multiply beneath restorations<sup>56</sup> (Fig 7).

### Development of resin dentinal adhesives

Buonocore et al<sup>57</sup> reported nearly four decades ago that a resin containing glycerophosphoric acid dimethacrylate could bond to hydrochloric acid-etched dentinal surfaces. However, the bond strengths of this early method of adhesion were greatly diminished by immersion in water. To overcome this problem, Bowen<sup>58</sup> synthesized N-phenylglycine glycidyl methacrylate (NPG-GMA), a "surface-active comonomer" that theoretically could mediate water-resistant chemical bonds of resins to dentinal calcium. However, commercial products based on NPG-GMA had very poor clinical results when they were used to restore cervical erosion lesions without mechanical retention.<sup>59,60</sup>

A second generation of dentinal bonding agents was developed for clinical use during the early 1980s. With the exception of Scotchbond Dual-Cure (3M Dental) and Bondlite (Kerr), second-generation bonding agents are no longer commercially available. Most of these materials were halophosphorous esters of unfilled resins such as bisphenol A-glycidyl methacrylate (bis-GMA) or hydroxyethyl methacrylate (HEMA).<sup>61,62</sup> The bonding mechanism involves a surface-wetting phenomenon as well as ionic interaction between the phosphate groups and dentinal calcium.<sup>62,63</sup> Shear dentinal bond strengths of only about 1 to 10 MPa have been reported for these bonding agents.<sup>61-64</sup> Bond strengths in this range are considered too weak to counteract the polymerization shrinkage of composite resin.<sup>27,29</sup> Furthermore, some evidence indicates that bonds between phosphonate esters and dentin are hydrolyzed by immersion in water.<sup>65</sup> Therefore, composite resin tends to separate from dentin, forming gaps at restoration margins.<sup>27</sup> These gaps allow considerable microleakage at margins in dentin or cementum.<sup>66,67</sup>

Several clinical studies of bonding agents that contain phosphonate esters have been reported.<sup>68-71</sup> The clinical performance of phosphonate esters used without enamel etching or mechanical retention was relatively poor, with fairly high percentages of cervical restoration loss over 1- to 3-year evaluation periods.

A major reason for the poor performance of these bonding agents is the fact that they bond to the smear layer rather than to the dentin itself. Hence, their bond strength is limited by the cohesive strength of the smear layer or by adhesion of the smear layer to the underlying dentin, which is tenuous at best.<sup>72,73</sup>

More recently developed dentinal bonding systems, sometimes called *third-generation* adhesives, either modify or completely remove the smear layer to allow resin penetration into the underlying dentin.<sup>74-78</sup> Shear dentinal bond strengths of agents such as Scotchbond 2 (3M Dental), Gluma (Bayer/Miles), Tenure (Den-Mat), Prisma Universal Bond 3 (Caulk/Dentsply), Syntac (Ivoclar Vivadent), and XR Bond (Kerr) usually are greater than those of the second-generation agents and can approach the typical bond strengths of resin to etched enamel. However, their performance is still unpredictable, even in laboratory studies. For a given bonding agent, bond strengths vary greatly not only among different studies, but also within studies.<sup>76-86</sup>

These dentinal adhesives are generally more effective than their predecessors in reducing microleakage at dentinal and cementum margins,<sup>82-89</sup> although they do not completely eliminate marginal leakage.<sup>90-93</sup> Composite resin restorations bonded with these adhesives can reinforce tooth structure that has been weakened by disease, trauma, or cavity preparation.<sup>94,95</sup> Clinically, 3-year studies of Scotchbond 2 and Gluma in cervical areas have demonstrated that these systems provide considerably better clinical performance (retention, marginal integrity, etc) than did earlier adhesives.<sup>96,97</sup>

### Current dentinal adhesives

Most of the current developments in dentinal bonding technology involve the "total-etch" technique, or simultaneous etching of enamel and dentin with phosphoric or other acids. An improvement in dentinal bond strengths by etching was first demonstrated by Fusayama et al<sup>98</sup> in 1979, and dentinal etching has since become a fairly common practice in Japan. However, the concept of total etching only recently has gained acceptance in the United States.<sup>99,100</sup> The shift towards total etching is a radical development in American restorative dentistry because etching of dentin traditionally has been discouraged. Data from studies conducted during the 1970s seemed to indicate that phosphoric acid etching of dentin caused pulpal inflammation.<sup>101-103</sup> However, very little acid actually penetrates



Fig 8a Surface view of dentin that was etched with 10% phosphoric acid for 15 seconds. The specimen was fixed and critical point dried. (Bar = 2  $\mu$ m.)



Fig 8b Lateral view of dentin that was etched with 10% phosphoric acid for 15 seconds. The specimen was fixed and critical point dried. (Bar = 2  $\mu$ m.)

dentin, so it seems unlikely that the acid is directly responsible for any pulpal damage that might occur.<sup>104</sup> Most evidence now indicates that lack of an adequate marginal seal is the primary cause of pulpal inflammation associated with permanent restorations. Little or no inflammation occurs if restorations are sealed well enough to prevent bacterial invasion of the pulp.<sup>105-107</sup> Furthermore, Kanca<sup>108</sup> hypothesized that in some studies pulpal inflammation was caused not by phosphoric acid, but by zinc oxide-eugenol materials used to seal deep acid-etched cavities.

Recent SEM and transmission electron microscopy (TEM) studies have provided significant information about how the current generation of adhesive systems bonds to dentin.<sup>13,109-114</sup> Although many different types of conditioners, primers, and adhesive resins are used, the bonding mechanisms of the various etched-dentin adhesive systems are remarkably similar. Acid etching removes the smear layer, opens the dentinal tubules, increases dentinal permeability, and decalcifies the intertubular and peritubular dentin (Figs 8a and 8b). The depth of decalcification is affected by various factors, including the pH, concentration, viscosity, and application time of the etchant.<sup>109,115</sup> Removal of hydroxyapatite crystals leaves a collagen meshwork that can collapse and shrink because of the loss of inorganic support.<sup>109,113</sup>

After the conditioner is rinsed off, a primer containing one or more hydrophilic resin monomers is applied (Fig 9). Primer molecules such as HEMA, biphenyl dimethacrylate (BPDm) and 4-methacryloxyethyl trimellitate anhydride (4-META) contain two functional groups—a hydrophilic group and a hydrophobic group.

The hydrophilic group has an affinity for the dentinal surface and the hydrophobic (methacrylate) group has an affinity for resin. The primer wets and penetrates the collagen meshwork, raising it almost to its original level. The primer also increases the surface energy, and hence the wettability, of the dentinal surface. Unfilled resin is applied to and penetrates the primed dentin, copolymerizing with the primer to form an intermingled layer of collagen and resin, termed the *resin-reinforced zone*, *resin-infiltrated layer*, or *hybrid layer* (Figs 10 and 11). Formation of this hybrid layer of dentin and resin, which was first described by Nakabayashi et al<sup>116</sup> in 1982, is thought to be the primary bonding mechanism of most current adhesive systems.<sup>109,117</sup> Bond strengths are generally lower when the bonding agent does not form a hybrid layer.<sup>13,117</sup> Data from a recent in vitro study indicated that resin infiltration (or hybridization) of the dentinal tubules and intertubular dentin accounted for a substantial proportion of the bond of resin to dentin.<sup>118</sup>

Scanning electron microscopy also reveals that many adhesives form long resin tags within the dentinal tubules of extracted teeth (see Fig 10). The tags are impressive in appearance and may convey some information about the wetting characteristics of a material. However, resin tags provide little or no retention unless they are firmly bonded to the tubule walls. Even conventional (hydrophobic) enamel bonding resins will form long tags in etched dentin, but provide no appreciable bond strength because the resin does not adequately wet or bond to the tubule walls.<sup>119</sup> Further evidence for the relative lack of importance of resin tags is the fact that bond strengths to deep, tubule-rich den-



Fig 9 Dentin etched with 10% phosphoric acid and primed with All-Bond primers A and B. The primers did not occlude the tubules in this area of the specimen. The specimen was fixed and critical point dried. (Bar = 2  $\mu$ m.)

