Chapter 23

Adhesive Restorative Materials: Bonding of Resin-based Materials

23.1 Introduction

The development and regular use of adhesive materials has begun to revolutionize many aspects of restorative and preventive dentistry. Attitudes towards cavity preparation are altering since, with adhesive materials, it is no longer necessary to produce large undercuts in order to retain the filling. These techniques are, therefore, responsible for the conservation of large quantities of sound tooth substance which would otherwise be victim to the dental bur. Microleakage, a major dental problem which is probably responsible for many cases of secondary caries, may be reduced or eliminated. New forms of treatment, such as the sealing of pits and fissures on posterior teeth, the coverage of badly stained or deformed teeth in order to improve appearance and the direct bonding of brackets in orthodontics have all grown from the development of adhesive systems.

Section 2.5 deals briefly with the general mechanistic aspects of adhesion. Three major approaches can be identified. (1), bonding through micromechanical attachment; in dentistry this is best illustrated through the bonding of resins to enamel using the *acid-etch technique*. (2), bonding through *chemical adhesion* to either enamel or dentine can be identified in many systems based on the use of coupling agents or cements containing polyacids. (3), bonding through a complex mechanism involving wetting, penetration and the formation of a layer of bound material at the interface between the restorative and the substrate. The latter describes the mode of action of many modern dentine bonding agents.

23.2 Acid-etch systems for bonding to enamel

The surface of enamel is smooth and has little potential for bonding by micromechanical attachment. On treatment with certain acids, however, the structure of the enamel surface may be modified considerably. Figure 23.1 shows the surface of human enamel following one minute of etching with a 37% solution of phosphoric acid, which is the acid of choice for most applications of the acid-etch technique. Solutions of phosphoric acid are difficult to control when applied to enamel, some acid inevitably contacts areas which are not required to be etched. One improvement in acid-etching procedures has been the development of acidified gels. These contain phosphoric acid in aqueous gel which is viscous enough to allow controlled placement in the required area. In addition, the gel is normally pigmented, a feature which further aids control.

The pattern of etching enamel can vary. The most common (type 1) involves preferential removal of the enamel prism cores, the prism peripheries remaining intact. The type 2 etching pattern is the opposite of the type 1, involving preferential removal of the peripheries with the cores being left intact. The type 3 etching pattern contains areas which resemble both type 1 and type 2 along with some less distinct areas where the pattern of etching appears to be unrelated to the enamel prism morphology.

The individual features evident in Fig. 23.1 correspond to the ends of enamel prisms, each being about 5 μm in diameter. This surface is now suitable for micromechanical attachment since it
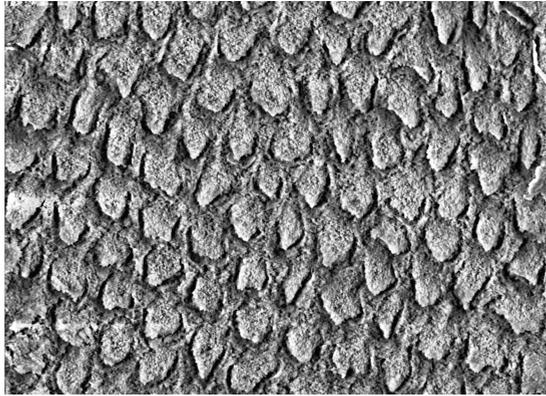
Fig. 23.1   Scanning electron micrograph of the surface of enamel after etching with 37% phosphoric acid followed by rinsing and drying (×2000 magnification).

Fig. 23.2   Pack of enamel bonding agent containing etching agent (37% phosphoric acid) and two fluid resins which begin to polymerize on mixing. Modern materials contain a single resin which is light activated.

contains a myriad of small undercuts into which resins can gain ingress, set and form a *mechanical lock*. The three major factors which affect the success or failure of acid-etch bonding systems are as follows:

(1)   The etching time. This should be sufficient to cause effective etching as evidenced by a white, chalky appearance on the treated section of enamel after washing and drying. Etching should not continue long enough for dissolved apatites to reprecipitate as phosphates onto the etched surface. The etching time normally used is between 10 and 60 seconds.
(2)   The washing stage. Following etching the enamel surface should be washed with copious amounts of water to remove debris. The washing time usually used is 60 seconds.
(3)   The drying stage. Drying is critical if the enamel is being coated with a hydrophobic resin (for example BisGMA), when oil free compressed air is used to give a chalky white appearance. The surface should be maintained in this dry state until resin application. An example of this would be the application of a fissure sealant. Conversely, when a Dentine Bonding Agent (DBA) is being used to attach resin to dentine, bonding to enamel can also be achieved when the etched enamel is damp.

The type of resin applied to the etched enamel surface depends upon the specific application

being used. For composite resins the mixed material may be applied directly to the etched enamel surface. Resin from the composite flows into the etched enamel and sets, forming rigid tags, typically 25 μm long, which retain the filling. Many manufacturers supply a fluid *bonding resin* which may enhance the adhesive bond strength (see Fig. 23.2). It consists of a resin similar to that used in the composite material but contains no filler particles. It is very fluid and readily flows into the etched enamel surface. The bonding resin may be a single component which is activated by light or may consist of two fluid resins, one containing initiator and the other activator, which require mixing before being applied to the etched enamel. The composite filling material is applied directly to the surface of the bonding resin. The need for the use of the intermediary layer of unfilled bonding resin varies depending upon the type of composite material used. For conventional composites it is likely that the materials contain sufficient excess resin to satisfy the requirements for attachment to etched enamel without the presence of the intermediate resin. For the more heavily filled and viscous products (mainly hybrid-type composites) it is necessary to use the unfilled resin layer in order to achieve adequate penetration of the etched enamel surface.

Bonding readily occurs at the unfilled resin to composite interface. This is aided by the fact that surface layers of resins polymerised by a free radical mechanism remain soft and unpolymerised due to the inhibiting effect which oxygen has on

the polymerisation mechanism. On applying a composite material to the surface of a 'cured' unfilled resin, mixing of the two resin systems occurs at the interface followed by a degree of copolymerisation and entangling which effectively bonds the filled and unfilled resins together. The resulting shear bond strength achieved between etched enamel and restorative resins is 16–20 MPa.