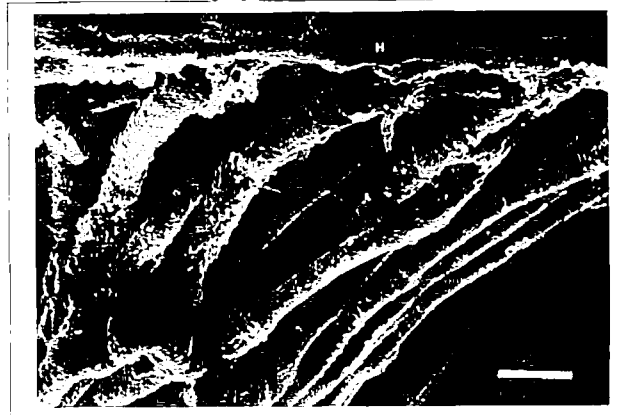


Fig 10 Resin tags and mixed zone of dentin and resin formed by the All-Bond 2 adhesive system. Dentin was dissolved by immersion in hydrochloric acid and sodium hypochlorite. Hybrid layer (H). (Bar = 5  $\mu$ m.)

tin are generally lower.<sup>120</sup> Finally, resin tags formed in vivo are probably shorter than those in extracted teeth because dentinal tubules are filled with fluid that reduces resin penetration.<sup>121</sup>

One important concern that has arisen from SEM and TEM studies is the potential for discrepancies between the depths of decalcification and resin penetration of etched-dentin adhesive systems.<sup>109,110,113</sup> The bond strength of an etched-dentin adhesive may rely on its ability to completely replace dissolved hydroxyapatite with polymerized resin. If dentin is decalcified so deeply that the decalcified zone cannot be thoroughly impregnated by resin, a fragile collagen layer may remain and degrade over time.<sup>109,122</sup> Although the primers currently in use are very hydrophilic, adequate resin impregnation may require the use of etching techniques that do not result in excessive decalcification depths. Shorter etching times or less aggressive acids may be used in the future.<sup>115</sup> However, one recent study indicated that hydrophilic resins could completely permeate decalcified dentin regardless of the aggressiveness of the etching procedure.<sup>123</sup>

Several major dental products manufacturers recently introduced a new generation of bonding systems that etch dentin with phosphoric or other acids. Examples include All-Bond 2 (Bisco Dental), Amalgambond (Parkell), Clearfil Liner Bond (Kuraray/J Morita), Imperva Bond (Shofu Dental), OptiBond (Kerr), and Scotchbond Multi-Purpose (3M Dental). Many of these systems are so new that almost no independent data regarding bond strengths or other properties have been reported. However, a fairly substantial amount of



Fig 11 Transmission electron micrograph of the resin-dentin interface created by All-Bond 2, showing the hybrid layer (H) and the underlying dentin (D). (Bar = 5  $\mu$ m.)

information about products such as All-Bond 2, Amalgambond, and Scotchbond Multi-Purpose is already available based on laboratory studies.

Several studies have indicated that shear bond strengths of All-Bond 2 exceed the typical enamel bond strength of 20 MPa, particularly when dentin is left visibly moist after etching.<sup>13,124-128</sup> Somewhat lower bond strengths have been reported in other studies.<sup>80,129,130</sup>

When All-Bond 2 is used, enamel and dentin are both etched with 10% phosphoric acid for 15 seconds. Phosphoric acid removes the smear layer, opens and widens the orifices of the dentinal tubules, and demineralizes intertubular dentin, reportedly to a depth of

about 7  $\mu\text{m}$ .<sup>109</sup> After etching and rinsing, the tooth surface is left visibly moist or is dried with compressed air and remoistened with water or an antibacterial solution (eg. chlorhexidine).<sup>131</sup> Maintaining a moist surface may be essential for optimal development of the hybrid layer when All-Bond and other hydrophilic bonding systems are used. Desiccation of the conditioned dentin can cause collapse of the unsupported collagen network, inhibiting adequate wetting and penetration by the primer. However, the clinician must be aware that pooled moisture should not be allowed to remain on the tooth because excess water can dilute the primer and render it less effective. A "glistening," hydrated surface is preferred.

Several coats of a primer mixture containing N-p-tolylglycine-glycidyl methacrylate (NTG-GMA) and BPDm in acetone are applied to the surface. Acetone apparently acts as a water chaser, displacing water and carrying the resin primers into the demineralized dentin.<sup>132</sup> An unfilled resin mixture (bis-GMA, urethane dimethacrylate [UDMA], and HEMA) is applied and visible light cured. The unfilled resin copolymerizes with the primer and the composite resin restorative material.<sup>124</sup>

Scotchbond Multi-Purpose Dental Adhesive uses 10% maleic acid to etch dentin and enamel for 15 seconds. Ten percent maleic acid decalcifies the dentin surface to a depth of 3  $\mu\text{m}$ .<sup>109</sup> After rinsing and drying are completed, a hydrophilic primer is applied to the surface and gently dried. The primer, an aqueous solution of HEMA and a polyalkenoate copolymer, infiltrates the etched dentin. Finally, an unfilled resin containing bis-GMA and HEMA is applied and cured with visible light. The manufacturer claims a shear bond strength of 24 MPa to dry dentin,<sup>133</sup> and there is some evidence that Scotchbond Multi-Purpose bonds as well or slightly better to moist dentin.<sup>134,135</sup> One study reported shear bond strengths of 21.8 MPa to moist dentin and 17.8 MPa to dry dentin.<sup>135</sup> The moisture resistance of Scotchbond Multi-Purpose is probably related to the formation of bonds between dentinal calcium and the polyalkenoic acid component of the primer. The presence of water facilitates ion exchange reactions.<sup>136</sup>

Concerns have been raised about the effectiveness of 10% maleic acid as an enamel etchant.<sup>41</sup> Therefore, some clinicians use a conventional phosphoric acid to etch enamel and use maleic acid strictly to condition dentin.<sup>137</sup> Dentin can be etched with phosphoric acid instead of maleic acid without significantly reducing the bond strength of Scotchbond Multi-Purpose, and

this product is now supplied with a 35% phosphoric acid etchant.<sup>38,138</sup>

Amalgambond is based on a dentinal bonding system developed in Japan by Nakabayashi and co-workers<sup>116</sup> more than a decade ago. Amalgambond uses a solution of 10% citric acid and 3% ferric chloride to remove the smear layer and demineralize the dentin to a depth of about 2  $\mu\text{m}$ .<sup>109</sup> A primer containing 35% HEMA in water is applied after the dentin is conditioned. Finally, a self-curing methyl methacrylate resin is applied to impregnate the primed dentin. The resin contains an adhesive monomer called 4-META.<sup>139</sup> As with All-Bond and Scotchbond Multi-Purpose, shear bond strengths for Amalgambond and similar 4-META products are generally close to or greater than 20 MPa.<sup>81,85,140-143</sup> In addition, 4-META systems appear to be less affected than are most other adhesives by dentinal depth and pulpal pressure.<sup>120,142-144</sup>

## Relevance of in vitro studies

Clinical studies of any dental material are time consuming and expensive. Cost is a particular drawback whenever technology is developing rapidly, as it is now in the area of dentinal bonding. There is no financial incentive for a manufacturer to spend hundreds of thousands of dollars to test a bonding system that may be replaced by a newer product before a 2- or 3-year clinical study can be completed. Therefore, dental products manufacturers and researchers rely largely on laboratory (in vitro) testing to predict the clinical (in vivo) performance of materials. Unfortunately, predicting the clinical performance of any dentinal adhesive system solely on the basis of in vitro data is extremely difficult and often unreliable. Nevertheless, laboratory testing can be used as a screening mechanism for predicting clinical performance.

The most commonly reported attribute of any bonding system is its shear bond strength to dentin. However, laboratory methods for measuring bond strength have little direct clinical relevance. In a typical test, extracted teeth are ground flat, an adhesive system is applied, and a composite resin post is bonded to the surface. A loading force is applied to the composite resin until it shears from dentin. Tests of this type do not take into account the three-dimensional nature of cavity preparations, and thus underestimate the effects of polymerization shrinkage.<sup>145</sup> Moreover, the effects of pulpal pressure, dentinal fluid, and tooth dynamics, such as flexural phenomena, are not typically taken into account.



Microleakage data are also commonly reported for dentinal bonding systems. Laboratory investigations typically involve restoration of Class V cavity preparations or simulated cervical abrasion lesions using a bonding system and composite resin. The specimens are usually thermocycled, ie, alternately placed in hot and cold solutions to simulate temperature changes that occur in the mouth. However, the relationship between thermocycling and actual clinical conditions is ambiguous. Finally, the specimens are immersed in some type of disclosing medium (eg, a dye or silver nitrate solution) that penetrates gaps at the interface between restorative material and tooth structure. Silver nitrate penetration is a very harsh test of the marginal seal because silver ions are considerably smaller than are bacteria.<sup>87</sup> In addition, the results of a recent study suggest that less leakage occurs *in vivo* than *in vitro*.<sup>146</sup>

Other factors that contribute to the lack of correlation between laboratory investigations and clinical results have been cited, including age and storage conditions of specimens, location and depth of the dentin, surface roughness, and type and duration of loading forces.<sup>145,147-149</sup> Perhaps the single most critical difference between laboratory and clinical conditions is that very few laboratory studies attempt to simulate the hydration or pulpal pressure of vital *in vivo* dentin.<sup>149</sup>

### Clinical factors in dentinal bonding

Several clinical factors unrelated to the bond strength of the adhesive system can contribute to the ultimate success or failure of a bonded restoration. First, the mineral content of dentin can increase with age, caries, or exposure to the oral cavity (as in cervical erosion or abrasion lesions). The width of peritubular dentin increases and dentinal tubules become obstructed by crystalline deposits. Dentin that has undergone such microstructural alterations is termed *sclerotic dentin* and is resistant to acidic conditioning solutions. Therefore, resin penetration of the dentin is limited and thinner hybrid layers are formed.<sup>150-153</sup> The clinical performance of dentinal adhesives is less satisfactory in sclerotic cervical lesions than in normal dentin.<sup>69,97</sup>

Second, there is increasing evidence that masticatory forces not only cause cervical erosion-abrasion lesions, but also contribute to the failure of bonded Class V restorations.<sup>69,153-156</sup> Bruxism or other unfavorable occlusion generates lateral forces that cause stress concentrations in the cervical area. Although these stresses may have a fairly low magnitude, repeated flexural

forces can ultimately result in fatigue failure of the bonding interface between dentin and resin. As a result, marginal breakdown can occur or restorations can be partially or completely dislodged.

A third factor that affects the longevity of a bonded restoration is the type of composite resin restorative material used.<sup>153</sup> Composite resins shrink during polymerization, and the volume of shrinkage depends on the filler content of the material. Microfilled composite resins shrink more than do heavily filled composite resins, but they also have a lower Young's modulus.<sup>153,157</sup> Low-modulus composite resins are able to relieve some of the polymerization contraction stresses by flow relaxation. Stiffer, high-modulus materials do not flow as well and therefore compensate less for polymerization contraction stresses. In addition, highly filled composite resins cannot flex adequately when subjected to flexural forces and may transfer stress to the bonding interface.

Reduced flow is a particular problem with light-curing composite resins because polymerization is initiated at the restoration surface, effectively eliminating that surface as a source of flow for stress relief.<sup>153,158</sup> One method for reducing overall restoration stiffness is the application of a low-viscosity, low-modulus intermediate resin between the bonding agent and restorative resin to act as an "elastic buffer" or "stress breaker" that can relieve contraction stresses and improve marginal integrity.<sup>153,158</sup> Recent research indicates that products such as OptiBond (unpublished data) and Clearfil Liner Bond,<sup>159</sup> which include a filled intermediate resin, reduce microleakage more effectively than do some other dentinal adhesives that have higher shear bond strengths. New stress-breaking liners of this type also protect the bonding interface from fatigue failure due to flexural forces.<sup>160</sup>

### New developments

#### *Desensitization*

Although evidence of efficacy remains largely anecdotal, many clinicians have begun to use dentinal bonding systems to treat hypersensitive exposed dentin and teeth prepared for crowns.<sup>161,162</sup> The mechanism by which adhesives reduce hypersensitivity probably involves hybrid layer formation and occlusion of the tubules by resin tags.<sup>117</sup> However, other factors may also be involved.<sup>163</sup> For example, All-Bond 2 primers are effective desensitizers even if no unfilled resin is applied, despite the observation that the primers may not com-

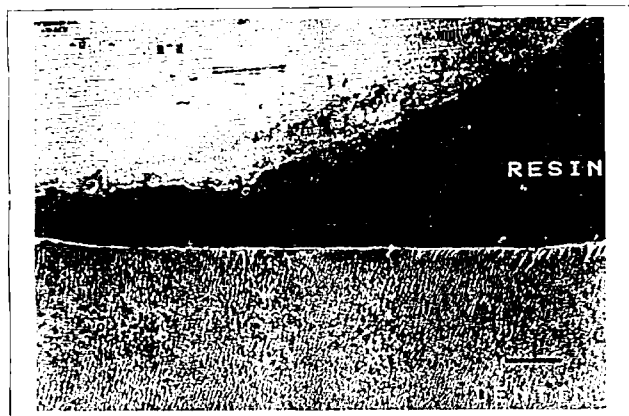


Fig 12a Scanning electron micrograph of tooth-restoration interface of a bonded amalgam. (Bar = 100  $\mu$ m.)

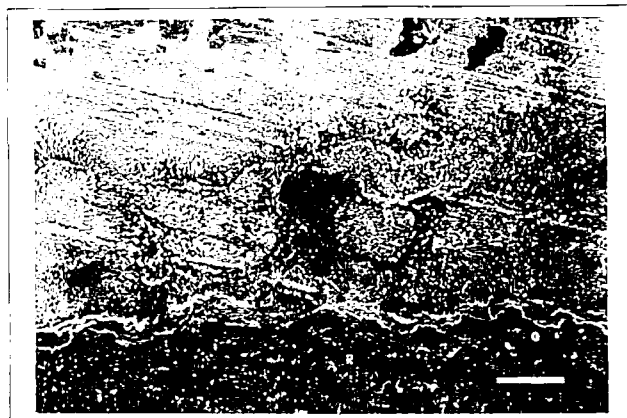


Fig 12b Higher magnification view of resin-amalgam interface. Note the intermixing of the two materials. Resin (R); amalgam (A). (Bar = 25  $\mu$ m.)

pletely occlude the dentin tubules (see Fig 9). Also, clinical studies have shown that Gluma primer can be used to desensitize teeth that have been prepared for crowns or that have hypersensitive erosion-abrasion lesions.<sup>164,165</sup> Gluma primer contains 5% glutaraldehyde, which is a biologic fixative. Glutaraldehyde may occlude dentinal tubules and reduce permeability by coagulating plasma proteins within the tubules.<sup>166</sup>

#### Indirect restorations

Several of the new adhesive systems are considered to be universal dental adhesives because they bond not only to dentin and enamel, but also to metal alloys, porcelain, and composite resin.<sup>124,125,133,167-169</sup> Ceramic and composite resin inlays, onlays, crowns, and veneers can be bonded to tooth structure with universal adhesives and resin cements. Conventional crowns and fixed partial dentures and resin-bonded prostheses also can be adhesively bonded to tooth structure with these materials after the proper surface treatments (such as sandblasting and tin plating) are completed.<sup>169</sup> A full discussion of indirect bonded restorations is beyond the scope of this article.