The way in which the enamel etch pattern affects bonding has never been conclusively proven. The nature of some enamel bonding systems has changed over recent years as some manufacturers have produced materials which can be used for both enamel and dentine bonding. Hence, some enamel bonding resins now contain primers and solvents which enable bonding to moist enamel to be achieved. This is contrary to the previous situation in which thorough drying of enamel was essential for effective bonding. This theme is developed further in Section 23.8.

23.3 Applications of the acid-etch technique

The acid-etch technique has many applications in dentistry. It is now widely used for most composite fillings as a means of aiding retention and reducing or preventing microleakage. For *class IV cavities* (incisal edge restorations) the acid-etch technique has replaced the gold inlay as the treatment of choice for restoring the tooth contours and function. In this example the use of an adhesive system allows the conservation of considerable quantities of tooth substance which would otherwise be lost in cavity preparation. Bonding of resins using the acid-etch technique has also been used as a means of strengthening or *splinting* teeth which have been weakened by cavity preparation. It can readily be shown that a tooth having a prepared cavity is weakened relative to an unprepared tooth. Under stress, fracture of the tooth is likely with cusp fracture being the most likely occurrence. Restoring the cavity with a non-adhesive restoration has little beneficial effect on the strength of the tooth whereas the use of an adhesive material will strengthen the tooth and help to prevent cusp fractures.

Fissure sealants are now widely used for preventing pit and fissure caries. The majority of products are based on dimethacrylate resin systems such as Bis GMA or urethane dimethacrylate.

The simplest products consist of two liquid components, each containing the dimethacrylate monomer or a mixture of the monomer and a diluent monomer such as triethylene glycol dimethacrylate (see Fig. 22.4). In addition, one component contains a peroxide initiator whilst the other contains an amine activator. The normal procedure is to mix together one drop of each liquid component in order to activate the polymerisation of the methacrylate groups. Chemically, these products are almost identical to the intermediary resin bonding agents referred to in the previous section. The mixed material is applied to the etched enamel of the occlusal surface of the selected tooth where it typically takes a few minutes to harden. The surface layer remains tacky due to air inhibition of the polymerisation and is generally wiped away to expose the fully cured material underneath.

Some products contain additives such as titanium dioxide in order to make the sealant more readily visible *in situ* (Fig. 23.3). With the unpigmented material the sealant can be difficult to detect on inspection due to the translucent nature of the resin. There has also been a trend towards adding glass filler to improve durability and those products containing filler may be considered as lightly filled composites. The filler content remains somewhat lower than that found in composite filling materials so that the viscosity is low enough to enable the materials to flow into the fissure pattern of the occlusal surface of the tooth.

Not surprisingly, the development of light-activated fissure sealant materials has followed the

Fig. 23.3   Pack of fissure sealant material which is similar in composition to the enamel bonding agent shown in Fig. 23.2. In this product one resin contains titanium dioxide in order to allow the sealant to be visualized in the pits and fissures after placement. Equivalent materials, provided as a single liquid resin component, are light activated.

development of light-activated composites. One of the most popular materials in use until a few years ago was activated using ultraviolet radiation. This is no longer used and has been replaced by products which are activated by light within the visible range. The visible light activation units which are used for curing composites can also be used to activate curing of fissure sealants so it is convenient for dentists who have such a unit to use it for several applications (see p. 204). The problems of limited depth of cure do not apply to these materials which are used in thin sections. The efficacy of fissure sealants is measured in one of two ways. One way is to monitor the survival of the sealant as a function of time. Apparent sealant loss may be due to detachment or wear. The other way is to monitor the caries reduction on sealed teeth compared with a group of unsealed control teeth. Surprisingly the two approaches do not produce the same result. Sealants, being unfilled or lightly filled resins, are relatively soft and readily undergo abrasive wear, although this is minimized in practice due to the fact that the material is in a protected environment in which it is unlikely to come under direct occlusal loads. In any event, wear of the sealant does not impair its efficacy since the surface enamel remains impregnated with resin. Likewise, if a sealant becomes detached it may still have some beneficial effect if it leaves behind an enamel surface which is resin impregnated.

The success of fissure sealants is mainly dependent on initial placement conditions and techniques. In order to get good resin tag formation the enamel must be properly etched and washed and thoroughly dried before the sealant is applied. It is the variability in levels of moisture which causes the wide variation in success rates recorded for fissure sealants. Attempts have been made to produce fluoride containing sealants so that the benefits of surface sealing can be combined with those of a sustained fluoride release. Release of fluoride from resin-based materials is difficult to achieve and the rate of release is generally much lower than is observed for glass ionomers. Fluoride releasing resin-modified glass ionomers (see Chapter 25) offer a potential for achieving the ideal of effective bonding durability and sustained fluoride release.

Most recently, chemically active luting resins have become available which will bond to oxide layers on the surface of non-precious metals and to copper oxide on heat treated gold casting alloys (see Section 23.9).

Resin systems are now widely used for attaching *orthodontic brackets*. These resins are normally supplied as two components carrying relatively high loadings of initiator and activator respectively. One component is applied to the etched enamel surface and the other to the bracket. When the two are pressed together rapid setting takes place. Alternatively, conventional composite resin materials can be used for this application.

Composites are gaining in popularity for the attachment of *bridges*. This involves a more conservative technique than the traditional methods, which involve considerable destruction of the abutment teeth in order to achieve retention. The principle of the resin-bonded systems is that the composite bonds mechanically to the etched enamel of the tooth and also to the surface of the cast alloy framework of the bridge. There are various means of achieving mechanical attachment between the resin and the alloy. One system employs the use of perforated 'wings' on the cast alloy bridge framework. The composite used for bonding flows through the perforations giving a mechanical lock onto the framework. Attachment to the abutment tooth is through resin penetration of acid-etched enamel. This type of bridge is known as a Rochette bridge. Another approach is to etch the wings of the bridge to produce a roughened surface with a myriad of small undercuts similar in appearance to the surface of etched enamel (Fig. 23.4). This surface is suitable for
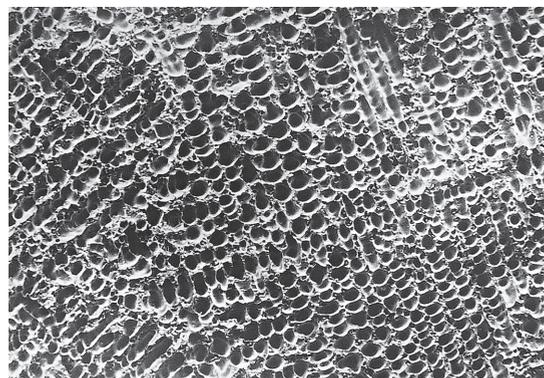

Fig. 23.4   A scanning electron micrograph of an electrolytically acid-etched metal surface showing the irregular etch pattern that can give micromechanical retention for attachment (×124).

Fig. 23.5 A chemically active resin luting cement which is used to bond laboratory made dental appliances and restorations to teeth.

achieving mechanical attachment with a composite. Etching is carried out electrolytically or in a strong acid. This second type of bridge is normally referred to as a Maryland bridge. Chemically active resins capable of attaching to both metals and tooth have been used to bond sand-blasted metal retainers to the supporting tooth. (see Fig. 23.5)

The active groups may be phosphate or melittic acid anhydride groups akin to those used in certain dentine bonding agents (see Section 23.4).

Another application of the acid-etch technique is the attachment of acrylic or porcelain labial veneers in order to improve the appearance of stained, discoloured or misshapen teeth. Acrylic veneers may be produced in a range of standard shapes and sizes which can be customized by heat adaptation to a cast of the patient's teeth. A composite of the correct shade is used to attach the veneer to the etched enamel surface. The fitting surface of the veneer is softened with a solvent primer to aid bonding between the veneer and composite. The acrylic laminate veneers have limited lifetime due to the fact that the acrylic resin is soft and readily abrades to expose regions of the underlying composite resin. Also the bond between the composite resin and veneer has a tendency to fail, probably due to stresses set up at the interface as a result of the differing values of

the coefficient of thermal expansion and water sorption for the two materials. The use of porcelain veneers is covered in Section 11.8. Essentially the veneers are custom made and bonding to the composite is achieved by etching the fitting surface of the veneer with hydrofluoric acid and using a silane coupling agent to chemically link silica groups in the porcelain to methacrylate groups in the resin. Porcelain veneers are much harder and more resistant to abrasion than acrylic veneers. Providing that etching and silane treatment is carried out carefully the bond to composite appears adequate. The brittle nature of the porcelain must be taken into account when considering the design of veneers if chipping at the incisal edge is to be avoided.

23.4 Bonding to dentine – background

The mechanism of bonding to enamel involves the penetration of resin into the relatively porous surface layer of the etched enamel to create a mechanical interlocking. It was recognized many years ago that a similar mechanism could potentially be used with dentine. This would involve etching of the surface of exposed dentine with acid to expose the patent dentinal tubules which could be penetrated by resin to form tags. Until quite recently this mechanism of bonding to dentine was rejected by most authorities as being both ineffective and unacceptable for the following reasons:

(1) Concerns over the potentially damaging effect of acids on vital dentine: these concerns were related to what was considered a well-established fact that acid-containing restoratives placed in contact with vital dentine cause irritation and/or irreversible pathological change to the pulp. Much of the evidence for these concerns involved experience with silicate restorative materials which contain phosphoric acid. Current philosophy on this important point is that most cases of pulpal irritation were not related to direct chemical traumatization with phosphoric acid but were as a result of ineffective sealing of cavity margins due to lack of adhesion. Hence, most authorities now accept that the dentine and pulp are able to withstand a greater chemical insult with acids than was once thought to be acceptable.

(2) Etching dentine opens dentinal tubules and encourages dentinal fluid flow. In view of the fact that most restorative resins are relatively hydrophobic, any increase in the moisture content of the surface of dentine is likely to make bonding more difficult to achieve. Ever since attempts to bond resins to dentine were first attempted, the inability of resins to 'wet' moist dentine and adapt closely enough to achieve bonding has been recognized as a major problem which has hindered development. Experience of bonding to enamel suggested that 'dryness' of the substrate was essential in order to achieve an effective bond, so it is easy to appreciate why the etching of dentine was considered unlikely to help in the production of an effective bond to this substrate. Most early attempts to achieve bonding emphasize the drying of dentine as an important step in the bonding procedure. Current thinking appreciates the damage which can be caused by desiccation of dentine and tries to overcome the moisture problem by the use of primers and solvents. Furthermore, it is now recognised that dentinal tubular fluid flow is negligible in anaesthetised teeth due to the reduction in pulpal blood flow as a consequence of the effect of the vasoconstrictor (usually epinephrine) in the local anaesthetic solution. Dentinal tubular fluid is a transudate from the blood vessels of the pulp, when pulpal perfusion pressure falls the rate of transudation also falls.

(3) The dentinal tubule openings occupy only about 5% of the cut dentine surface in superficial dentine (near the amelodentinal junction). This rises to near 20% in deep dentine. Hence, it was suggested that in inserting resin tags into dentinal tubules the effectiveness of the bond to dentine would be limited by the relatively small proportion of the area being utilized. It is currently accepted that whereas tags in dentinal tubules can contribute to bonding, other mechanisms involving all the exposed dentine surface are at least equally as important. In the 1970s and 1980s, when dentine bonding was considered desirable but when etching of dentine was considered unacceptable, emphasis was placed on trying to achieve bonding to dentine through the formation of chemical links between restoratives and chemical moieties in the dentine surface.
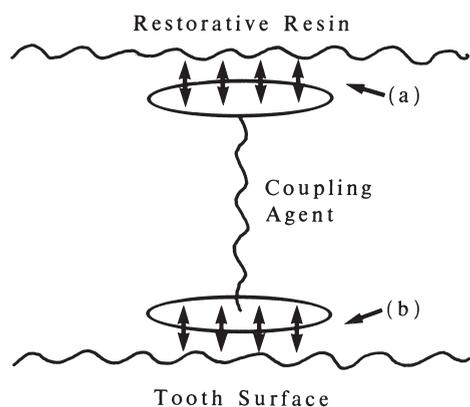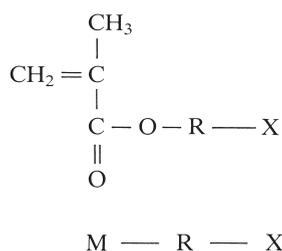
Attempts at chemical bonding

When attempting to form chemical links with the tooth surface it is obviously necessary to pay some attention to the chemical nature of the substrate tooth material. Dentine contains approximately 50% hydroxyapatite and 30% polypeptides (e.g. collagen), the balance being aqueous solutions which occupy the dentinal tubules. Enamel, on the other hand, contains only about 1% protein and 97% hydroxyapatite. Forming chemical links with enamel therefore inevitably involves forming a union with hydroxyapatite. Adhesive systems which attach to hydroxyapatite will form links with both enamel and dentine, although the bond to enamel for such materials is generally significantly stronger than the bond to dentine. Dentine offers the possibility of utilizing reactive groups, such as – NH which are present in dentine proteins, for achieving chemical union with adhesives. For adhesives of this type a significant bond strength may be demonstrated with dentine but no appreciable adhesion is observed with enamel.