#### Bonded amalgam restorations

One particularly interesting application of universal adhesives is the bonded amalgam restoration. Numerous laboratory studies have shown that certain resins, including All-Bond 2, Amalgambond, and Panavia (Kuraray/J Morita), can be used to bond amalgam to dentin. The nature of the bond between resin and amal-

gam is not clear. It appears to be at least partly mechanical, as amalgam mixes with the fluid resin during condensation (Figs 12a and 12b). Although one recent study reported a shear bond strength of 13.0 MPa for amalgam bonded to dentin with All-Bond 2,<sup>130</sup> the bond strengths of amalgam are generally lower (less than 10 MPa) than those of composite resin.<sup>140,141,170-174</sup>

Nevertheless, studies suggest that the use of adhesive liners to bond amalgam may provide several benefits. First, the amount of force required to dislodge an amalgam restoration is increased by bonding, thus reducing the need for retentive devices such as dovetails, grooves, and pins.<sup>175-177</sup> Second, teeth restored with bonded amalgam may be more resistant to fracture than are teeth restored in the conventional manner.<sup>178</sup> Third, adhesive resin liners reduce leakage around amalgam restorations more effectively than do traditional cavity varnishes.<sup>170,175,179-182</sup> The reduced leakage could result in less recurrent carious activity at restoration margins.<sup>183</sup> Finally, clinical experience indicates that the use of dentinal adhesives as amalgam liners reduces the incidence of postoperative sensitivity.<sup>184</sup> This effect is probably the result of marginal sealing and reduced permeability by the adhesive, in addition to the seal provided by amalgam itself.<sup>171,185,186</sup>

Because bonded amalgam restorations are a new treatment modality, there is no documented clinical evidence of their durability or superiority over conventional amalgam restorations. One potential problem is the incorporation of resin into the amalgam, which may weaken the restoration.<sup>187</sup>

The use of resin adhesives to repair existing amalgam restorations is not particularly successful. Studies indi-

cate that adhesives have little or no effect on repair strengths, and fracture resistance remains much less than that of intact amalgam.<sup>188-192</sup>

### *Resin-modified glass-ionomer cements*

Glass-ionomer cements were developed in the early 1970s as a hybrid of silicate and polycarboxylate cements.<sup>193</sup> Different formulations of glass-ionomer cements are now used as crown and fixed partial denture cements, cavity liners and bases, core buildups, and direct restorative materials. The two major advantages of glass-ionomer cements are their adhesion to tooth structure and fluoride release.<sup>194,195</sup>

Tooth-colored glass-ionomer restorative materials are generally reserved for use in Class III and root-surface lesions. Clinical studies have shown that glass-ionomer cements have high retention rates in cervical lesions.<sup>196-198</sup> In addition, laboratory studies predict that use of glass-ionomer cements will decrease the frequency and severity of recurrent caries.<sup>199-201</sup> However, the glass-ionomer cements have a slow setting reaction that necessitates delayed finishing and are sensitive to moisture contamination and desiccation.<sup>194,195</sup> These factors, plus concern about their strength and esthetic qualities, have limited the use of tooth-colored glass-ionomer restorative materials in the United States.<sup>202</sup>

Some clinicians use the so-called sandwich technique to combine the advantages of glass-ionomer cement and composite resin in a single restoration.<sup>203</sup> A glass-ionomer base or restorative material, which bonds to tooth structure, replaces missing dentin. The glass-ionomer cement is covered with composite resin, which has more enamel-like qualities, such as translucency and polishability. Recently, several manufacturers introduced products that combine the properties of glass-ionomer cement and composite resin in a single material. Several light-activated glass-ionomer restorative materials (also called *hybrid glass-ionomer cements* or *resin-modified glass-ionomer cements*) are commercially available, including Fuji II LC (GC America), Photac-Fil (ESPE), and Vitremer (3M Dental). Some of these products are closely related to conventional glass-ionomer cements, while others more closely resemble composite resins.<sup>204</sup> Fluoride release varies among materials,<sup>204</sup> but one recent study showed that Photac-Fil and Fuji II LC released as much as or more fluoride than do conventional glass-ionomer cements.<sup>205</sup>

Like the light-activated glass-ionomer liners that were developed earlier, true resin-modified glass-

ionomer restorative materials actually undergo a dual-cure setting mechanism.<sup>206</sup> Mixing of the two components of a material initiates the conventional glass-ionomer acid-base setting reaction. In addition, exposure to visible light initiates polymerization of water-soluble resin monomers and methacrylate groups attached to the glass-ionomer acid chains. The manufacturer<sup>207</sup> has stated that Vitremer has a third and separate setting reaction that is initiated by oxidation and reduction catalysts. This reaction supposedly ensures complete cure of the material even in areas that are not accessible to the visible light beam.<sup>207</sup> GC America also claims that its Fuji II LC material has a triple-curing mechanism. The third curing mechanism appears to be spontaneous polymerization of HEMA. In addition, postirradiation may occur, as in composite resins. Polymerization of composite resins continues for up to 24 hours after visible light activation ceases.<sup>208</sup>

Light activation allows a longer working time and shorter setting time than are possible with conventional glass-ionomer materials, so placement and finishing procedures are less complex.<sup>204</sup> Manufacturers' data indicates that the physical properties of the resin-modified glass-ionomer cements are better than those of the conventional glass-ionomer cements, and early studies confirm these data.<sup>204,209-211</sup> The light-activated glass-ionomer cements have higher dentinal bond strengths than do conventional glass-ionomer restoratives.<sup>211-213</sup> Bond strengths of some resin-modified glass-ionomer materials may be improved by the application of adhesive systems.<sup>214</sup> Early reports on microleakage of the resin-modified glass-ionomer restorative materials have been quite good.<sup>215,216</sup>

### **Summary**

Advances in adhesive dental technology have radically changed restorative dentistry. The acid-etch technique for enamel bonding led to the development of a myriad of restorative, preventive, and esthetic treatment alternatives. Recent advances in dentinal bonding have taken adhesive dentistry to an even higher level. Currently, numerous systems are available for strongly bonding resin to dentin. Most systems condition dentin with an acid and use a hydrophilic primer to mediate a strong micromechanical bond with the dentinal substrate.

Some materials also bond to metal, leading to innovative applications, such as for bonded amalgam restorations and crowns. Other materials, such as the new resin-modified glass-ionomer cements, aim to incorpo-

rate adhesive and anticaries properties in esthetic restoratives. These and other developments in adhesive dental technology have ushered in a new age of restorative dentistry characterized by conservation of tooth structure, improved restorations, and enhanced esthetics.