In order to bridge the gap between the tooth surface and the resin-based restorative a series of difunctional chemical coupling agents were developed. Resin-based restorative materials were bonded to either dentine or enamel using coupling agents or adhesion promoters comprising difunctional molecules, one part of which enters into chemical union with the tooth surface whilst the other attaches to the resin, as illustrated in Fig. 23.6. The method of use was to apply the coupling agent to the clean, dry tooth surface followed by the resin filling material, normally a composite. The adhesion promoters had a general formula of the type shown in Fig. 23.7 where M represents a methacrylate group which eventually becomes bound to the resin by co-polymerisation, X represents a reactive group which interacts with the tooth surface and R is a linking and spacing group. Examples of such molecules are N-phenylglycineglycidylmethacrylate, NPG-GMA (Fig. 23.8 and 23.9), 4-methacryloxyethyltrimelliticanhydride (4-META) (Fig. 23.10) and phosphate-methacrylates such as that shown in Fig. 23.11. In these, the mineral component of the tooth was thought to bind with the glycine, mellitic acid and phosphate groups respectively.
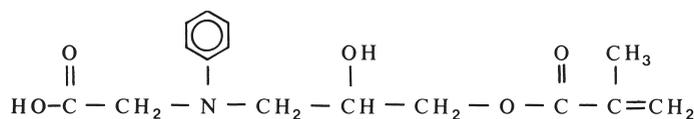
The coupling agents referred to above are all polymerizable monomers containing groups capable of interacting with the tooth surface. In the presence of the required initiators and activators the monomers are readily polymerised to form resins. Hence some of the products were supplied as two components, one containing a chemical activator (e.g. a tertiary amine), the other containing a polymerisation initiator (e.g. a peroxide). Over the years there has been a trend for

chemically activated resin systems to be replaced by light-activated materials. As a result, some products are supplied as one component containing the adhesive and a light-sensitive polymerisation activator.

The adhesive systems described above worked primarily through affinity for calcium in the organic component of dentine. Consequently, whereas each material was primarily designed as a dentine adhesive they all formed a more tenacious bond to enamel. Some direct bonding between reactive groups in dentinal collagen and reactive groups in the adhesives was thought possible.

Some adhesive systems were developed specifically with the aim of grafting to the organic collagenous component of dentine. Collagen has several reactive groups which make this a feasible proposition. The groups which have received most attention are the hydroxyl and amine groups. One commercial product relied on the addition reaction which occurs between isocyanate groups and both hydroxyl and amine groups. Another commercial product relied on the reaction which readily occurs between aldehyde groups and amine groups.

Attempts at bonding restorative resins to dentine by direct chemical coupling led to limited clinical success in the absence of any form of dentine

Fig. 23.6   Diagram illustrating the principle of bonding with a coupling agent. (a) Part of molecule which enters into bonding with restorative resin. (b) Part of molecule which enters into bonding with tooth surface.

Fig. 23.7   General structural formula of a resin–tooth coupling agent. X represents a chemical group which interacts with enamel or dentine. R represents a linking group which joins X to the methacrylate (M).
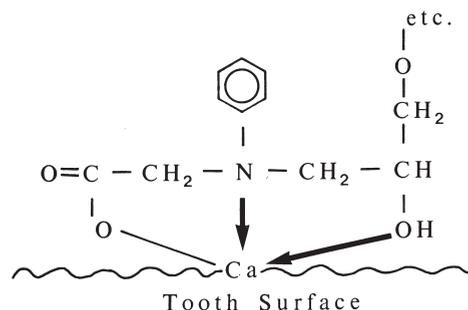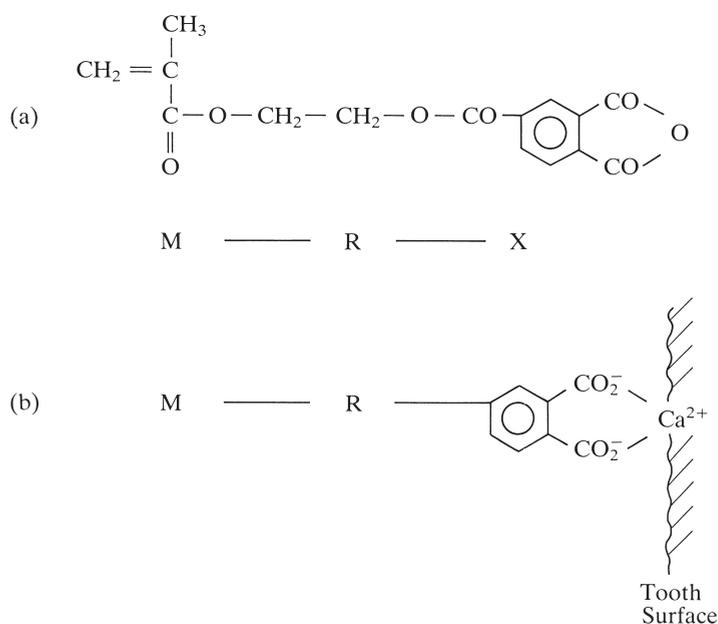

Fig. 23.9   Diagram illustrating the probable mechanism of adhesion between NPG-GMA and the tooth surface.

Fig. 23.8   Structural formula of *N*-phenylglycine-glycidylmethacrylate (NPG-GMA). Used as a coupling agent to link composite resin restorative materials with tooth substance.

(a)

CH₃

CH₂ = C

$\overset{\overset{\text{CH}_3}{|}}{\underset{\underset{\text{O}}{\parallel}}{\text{C}}}$ — O — CH₂ — CH₂ — O — CO — [benzene ring] — CO⟩O, CO⟩

M ——— R ——— X

(b)

M ——— R —— [benzene ring] — CO₂⁻, CO₂⁻ — Ca²⁺

Tooth Surface

Fig. 23.10   Structure of 4-META (4-methacryloxyethyltrimelliticanhydride) and its mode of bonding to tooth substance. (a) Structure of 4-META. (b) 4-META bound to calcium in tooth substance.

(a)

CH₃

CH₂ = C

C — O — CH₂ — CH₂ — O — P=O, with OH above and O—[benzene ring] below
‖
O

M — R — X

(b)

M — R — O, O⁻ → Ca²⁺

P⁺

[benzene ring] — O, O⁻ →

Tooth Surface
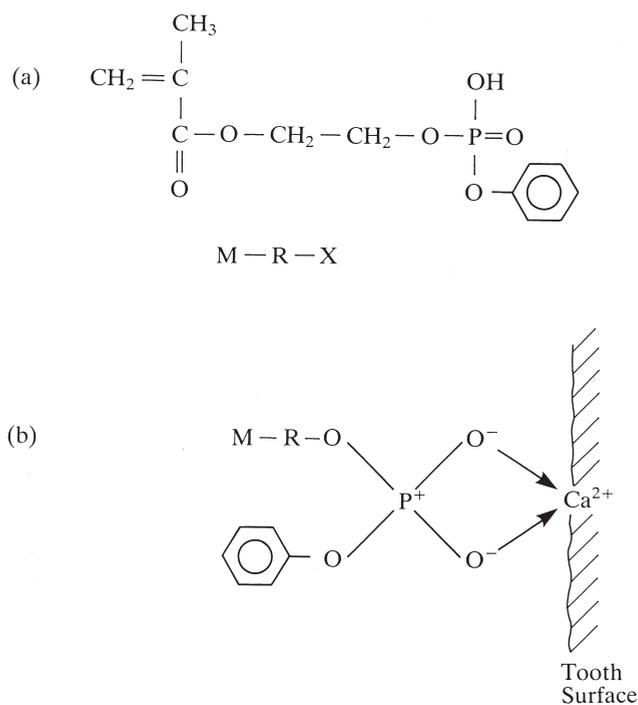
Fig. 23.11   Structure of a phosphate ester suggested as a dental adhesive. (a) Structure of the ester which is essentially a product of an aromatic phosphate and hydroxyethylmethacrylate (HEMA). (b) Proposed method of bonding to tooth substance.

pre-treatment or conditioning. Table 23.1 shows values of shear bond strength to acid-etched enamel and unconditioned dentine. The significantly lower bond strengths to dentine explain the lack of clinical efficacy. Microleakage studies also showed that a less than perfect marginal seal to dentine was achieved, indicating that close adaptation between the restorative and dentine had not been developed over a significant proportion of the dentine surface.
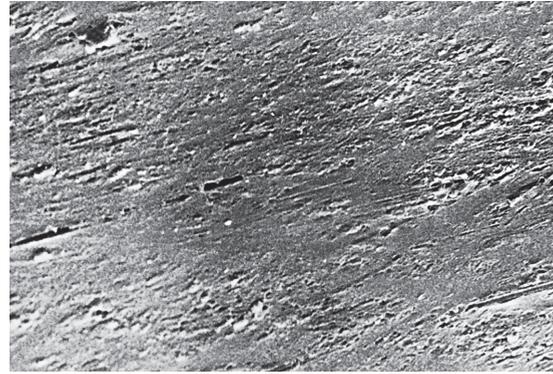
Table 23.1   Shear bond strength of various bonding systems to etched enamel, conditioned or unconditioned dentine.

Bonding system	Bond strength (MPa)
Acid-etched enamel + resin	16–20
Unconditioned dentine + adhesive	3–5
Conditioned dentine with total etch bonding	15–25
Conditioned dentine with self-etching primer system	15–25

Fig. 23.12   Surface of the dentine smear layer formed after cavity preparation.

Table 23.2   Commonly used dentine conditioners.

35–37% Phosphoric acid
10% Phosphoric acid
10% Maleic acid
17% EDTA
10% Citric acid + 3% ferric chloride

Improvements in the ability to bond to dentine and to form an effective seal at the tooth restoration interface were not possible until a greater understanding of the nature of the dentine surface and the changes which could be produced by conditioning was achieved. For those materials discussed in this section, drying of the dentine surface was considered a prerequisite for effective bonding. The higher values of shear bond strength to dentine (Table 23.1) were achieved only after effective drying. Work on dentine conditioning and the use of primers was to cause a complete re-think of how bonding to dentine is best achieved.

23.5 Dentine conditioning – the smear layer

There are several possible reasons why the bond strength to dentine was so much lower than that which could be achieved with enamel (Table 23.1). The proposed mechanism was different and relied upon the very close adaptation of bonding agent to substrate in order to allow chemical bonding to occur. The inherent problem involved in bonding a hydrophobic resin to a hydrophilic substrate was thought to be a major factor in this regard. It became clear, however, that one of the most significant factors which limits bonding, in the absence of any form of dentine pre-treatment, is the presence of the dentine smear layer. This layer, which is 3–15 μm thick, prevents interaction of the adhesive with the bulk dentine and this prevents the formation of any effective or durable bond. Any bond which is formed is to the surface of the smear layer itself and since this may not be strongly bound to the underlying dentine the bond strength and sealing ability are compromised. The smear layer (Fig. 23.12) is formed by the process

of cavity preparation and extends over the whole prepared surface of the dentine and into the dentinal tubules (smear plug). It is a loosely bound layer of cutting debris including dentine chips, micro-organisms, salivary protein and collagen from the dentine. A smear layer is present on the surface of freshly cut dentine irrespective of the method of mechanical tooth preparation.

It is now recognized that in order to form an effective bond and seal between a restorative resin and dentine the smear layer must be removed, disturbed or modified in some way which allows access to the underlying bulk dentine. The liquids used for dentine pre-treatments prior to bonding are called *conditioners*. They are generally acid solutions which are capable of dissolving or at least *solubilizing* the smear layer, exposing the underlying dentine to the bonding agent. Many acidic solutions have been employed as conditioners. Some of the more common agents are listed in Table 23.2.