## References

- Buonocore MG. A simple method of increasing the adhesion of acrylic filling materials to enamel surfaces. *J Dent Res* 1955;34:849-853.
- Gwinnett AJ, Matsui A. A study of enamel adhesives. The physical relationship between enamel and adhesive. *Arch Oral Biol* 1967;12:1615-1620.
- Buonocore MG, Matsui A, Gwinnett AJ. Penetration of resin dental materials into enamel surfaces with reference to bonding. *Arch Oral Biol* 1968;13:61-70.
- Retief DH. Effect of conditioning the enamel surface with phosphoric acid. *J Dent Res* 1973;52:333-341.
- Silverstone LM. Fissure sealants: Laboratory studies. *Caries Res* 1974;8:2-26.
- Gwinnett AJ. Histologic changes in human enamel following treatment with acidic adhesive conditioning agents. *Arch Oral Biol* 1971;16:731-738.
- Silverstone LM, Saxton CA, Dogon IL, Fejerskov O. Variation in the pattern of acid etching of human dental enamel examined by scanning electron microscopy. *Caries Res* 1975;9:373-387.
- Gwinnett AJ, Buonocore MG. Adhesion and caries prevention. A preliminary report. *Br Dent J* 1965;119:77-80.
- Chow LC, Brown WE. Phosphoric acid conditioning of teeth for pit and fissure sealants. *J Dent Res* 1973;52:1158.
- Manson-Rahemtulla B, Retief DH, Jamison HC. Effect of concentrations of phosphoric acid on enamel dissolution. *J Prosthet Dent* 1984;51:495-498.
- Soetopo A, Beech DR, Hardwick JL. Mechanism of adhesion of polymers to acid-etched enamel. Effect of acid concentration and washing on bond strength. *J Oral Rehabil* 1978;5:69-80.
- Gottlieb EW, Retief DH, Jamison HC. An optimal concentration of phosphoric acid as an etching agent. Part I. Tensile bond strength studies. *J Prosthet Dent* 1982;48:48-51.
- Gwinnett AJ, Kanca J. Micromorphology of the bonded dentin interface and its relationship to bond strength. *Am J Dent* 1992;5:73-77.
- Mardaga WJ, Shannon IL. Decreasing the depth of etch for direct bonding in orthodontics. *J Clin Orthod* 1982;16:130-132.
- Nordenvall K-J, Brännström M, Malmgren O. Etching of deciduous teeth and young and old permanent teeth. A comparison between 15 and 60 seconds of etching. *Am J Orthod* 1980;78:99-108.
- Barkmeier WW, Gwinnett AJ, Shaffer SE. Effects of enamel etching on bond strength and morphology. *J Clin Orthod* 1985;19:36-38.
- Barkmeier WW, Shaffer SE, Gwinnett AJ. Effects of 15 vs 60 second enamel acid conditioning on adhesion and morphology. *Oper Dent* 1986;11:111-116.
- Bastos PAM, Retief DH, Bradley EL, Denys FR. Effect of etch duration on the shear bond strength of a microfill composite resin to enamel. *Am J Dent* 1988;1:151-157.
- Gilpatrick RO, Ross JA, Simonsen RJ. Resin-to-enamel bond strengths with various etching times. *Quintessence Int* 1991;22:47-49.
- Shaffer SE, Barkmeier WW, Kelsey WP. Effects of reduced acid conditioning time on enamel microleakage. *Gen Dent* 1987;35:278-280.
- Crim GA, Shay JS. Effect of etchant time on microleakage. *J Dent Child* 1987;54:339-340.
- Stephen KW, Kirkwood M, Main C, Gillespie FC, Campbell D. Retention of a filled fissure sealant using reduced etch time. *Br Dent J* 1982;153:232-233.
- Eidelman E, Shapira J, Houpt M. The retention of fissure sealants using twenty-second etch time. Part I. A clinical trial. *J Dent Child* 1984;51:422-424.
- Hegdahl T, Gjerdet NR. Contraction stresses of composite filling materials. *Acta Odontol Scand* 1977;35:191-195.
- Bowen RL, Nemoto K, Rapson JE. Adhesive bonding of various materials to hard tooth tissue: Forces developing in composite materials during hardening. *J Am Dent Assoc* 1983;106:475-477.
- Davidson CL, de Gee AJ. Relaxation of polymerization contraction stresses by flow in dental composites. *J Dent Res* 1984;63:146-148.
- Davidson CL, de Gee AJ, Feilzer A. The competition between the composite-dentin bond strength and the polymerization contraction stress. *J Dent Res* 1984;63:1396-1399.
- Feilzer A, de Gee AJ, Davidson CL. Setting stress in composite resin in relation to configuration of the restoration. *J Dent Res* 1987;66:1636-1639.
- Munksgaard EC, Irie M, Asmussen E. Dentin-polymer bond promoted by Gluma and various resins. *J Dent Res* 1985;64:1409-1411.
- Morin D, DeLong R, Douglas WH. Cusp reinforcement by the acid-etch technique. *J Dent Res* 1984;63:1075-1079.
- McCulloch AJ, Smith BGN. In vitro studies of cuspal movement produced by adhesive restorative materials. *Br Dent J* 1986;161:405-409.
- Oliveira FC, Denehy GE, Boyer DB. Fracture resistance of endodontically prepared teeth using various restorative materials. *J Am Dent Assoc* 1987;115:57-60.
- Donly KJ, Wild T, Jensen ME. Cuspal reinforcement in primary teeth: An in vitro comparison of three restorative materials. *Pediatr Dent* 1988;10:102-104.
- Hansen EK. In vivo cusp fracture of endodontically treated premolars restored with MOD amalgam or MOD resin fillings. *Dent Mater* 1988;4:169-173.
- Reeh ES, Douglas WH, Messer HH. Stiffness of endodontically-treated teeth related to restoration technique. *J Dent Res* 1989;68:1540-1544.
- Barghi N, Knight GT, Berry TG. Comparing two methods of moisture control in bonding to enamel: A clinical study. *Oper Dent* 1991;16:130-135.
- Gwinnett AJ, Garcia-Godoy F. Effect of etching time and acid concentration on resin shear bond strength to primary tooth enamel. *Am J Dent* 1992;5:237-239.
- Aasen SM, Ario PD. Bonding systems: A comparison of maleic and phosphoric acids [abstract 269]. *J Dent Res* 1993;72:137.
- Berry TG, Barghi N, Knight GT, Conn LJ. Effectiveness of nitric-NPG as a conditioning agent for enamel. *Am J Dent* 1990;3:59-62.

40. Saunders WP, Strang R, Ahmad I. Shear bond strength of Mirage Bond to enamel and dentin. *Am J Dent* 1991;4:265-267.
41. Swift EJ, Cloe BC. Shear bond strengths of new enamel etchants. *Am J Dent* 1993;6:162-164.
42. Triolo PT, Swift EJ, Mudgil A, Levine A. Effect of etching time on enamel bond strengths. *Am J Dent* 1993;6:302-304.
43. Aasen SM. History of dentinal bonding. *Esthet Dent Update* 1990;1:43-46.
44. Thomas HF, Carella P. Correlation of scanning and transmission electron microscopy of human dentinal tubules. *Arch Oral Biol* 1984;29:641-646.
45. Terkla LG, Brown AC, Hainisch AP, Mitchem JC. Testing sealing properties of restorative materials against moist dentin. *J Dent Res* 1987;66:1758-1764.
46. Andreasson SB, Bayne SC, Heymann HO, Kanoy BE. Intrapulpal composition and fluid flow effects on dentin bond strengths [abstract 1114]. *J Dent Res* 1989;67:321.
47. Thomas HF. The dentin-predentin complex and its permeability: Anatomical overview. *J Dent Res* 1985;64:607-612.
48. Garberoglio R, Brännström M. Scanning electron microscopic investigation of human dentinal tubules. *Arch Oral Biol* 1976;21:355-362.
49. Pashley DH. Clinical correlations of dentin structure and function. *J Prosthet Dent* 1991;66:777-781.
50. Heymann HO, Bayne SC. Current concepts in dentin bonding: Focusing on dentinal adhesion factors. *J Am Dent Assoc* 1993;124:27-36.
51. Pashley DH, Andringa HJ, Derkson GD, Derkson ME, Kalathoor SR. Regional variability in the permeability of human dentine. *Arch Oral Biol* 1987;32:519-523.
52. Pashley DH, Pashley EL. Dentin permeability and restorative dentistry: A status report for the American Journal of Dentistry. *Am J Dent* 1991;4:5-9.
53. Eick JD, Wilko RA, Anderson CH, Sorensen SE. Scanning electron microscopy of cut tooth surfaces and identification of debris by use of the electron microprobe. *J Dent Res* 1970;49:1359-1368.
54. Gwinnett AJ. Smear layer: Morphological considerations. *Oper Dent* 1984;9(suppl 3):3-12.
55. Pashley DH, Michelich V, Kehl T. Dentin permeability: Effects of smear layer removal. *J Prosthet Dent* 1981;46:531-537.
56. Brännström M. Smear layer. Pathological and treatment considerations. *Oper Dent* 1984;(suppl 3):35-42.
57. Buonocore M, Wileman W, Brudevold F. A report on a resin composition capable of bonding to human dentin surfaces. *J Dent Res* 1956;35:846-851.
58. Bowen RL. Adhesive bonding of various materials to hard tooth tissues. II. Bonding to dentin promoted by a surface-active comonomer. *J Dent Res* 1965;44:895-902.
59. Jendresen MD. Clinical performance of a new composite resin for Class V erosion [abstract 1057]. *J Dent Res* 1978;57:339.
60. Flynn M. Six-year evaluation of in vivo performance of cervical restorative materials [abstract 322]. *J Dent Res* 1982;61:214.
61. American Dental Association. Council on Dental Materials, Instruments, and Equipment. Dentin bonding systems: an update. *J Am Dent Assoc* 1987;114:91-95.
62. Eliades GC, Caputo AA, Vougiouklakis GJ. Composition, wetting properties and bond strength with dentin of 6 new dentin adhesives. *Dent Mater* 1985;1:170-176.
63. Causton BE. Improved bonding of composite restorative to dentine. *Br Dent J* 1984;156:93-95.
64. Chan DCN, Reinhardt JW, Boyer DB. Composite resin compatibility and bond longevity of a dentin bonding agent. *J Dent Res* 1985;64:1402-1404.
65. Eliades GC, Vougiouklakis GJ. <sup>31</sup>P-NMR study of P-based dental adhesives and electron probe microanalysis of simulated interfaces with dentin. *Dent Mater* 1989;5:101-108.
66. Leinfelder KF, Russell CM, Thornton RJ, Cowen RG, Walker CK. Efficacy of dentin bonding agents: Their effectiveness in reducing microleakage. *J Ala Dent Assoc* 1986;70:13-20.
67. Barkmeier WW, Cooley RL. Resin adhesive systems: In vitro evaluation of dentin bond strength and marginal microleakage. *J Esthet Dent* 1989;1:67-72.
68. Ziemecki TL, Dennison JB, Charbeneau GT. Clinical evaluation of cervical composite resin restorations placed without retention. *Oper Dent* 1987;12:27-33.
69. Heymann HO, Sturdevant JR, Brunson WD, Wilder AD, Sluder TB, Bayne SC. Twelve-month clinical study of dentinal adhesives in Class V cervical lesions. *J Am Dent Assoc* 1988;116:179-183.
70. Tyas MJ, Burns GA, Byrne PF, Cunningham PJ, Dobson BC, Widdop FT. Clinical evaluation of Scotchbond: Three-year results. *Aust Dent J* 1989;34:277-279.
71. Tyas MJ. Three-year clinical evaluation of dentine bonding agents. *Aust Dent J* 1991;36:298-301.
72. Tao L, Pashley DH, Boyd L. Effect of different types of smear layers on dentin and enamel shear bond strengths. *Dent Mater* 1988;4:208-216.
73. Yu XY, Joynt RB, Wiecekowsky G, Davis EL. Scanning electron microscopic and energy dispersive x-ray evaluation of two smear layer-mediated dentinal bonding agents. *Quintessence Int* 1991;22:305-310.
74. Joynt RB, Davis EL, Wiecekowsky G, Yu XY. Dentin bonding agents and the smear layer. *Oper Dent* 1991;16:186-191.
75. Erickson RL. Mechanism and clinical implications of bond formation for two dentin bonding agents. *Am J Dent* 1989;2:117-123.
76. Prati C, Biagini G, Rizzoli C, Nucci C, Zucchini C, Montanari G. Shear bond strength and SEM evaluation of dentinal bonding systems. *Am J Dent* 1990;3:283-288.
77. Chappell RP, Eick JD, Theisen FC, Carracho AJL. Shear bond strength and scanning electron microscopic observation of current dentinal adhesives. *Quintessence Int* 1991;22:831-839.
78. Retief DH. Adhesion to dentin. *J Esthet Dent* 1991;3:106-113.
79. Barkmeier WW, Cooley RL. Shear bond strength of the Tenure Solution dentin bonding system. *Am J Dent* 1989;2:263-265.
80. Dickinson GL, Stevens JT, Overberger JE, McCutcheon WR. Comparison of shear bond strengths of some third-generation dentin bonding agents. *Oper Dent* 1991;16:223-230.
81. Triolo PT, Swift EJ. Shear bond strengths of ten dentin adhesive systems. *Dent Mater* 1992;8:370-374.
82. Barkmeier WW, Cooley RL. Resin adhesive systems. In vitro evaluation of dentin bond strength and marginal microleakage. *J Esthet Dent* 1989;1:67-72.
83. Barkmeier WW, Cooley RL. Shear bond strength, microleakage, and SEM study of the XR Bond adhesive system. *Am J Dent* 1989;2:111-115.
84. Barkmeier WW, Huang CT, Hammesfahr PD, Jefferies SR. Bond strength, microleakage, and scanning electron microscopy examination of the Prisma Universal Bond 2 adhesive system. *J Esthet Dent* 1990;2:134-139.

85. Prati C, Nucci C, Montanari G. Shear bond strength and microleakage of dentin bonding systems. *J Prosthet Dent* 1991;65:401-407.
86. Retief DH, Mandras RS, Russell CM, Denys FR. Evaluation of the Syntac bonding system. *Am J Dent* 1993;6:17-21.
87. Pintado MR, Douglas WH. The comparison of microleakage between two different dentin bonding resin systems. *Quintessence Int* 1988;19:905-907.
88. Mixson JM, Eick JD, Moore DL, Tira DE. Effect of two dentin bonding agents on microleakage in two different cavity designs. *J Prosthet Dent* 1992;67:441-445.
89. Crim GA. Prepolymerization of Gluma 4 sealer: Effect on bonding. *Am J Dent* 1990;3:25-27.
90. Swift EJ, Hansen SE. Effect of new bonding systems on microleakage. *Am J Dent* 1989;2:77-80.
91. Kanca J. Microleakage of the Gluma system. *Am J Dent* 1990;3:105-107.
92. Swift EJ. Microleakage of dentin adhesive systems. *J Esthet Dent* 1991;3:91-94.
93. Fitchie JG, Reeves GW, Scarbrough AR, Hembree JH. Microleakage of two new dentinal bonding systems. *Quintessence Int* 1990;21:749-752.
94. Sheth JJ, Fuller JL, Jensen ME. Cuspal deformation and fracture resistance of teeth with dentin adhesives and composites. *J Prosthet Dent* 1988;60:560-569.
95. Fissore B, Nicholls JJ, Yuodelis RA. Load fatigue of teeth restored by a dentin bonding agent and a posterior composite resin. *J Prosthet Dent* 1991;65:80-85.
96. Hansen EK. Three-year study of cervical erosions restored with resin and dentin-bonding agent. *Acta Odontol Scand* 1989;47:301-306.
97. Duke ES, Robbins JW, Snyder DS. Clinical evaluation of a dentinal adhesive system: three-year results. *Quintessence Int* 1991;22:889-895.
98. Fusayama T, Nakamura M, Kurosaki N, Iwaku M. Non-pressure adhesion of a new adhesive restorative resin. *J Dent Res* 1979;58:1364-1370.
99. Kanca J. Bonding to tooth structure: A rational rationale for a clinical protocol. *J Esthet Dent* 1989;1:135-138.
100. Bertolotti RL. Total-etch—The rational dentin bonding protocol. *J Esthet Dent* 1991;3:1-6.
101. Retief DH, Austin JC, Fatti LP. Pulpal response to phosphoric acid. *J Oral Pathol* 1974;3:114-122.
102. Stanley HR, Going RE, Chauncey HH. Human pulp response to acid pretreatment of dentin and to composite restoration. *J Am Dent Assoc* 1975;91:817-825.
103. Macko DJ, Rutberg M, Langeland K. Pulpal response to the application of phosphoric acid to dentin. *Oral Surg Oral Pathol* 1978;45:930-946.
104. Lee HL, Orlowski JA, Scheidt GC, Lee JR. Effects of acid etchants on dentin. *J Dent Res* 1973;52:1228-1233.
105. Skogedal O, Eriksen HM. Pulpal reactions to surface-sealed silicate cements and composite resin restorations. *Scand J Dent Res* 1976;84:381-385.
106. Cox CF, Keall CL, Keall HJ, Ostro E, Bergenholz G. Biocompatibility of surface-sealed dental materials against exposed pulps. *J Prosthet Dent* 1987;57:1-8.
107. Fuks AB, Funnell B, Cleaton-Jones P. Pulp response to a composite resin inserted in deep cavities with and without a surface seal. *J Prosthet Dent* 1990;63:129-134.
108. Kanca J. An alternative hypothesis to the cause of pulpal inflammation in teeth treated with phosphoric acid on the dentin. *Quintessence Int* 1990;21:83-86.
109. Van Meerbeek B, Inokoshi S, Braem M, Lambrechts P, Vanherle G. Morphological aspects of the resin-dentin interdiffusion zone with different dentin adhesive systems. *J Dent Res* 1992;71:1530-1540.
110. Eick JD, Robinson SJ, Cobb CM, Chappell RP, Spencer P. The dentinal surface: its influence on dentinal adhesion. Part III. *Quintessence Int* 1993;24:571-582.
111. Erickson RL. Surface interactions of dentin adhesive materials. *Oper Dent* 1992;17(Suppl 5):81-94.
112. Van Meerbeek B, Dhem A, Goret-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.
113. Inokoshi S, Hosoda H, Harnirattisai C, Shimada Y. Interfacial structure between dentin and seven dentin bonding systems revealed using argon ion beam etching. *Oper Dent* 1993;18:8-16.
114. Perdigao J, Swift EJ. Analysis of dental adhesive systems using scanning electron microscopy. *Int Dent J* 1994;44:349-359.
115. Pashley DH. The effects of acid etching on the pulpodentin complex. *Oper Dent* 1992;17:229-242.
116. Nakabayashi N, Kojima K, Masuhara E. The promotion of adhesion by the infiltration of monomers into tooth substrates. *J Biomed Mater Res* 1982;16:265-273.
117. Nakabayashi N, Nakamura M, Yasuda N. Hybrid layer as a dentin-bonding mechanism. *J Esthet Dent* 1991;3:133-138.
118. Gwinnett AJ. Quantitative contribution of resin infiltration/hybridization to dentin bonding. *Am J Dent* 1993;6:7-9.
119. Brännström M, Nordenvall KJ. The effect of acid etching on enamel, dentin and the inner surface of the resin restoration: A scanning electron microscopic investigation. *J Dent Res* 1977;56:917-923.
120. Tagami J, Tao L, Pashley DH. Correlation among dentin depth, permeability, and bond strength of adhesive resins. *Dent Mater* 1990;6:45-50.
121. Iwaku M, Nakamichi I, Nakamura K, Horie K, Suizu S, Fusayama T. Tags penetrating dentin of a new adhesive resin. *Bull Tokyo Med Dent Univ* 1981;28:45-51.
122. Kiyomura M. Bonding strength to bovine dentin with 4-META/MMA-TBB resin: Long-term stability and influence of water. *J Jpn Dent Mater* 1987;6:860-872.
123. Van Meerbeek B, Mohrbacher H, Celis JP, Roos JR, Braem M, Lambrechts P, Vanherle G. Chemical characterization of the resin-dentin interface by micro-Raman spectroscopy. *J Dent Res* 1993;72:1423-1428.
124. Kanca J. Dental adhesion and the All-Bond system. *J Esthet Dent* 1991;3:129-132.
125. Barkmeier WW, Suh BI, Cooley RL. Shear bond strength to dentin and Ni-Cr-Be alloy with the All-Bond universal adhesive system. *J Esthet Dent* 1991;3:148-153.
126. Kanca J. Resin bonding to wet substrate. I. Bonding to dentin. *Quintessence Int* 1992;23:39-41.
127. Gwinnett AJ. Moist versus dry dentin: Its effect on shear bond strength. *Am J Dent* 1992;5:127-129.
128. Perdigao J, Swift EJ, Cloe BC. Effects of etchants, surface moisture, and composite resin on dentin bond strengths. *Am J Dent* 1993;6:61-64.
129. Retief DH, Mandras RS, Russell CM, Denys FR. Phosphoric acid as a dentin etchant. *Am J Dent* 1992;5:24-28.
130. Souza MHS, Retief DH, Russell CM, Denys FR. Shear bond strength and microleakage of All-Bond. *Am J Dent* 1993;6:148-154.
131. Gwinnett AJ. Effect of cavity disinfection on bond strength to dentin. *J Esthet Dent* 1992;4(suppl):11-13.