It is advantageous if the acid used for dentine conditioning can also be used for acid-etching enamel and there is a growing trend now for manufacturers to supply a single agent for both purposes. Since 37% phosphoric acid has a proven

track record as an enamel etchant its popularity as a dentine conditioner is increasing. In many ways, dental research has come full circle in accepting acidic dentine conditioning using strong etchants as part of a normal treatment regime. There is mounting evidence that etching can be tolerated, without adverse effects, even in the deepest dentine and the use of cavity liners under resin-based restorative materials is declining. A prerequisite to the tolerance of acidic dentine conditioning is the ability to form a strong bond with an adequate seal at the end of the treatment.

The option for removing or just disturbing the smear layer depends on whether the manufacturer recommends rinsing after the conditioning stage. A rinse at this stage is likely to remove the smear layer completely, leaving a relatively smooth dentine surface with patent dentinal tubules (Fig. 23.13). When there is no rinsing stage after conditioning the smear layer becomes re-deposited on the dentine surface. The latter approach is used when manufacturers attempt to reduce the number of steps required to form a bond. The conditioning stage can be viewed as the first of three stages – the other two being priming and bonding. Many manufacturers now try to combine at least two of the three stages.

23.6 Priming and bonding

Having conditioned the dentine in order to remove or modify the smear layer, the next stage is the priming stage. This is a key stage in the procedure as it is designed to change the chemical nature of
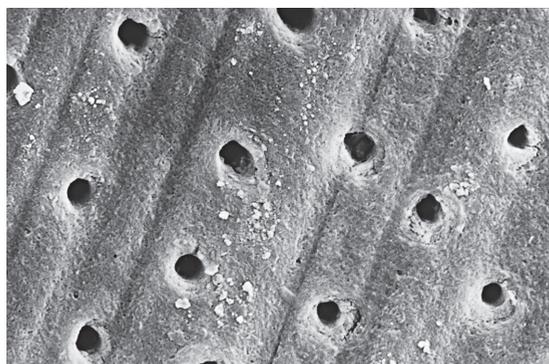
Fig. 23.13   Surface of dentine after conditioning with 37% phosphoric acid followed by rinsing. The smear layer is removed, the dentinal tubules opened and the intertubular dentine partially decalcified (×1690).

the dentine surface and to overcome the normal repulsion between the hydrophilic dentine and the hydrophobic resin. The priming agents are similar in nature to the di-functional chemical coupling agents described in Section 23.4. Their nature is described in general terms in Fig. 23.6. They are difunctional materials with a methacrylate group (having affinity for the resin) and another reactive group having affinity for the dentine. This other reactive group may be an amino group, a phosphate group or a 4-META group as described in Section 23.4. However, the most commonly used primer is hydroxyethylmethacrylate (HEMA) in which the R–X group in Fig. 23.7 is simply a C_2H_4OH group. It is the hydrophilic nature of the hydroxyl group which makes HEMA such an effective priming agent. Much more emphasis is now placed on the affinity between the reactive groups and the dentine and less emphasis is placed on the ability to form a chemical bond with components of dentine, although this is still recognized as being a possibility with some materials. After priming, the nature of the dentine surface is significantly changed – it being more hydrophobic and ready to accept the resin-based bonding agent.

The bonding agent is normally a fluid resin similar in composition to the products described for enamel bonding (Section 23.2). The fluid resin is able to flow over and *wet* the primed surface to complete the formation of an effective bond. Curing of the bonding agent is activated by light for single component materials or chemically for two component materials.

The achievement of a satisfactory bond to dentine through three stages of conditioning, priming and bonding enables us to appreciate the complex nature of some bonding systems (Fig. 23.14).

Manufacturers have responded to the needs of clinicians by trying to simplify the application procedures for conditioners, primers and bonding agents and by combining these procedures into one in some cases (Figs 23.15, 23.16 and 23.17). Hence, the primer is sometimes incorporated with the conditioner and following the combined conditioning/priming the smear layer is incorporated within the primer which now has direct contact with the bulk dentine surface. Alternatively, the primer may be incorporated with the bonding resin and the combined liquid applied to the conditioned and rinsed dentine surface. A previously

Fig. 23.14   This pack of a dentine bonding agent contains all the ingredients required to bring about bonding between restorative materials such as composites and tooth substance. The different components essentially enable acid etching or conditioning, priming and finally bonding to be achieved. Multiple stages are often required and the systems may be highly complex.

Fig. 23.16   An alternative approach to achieving bonding to dentine is the so-called self-etching primer approach. In this sort of material one bottle contains an acidic primer which can act as both an etching agent and a priming agent, hence the term self-etching primer. The other bottle contains a resin in order to bring about completion of the bond.

Fig. 23.15   A simplified approach to bonding can be achieved by combining together the priming and bonding agent into one container and hence in this case only two bottles of liquid are required. The bottle on the left contains acid in the form of a gel which is used for etching or conditioning. The dark bottle on the right contains a mixture of resin and priming agent which is applied after etching and drying.
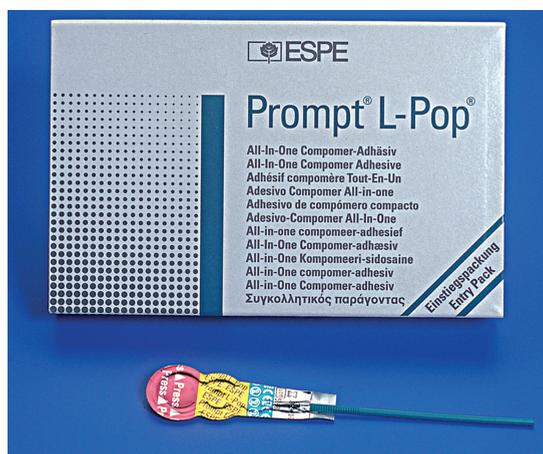
Fig. 23.17   In an attempt to help the dentist, some manufacturers have tried to simplify the approach to bonding as much as possible and here we see a device in which the manufacturers have combined together all the necessary ingredients for bonding and the conditioner, primer and the resin all into the one device. Mixing is carried out in the device prior to application with the applicator.

unmentioned component of the priming agent is the solvent carrier. The role of this solvent becomes evident when the overall concept of bonding is considered.