132. Kanca J. Effect of resin primer solvents and surface wetness on resin composite bond strength to dentin. *Am J Dent* 1992; 5:213-215.
133. Scotchbond Multi-Purpose Dental Adhesive System technical product profile. St Paul, MN: 3M Dental Products Division, 1992.
134. Glasspoole EA, Erickson RL, Pashley DH. In vitro bonding to wet dentin [abstract 795]. *J Dent Res* 1992;72:615.
135. Swift EJ, Triolo PT. Bond strengths of Scotchbond Multi-Purpose to moist dentin and enamel. *Am J Dent* 1992;5:318-320.
136. Eliades GC. Dentin bonding systems. In: Vanherle G, De-grange M, Willems G (eds). *Proceedings of the International Symposium on State of the Art on Direct Posterior Filling Materials and Dentine Bonding*. Leuven, Belgium: Van der Poorten, 1993:49-74.
137. Miller MB (ed). *The reviews: Microleakage and adhesion. Reality Now* 1993;45:11.
138. Swift EJ, Denehy GE, Beck MD. Use of phosphoric acid etchants with Scotchbond Multi-Purpose. *Am J Dent* 1993; 6:88-90.
139. Nakabayashi N, Watanabe A, Gendusa NJ. Dentin adhesion of a "modified" 4-META/MMA-TBB resin: function of HEMA. *Dent Mater* 1992;8:259-264.
140. Cooley RL, Tseng EY, Barkmeier WW. Dentinal bond strengths and microleakage of a 4-META adhesive to amalgam and composite resin. *Quintessence Int* 1991;22:979-983.
141. Hasegawa T, Retief DH, Russell CM, Denys FR. A laboratory study of the Amalgambond Adhesive System. *Am J Dent* 1992;5:181-186.
142. Tao L, Tagami J, Pashley DH. Pulpal pressure and bond strengths of SuperBond and Gluma. *Am J Dent* 1991;4:73-76.
143. Elhabashy A, Swift EJ, Boyer DB, Denehy GE. Effects of dentin permeability and hydration on the bond strengths of dentin bonding systems. *Am J Dent* 1993;6:123-126.
144. Pashley EL, Tao L, Matthews WG, Pashley DH. Bond strengths to superficial, intermediate and deep dentin in vivo with four dentin bonding systems. *Dent Mater* 1993;9:19-22.
145. Finger WJ. Dentin bonding agents. Relevance of in vitro investigations. *Am J Dent* 1988;1:184-188.
146. Barnes DM, Thompson VP, Blank LW, McDonald NJ. Microleakage of Class 5 composite resin restorations: a comparison between in vivo and in vitro. *Oper Dent* 1993;18:237-245.
147. Rueggeberg FA. Substrate for adhesion testing to tooth structure—Review of the literature. *Dent Mater* 1991;7:2-10.
148. Söderholm K-JM. Correlation of in vivo and in vitro performance of adhesive restorative materials: A report of the ASC MD156 Task Group on Test Methods for the Adhesion of Restorative Materials. *Dent Mater* 1991;7:74-83.
149. Pashley DH. In vitro simulations of in vivo bonding conditions. *Am J Dent* 1991;4:237-240.
150. Duke ES, Lindemuth J. Polymeric adhesion to dentin: Contrasting substrates. *Am J Dent* 1991;4:241-246.
151. Gwinnett AJ, Kanca J. Interfacial morphology of resin composite and shiny erosion lesions. *Am J Dent* 1992;5:315-317.
152. Harnirattisai C, Inokoshi S, Shimada Y, Hosoda H. Adhesive interface between resin and etched dentin of cervical erosion/abrasion lesions. *Oper Dent* 1993;18:138-143.
153. Van Meerbeek B, Lambrechts P, Inokoshi S, Braem M, Vanherle G. Factors affecting adhesion to mineralized tissues. *Oper Dent* 1992;17(suppl 5):111-124.
154. Lee WC, Eakle WS. Possible role of tensile stress in the etiology of cervical erosive lesions of teeth. *J Prosthet Dent* 1984;52:374-380.
155. Heymann HO, Sturdevant JR, Bayne S, Wilder AD, Sluder TB, Brunson WD. Examining tooth flexure effects on cervical restorations: A two-year clinical study. *J Am Dent Assoc* 1991;122:41-47.
156. Braem M, Lambrechts P, Vanherle G. Stress-induced cervical lesions. *J Prosthet Dent* 1992;67:718-722.
157. Miyazaki M, Hinoura K, Onose H, Moore BK. Effect of filler content of light-cured composites on bond strength to bovine dentine. *J Dent* 1991;19:301-303.
158. Kemp-Scholte CM, Davidson CL. Marginal integrity related to bond strength and strain capacity of composite resin restorative systems. *J Prosthet Dent* 1990;64:658-664.
159. Staninec M, Kawakami M. Adhesion and microleakage tests of a new dentin bonding system. *Dent Mater* 1993;9:204-208.
160. Kemp-Scholte CM, Davidson CL. Complete marginal seal of Class V resin composite restorations effected by increased flexibility. *J Dent Res* 1990;69:1240-1243.
161. Dentin bonding: State of the art. *Clin Res Assoc Newsletter* 1991;15(12):1-3.
162. Tooth desensitization before crown cementation—'93. *Clin Res Assoc Newsletter* 1993;17(8):2-3.
163. Watanabe T, Sano M, Itoh K, Wakumoto S. The effects of primers on the sensitivity of dentin. *Dent Mater* 1991;7:148-150.
164. Felton DA, Bergenholz G, Kanoy BE. Evaluation of the desensitizing effect of Gluma Dentin Bond on teeth prepared for complete-coverage restorations. *Int J Prosthodont* 1991; 4:292-298.
165. Dondi dall'Orologio G, Malferrari S. Desensitizing effects of Gluma and Gluma 2000 on hypersensitive dentin. *Am J Dent* 1993;6:283-286.
166. Bergenholz G, Jontell M, Tuttle A, Knutsson G. Inhibition of serum albumin flux across exposed dentine following conditioning with GLUMA primer, glutaraldehyde or potassium oxalates. *J Dent* 1993;21:220-227.
167. Watanabe F, Powers JM, Lorey RE. In vitro bonding of prosthodontic adhesives to dental alloys. *J Dent Res* 1988;67:479-483.
168. Barkmeier WW, Menis DL, Barnes DM. Bond strength of a veneering porcelain using newer generation adhesive systems. *Pract Periodont Aesthet Dent* 1993;5:50-55.
169. Albers HIF (ed). *Metal-resin bonding. ADEPT Report* 1991;2:25-40.
170. Pashley EL, Comer RW, Parry EE, Pashley DH. Amalgam buildups: Shear bond strength and dentin sealing properties. *Oper Dent* 1991;16:82-89.
171. Covey DA, Moon PC. Shear bond strength of dental amalgam bonded to dentin. *Am J Dent* 1991;4:19-22.
172. Miller BH, Arita K, Tamura N, Nishino M, Guo I, Okabe T. Bond strengths of various materials to dentin using Amalgambond. *Am J Dent* 1992;5:272-276.
173. Chang J, Scherer W, Tawk BA, Martini R. Shear bond strength of a 4-META adhesive system. *J Prosthet Dent* 1992;67:42-45.
174. Bagley A, Wakefield CW, Robbins JW. In vitro comparison of filled and unfilled universal bonding agents of amalgam to dentin. *Oper Dent* 1994;19:97-101.
175. Charlton DG, Moore BK, Swartz ML. In vitro evaluation of the use of resin liners to reduce microleakage and improve retention of amalgam restorations. *Oper Dent* 1992;17:112-119.
176. Ianzano JA, Mastrodomenico J, Gwinnett AJ. Strength of amalgam restorations bonded with Amalgambond. *Am J Dent* 1993;6:10-12.

177. Staninec M. Retention of amalgam restorations: Undercuts versus bonding. *Quintessence Int* 1989;20:347-351.
178. Eakle WS, Staninec M, Lacy AM. Effect of bonded amalgam on the fracture resistance of teeth. *J Prosthet Dent* 1992;68:257-260.
179. Varga J, Matsumura H, Masuhara E. Bonding and amalgam filling to tooth cavity with adhesive resin. *Dent Mater J* 1986;5:158-164.
180. Simizu A, Ui T, Kawakami M. Microleakage of amalgam restoration with adhesive resin cement lining, glass ionomer base and fluoride treatment. *Dent Mater J* 1987;6:64-69.
181. Staninec M, Holt M. Bonding of amalgam to tooth structure: Tensile adhesion and microleakage tests. *J Prosthet Dent* 1988;59:397-402.
182. Edgren BN, Deney GE. Microleakage of amalgam restorations using Amalgambond and Copalite. *Am J Dent* 1992;5:296-298.
183. Torii Y, Staninec M, Kawakami M, Imazato S, Torii M, Tsuchitani Y. Inhibition in vitro of caries around amalgam restorations by bonding amalgam to tooth structure. *Oper Dent* 1989;14:142-148.
184. Masaka N. Restoring the severely compromised molar through adhesive bonding of amalgam to dentin. *Compend Contin Educ Dent* 1991;12:90-98.
185. Pashley DH, Derkson GD, Tao L, Derkson M, Kalathoor S. The effects of a multi-step dentin bonding system on dentin permeability. *Dent Mater* 1988;4:60-63.
186. Hansen SE, Swift EJ, Krell KV. Permeability effects of two dentin adhesive systems. *J Esthet Dent* 1992;4:169-172.
187. Charlton DG, Murchison DF, Moore BK. Incorporation of adhesive liners in amalgam: Effect on compressive strength and creep. *Am J Dent* 1991;4:184-188.
188. Hadavi F, Hey JH, Ambrose ER, Elbadrawy HE. The influence of an adhesive system on shear bond strength of repaired high copper amalgams. *Oper Dent* 1991;16:175-180.
189. Roeder LB, DeSchepper EJ, Powers JM. In vitro bond strength of repaired amalgam with adhesive bonding systems. *J Esthet Dent* 1991;3:126-128.
190. Leelawat C, Scherer W, Chang J, Vijayaraghavan T, LeGeros J. Bonding fresh amalgam to existing amalgam: A shear and flexural strength study. *J Esthet Dent* 1992;4:46-49.
191. Hadavi F, Hey JH, Ambrose ER, Elbadrawy HE. Repair of high-copper amalgam with and without an adhesive system: In vitro assessment of microleakage and shear bond strength. *Gen Dent* 1992;41:49-53.
192. Lacy AM, Rupprecht R, Watanabe L. Use of self-curing composite resins to facilitate amalgam repair. *Quintessence Int* 1992;23:53-59.
193. Wilson AD, Kent BE. A new translucent cement for dentistry: The glass ionomer cement. *Br Dent J* 1972;132:133-135.
194. Walls AWG. Glass polyalkenoate (glass-ionomer) cements: A review. *J Dent* 1986;14:231-246.
195. Mount GJ. Polyacrylic cements in dentistry. *Am J Dent* 1990;3:79-84.
196. Tyas MJ, Beech DR. Clinical performance of three restorative materials for non-undercut cervical abrasion lesions. *Aust Dent J* 1985;30:260-264.
197. Osborne JW, Berry TG. A 3-year clinical evaluation of glass ionomer cements as Class III restorations. *Am J Dent* 1990;3:40-43.
198. Powell LV, Gordon GE, Johnson GH. Clinical comparison of Class V resin composite and glass ionomer restorations. *Am J Dent* 1992;5:249-252.
199. Hicks MJ. Artificial lesion formation around glass ionomer restorations in root surfaces: A histologic study. *Gerodontology* 1986;2:108-114.
200. Kambhu PP, Ettinger RL, Wefel JS. An in vitro evaluation of artificial caries-like lesions on restored overdenture abutments. *J Dent Res* 1988;67:582-584.
201. Swift EJ. In vitro caries-inhibitory properties of a silver cement. *J Dent Res* 1989;68:1088-1093.
202. Reinhardt JW, Swift EJ, Bolden AJ. A national survey on the use of glass ionomer cements. *Oper Dent* 1993;18:56-60.
203. McLean JW, Powis DR, Prosser HJ, Wilson AD. The use of glass-ionomer cements in bonding composite resins to dentine. *Br Dent J* 1985;158:410-414.
204. Glass ionomer-resin—state-of-art. *Clin Res Assoc Newsletter* 1993;17(3):1-2.
205. Momoi Y, McCabe JF. Fluoride release from light-activated glass ionomer restorative cements. *Dent Mater* 1993;9:151-154.
206. Mitra SB. Adhesion to dentin and physical properties of a light-cured glass ionomer liner/base. *J Dent Res* 1991;70:72-74.
207. Vitremer Tri-Cure Glass Ionomer System technical product profile. St Paul, MN: 3M Dental Products Division, 1992.
208. Leung RL, Fan PL, Johnston WM. Post-irradiation polymerization of visible light-activated composite resin. *J Dent Res* 1983;62:363-365.
209. Nathanson D, Buithieu H. Mechanical properties of new glass ionomers [abstract 743]. *J Dent Res* 1993;72:196.
210. Kitamura A, Aoyama M, Miyazaki T. Direct tensile strength of a light-cured glass ionomer [abstract 1649]. *J Dent Res* 1993;72:309.
211. Moon PC, Covey DA, Hass TW. Mechanical properties and dentin bonding strength of glass ionomer materials [abstract 2273]. *J Dent Res* 1993;72:387.
212. Burgess JO, Burkett L. Shear bond strength of four glass ionomers to enamel and dentin [abstract 2276]. *J Dent Res* 1993;72:388.
213. Pawlus MA, Swift EJ, Vargas MA. Shear bond strengths of resin ionomer restorative materials [abstract 1812]. *J Dent Res* 1994;73:328.
214. Vargas MA, Fortin D, Swift EJ. Dentin bond strength of VLC glass ionomers using All-Bond 2 [abstract 1813]. *J Dent Res* 1994;73:328.
215. Crim GA. Marginal leakage of visible light-cured glass ionomer restorative materials. *J Prosthet Dent* 1993;69:561-563.
216. Crim GA. Effect of aging on microleakage of restorative systems. *Am J Dent* 1993;6:192-194. □