23.7 Current concepts in dentine bonding – the hybrid layer

In Sections 23.5 and 23.6 the importance of dentine conditioning and priming has been stressed. Modern dentine bonding systems are able to produce bond strength values equivalent to or greater than the value obtained in bonding resins to acid-etched enamel. An indication of the tenacious nature of the bond which can be achieved is obtained from the mode of failure during bond testing. This is often cohesive in nature – either within the adhesive or within the dentine. Table 23.1 gives an indication of the bond strength values which can be achieved with some systems. Values of this magnitude suggest that the mechanism of bonding must involve something other than weak interfacial bonding caused by good wetting and close adaptation.

Painstaking work in Japan and the USA has gone some way towards explaining the mechanism of bonding of most modern materials and the reason why high bond strength values are achieved. It is now believed that efficient dentine conditioning not only involves removal of the smear layer and smear plug but also causes a significant decalcification of inter-tubular dentine to a depth of a few microns. The decalcification process leaves a three-dimensional collagenous network which can be infiltrated by primer and resin to form a *resin infiltrated/reinforced layer* or *hybrid layer* at the interface between the bulk dentine and the resin. This hybrid layer is illustrated in Fig. 23.18 and can be considered to have a composite structure of two continuous phases, the resin phase and the fibrous collagenous phase, which when the resin is polymerised, strongly binds the resin and dentine together. In Fig. 23.18 it can be seen that the resin also penetrates the dentinal tubules and this is likely to contribute to the overall efficacy of the bond.

The ability of primers and resins (or mixtures of the two) to penetrate the demineralized dentine surface is the key to the formation of the hybrid layer.
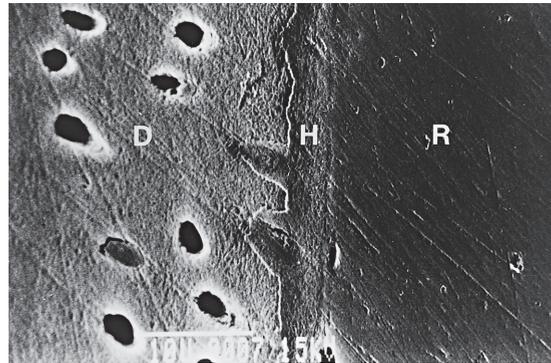
Fig. 23.18   Interface of conditioned, primed dentine and resin bonding agent illustrating the presence of the resin reinforced or hybrid layer. (Kindly supplied by Professor N. Nakabayashi. Originally published in *Oper. Dent*. Suppl. 5, 197 (1992), reproduced with permission from the editor.) In this case bonding was achieved using a 4-META system (×1472).

Two different approaches have been developed to achieve hybrid layer formation: the *total-etch* method and the *self-etching primer* method.

Total etch method

This method involves application of a strong acid (commonly 37% phosphoric acid) followed by rinsing with water in order to completely remove the smear layer and demineralize the surface of the bulk dentine. Following demineralization the collagenous network is supported only by moisture and any attempt to rigorously dry the dentine at this stage will lead to the collapse of collagen fibres and impair the formation of a hybrid layer. Most manufacturers now recommend that dentine is maintained in a moist state immediately prior to application of the primer in order to prevent collapse of the demineralized collagenous network. This represents a strange turn of events for dentists who had previously believed dryness to be critical when bonding to both enamel and dentine. Published results for many products confirm that the bond strength to moist dentine is often greater than that to dry dentine. The ability of primer solutions to wet and penetrate moist dentine is a function of the hydrophilic group in the primer molecule and the presence of a solvent such as acetone. This type of solvent is able to 'chase' away the water in the porous dentine surface, allowing the spaces to be filled by primer and

resin. Before curing of the resin the solvent is lost by evaporation. Another approach to wetting and penetration is to use aqueous primer solutions in which infiltration of primer is achieved by diffusion.

One advantage of the total etch method is that conventional and effective etching of enamel with phosphoric acid can be performed at the same time as conditioning of the dentine.

Self-etching primer method

This method involves application of a solution containing an acidic primer which can solubilize the smear layer and at the same time perform the functions of a difunctional primer. The application of the self-etching primer is not followed by rinsing as this would remove the primer and interfere with bond formation. Primers are similar in nature to certain chemicals described earlier (e.g., Fig. 23.11). Following the application of the self-etching primer the bonding resin is applied and polymerised. In some materials the manufacturers have combined the bonding resin with acidic primer to form single component systems which are designed to appeal to dentists through their simplicity of approach. Hence, the -OH group in figure 23.11(a) is highly acidic and able to condition dentine and also function as a primer. One potential advantage of the self-etching primer systems is that there is no stage in the proceedings when there are open dentinal tubules exposed and no danger of over drying following a rinse stage (as required for the total etch system). On the other hand one potential problem is that the self-etching systems may not be as effective at etching enamel as phosphoric acid. Some manufacturers provide a solution of phosphoric acid for the purposes of enamel etching during bonding procedures with self-etching primer systems but this rather defeats the object.

23.8 Classification of dentine bonding systems

In an attempt to help the dentist, manufacturers and researchers have used various descriptive terms to describe bonding systems. Of these the system of 'generations' of dentine bonding agents has been very widely employed and has led to frequent races amongst manufacturers to produce the 'next generation'. Implied within this method of classification is the message that new developments lead inevitably to improvements and that the nth generation is automatically an improvement upon the n-1th generation. Inspection of materials which represent the various generations reveal two surprising findings. First, new generations are often claimed for very small developments and modifications. Second, there is a tendency for the generation scale to follow a somewhat circular route, as even a cursory inspection shows that a recently developed generation bears a striking resemblance to a much earlier one. Other curious methods of classification involve reference to the number of steps used in the application or the number of bottles in the kit. There is an implication that fewer steps and fewer bottles represents progress of some sort. Nevertheless, closer inspection often reveals that all is not as simple as may first appear. For example, multiple applications from a single bottle may be applied. The main limitation of all these methods of classification is that there is no direct reference to the mechanism of bonding and the principles involved. On the other hand descriptions such as 'self-etching primer' and 'total-etch' are helpful as they do refer to the mechanism of bonding which is employed.

The mechanism of bonding which involves the formation of the hybrid layer produces some impressive values of bond strength. Most bond failures above 20 MPa occur through fracture within dentine (cohesive failure).

Reported values of shear bond strength to dentine in the range 15 to 30 MPa are not uncommon and this illustrates the marked improvement in bond strength which has followed the improvement in the understanding of the structure of the resin–dentine interface. The thickness of the hybrid layer is not considered an important factor which controls bonding. In most cases the layer is thought to be 2–10 μm thick and the important feature as far as bonding is concerned is that the demineralised dentine is completely infiltrated to give close adaptation of the resin to the irregular surface of the bulk dentine.

Values of bond strengths can only be used as a rough guide to bond quality, as the value is likely to vary markedly within a population of specimens. The values quoted are normally mean values and this may disguise the fact that there is a reasonable probability of finding a proportion of weak bonds which account for some clinical failures. Weaker bonds within a population may be

related to the technique sensitivity associated with the use of some of these materials.

It is not known what value of bond strength is required in order to prevent debonding during the setting of a composite restorative. The stress set up caused by shrinkage during setting is a function of cavity shape and size as well as the nature of the material, as described in Section 22.5. One method adopted by some manufacturers to prevent the disruption of bonding resins by polymerisation shrinkage of composites is to incorporate elastomeric resins into the bonding material. These may allow the bonded layer to deform elastically without destroying the bond. Another approach is to advise the application of multiple layers of bonding resin in order to create a more flexible buffer layer between the tooth and the composite. Since dentists demand the availability of bonding systems which can be used simultaneously with both dentine and enamel the products described in this section have become widely used as enamel bonding agents. The mechanism of bonding to enamel is essentially similar to that for conventional enamel bonding systems (Section 23.2). Application of the conditioning (or etching) agent results in the familiar change in the surface of the enamel (Fig. 23.1). This is then impregnated by the primer and bonding resin. The developments in dentine primers, which are now also used for enamel bonding, have led to the emphasis on enamel dryness becoming less of an issue with these modern systems. Also, there is evidence that an enamel–resin hybrid layer analogous to the dentine hybrid layer can form during enamel bonding. Figure 23.19 shows the interface of a resin–enamel bond after partial removal of enamel with hydrochloric acid. The area at the interface where resin had impregnated the porous enamel surface is clearly visible.

23.9 Bonding to alloys, amalgam and ceramics

In the previous sections, emphasis has been placed on the use of enamel and dentine bonding agents used to improve bonding to tooth substance during the placement of direct composite restorations. In Section 23.3 reference was made to the fact that composite type materials are used for bonding of orthodontic brackets and resin-retained bridges. In these situations the bond between the composite and metal may rely upon mechanical
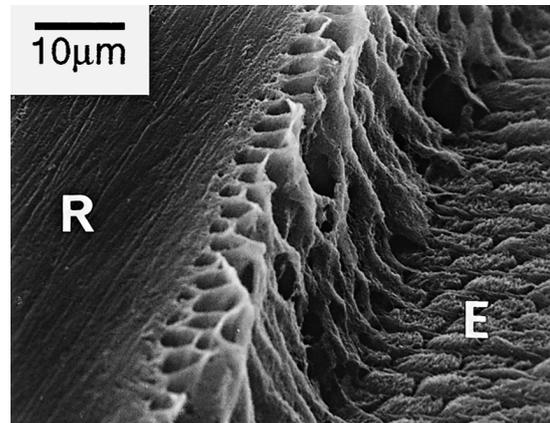
Fig. 23.19 The interface of a resin–enamel bond (mediated by a 4-META primer) after partial removal of enamel with hydrochloric acid. (Kindly supplied by Professor N. Nakabayashi. First published in *Dent. Mat.* **8**, 175 (1992), reproduced with permission from the editor (×1000).

retention, either by building in retention into the design of the metal structure (e.g. the base of the orthodontic bracket) or by creating a retentive surface through electrolytic etching or abrasion. For these and other applications where a strong durable bond is required in the absence of any natural retentive forces a resin-based luting agent may be preferred to a conventional cement. The ability of the resin to achieve a chemical union with the alloy may improve retention whilst at the same time reducing the amount of preparative work required to be performed on the alloy.

Virtually all the bonding agents described in the previous section can be used to achieve bonding with a variety of alloys – normally in conjunction with a low viscosity composite luting cement. Some specialist resin-based adhesive luting cements have become widely used over recent years. One such system, originally supplied as a powder and liquid, was essentially a self-curing composite in which the powder was primarily a quartz filler along with some initiator and the liquid consisted of a mixture of dimethacrylate monomers and a methacrylate–phosphate coupling agent along with a small amount of a chemical activator. The mixed material combined adhesive characteristics with an ideal consistency for luting purposes. A material of similar composition is now available in two-paste form (Fig. 23.5). One feature of this particular type of resin-based cement was a

marked sensitivity of the polymerisation reaction to the presence of oxygen. In order to enable the material to set properly oxygen must be excluded from the exposed surface of the cement. This is achieved by the application of a gel-type barrier which can be washed away after setting (see also section 23.11).

Another powder–liquid type luting cement in common use is based upon the 4-META system referred to in the previous section (Fig. 23.10). The powder contains polymethylmethacrylate (PMMA) whilst the liquid contains a mixture of methylmethacrylate monomer (MMA), 4-META and tri-butylborane (TBB). The TBB liberates free radicals on contact with moisture (e.g. on the tooth surface) and causes polymerisation of the MMA (see also section 23.11).

The nature of the metal surface required for bonding has received some attention – particularly with regard to crown and bridge alloys. Bonding of most materials to base metal alloys appears to be quite straightforward with bond strengths in excess of 20 MPA being normal. The naturally formed oxide layer on the alloy surface is thought to be involved in the bonding process and the only preparation required is a moderate roughening using sand blasting followed by steam cleaning. Bonding to precious alloys can be more difficult, Tin plating is recommended for some products in order to generate an oxide layer. It is not clear whether this treatment aids bonding by producing a surface suitable for chemical bonding or through the formation of a roughened surface coated with tin oxide crystals. For other alloy/adhesive systems heating of the alloy to 400°C in air for 10 minutes generates a copper oxide layer on the metal surface, whilst other products claim to bond adequately to a sand blasted alloy surface.

Much of the work in this area relates to luting adhesive bridgework and a wide variety of techniques have been described for roughening the surface to produce either macro or micro mechanical irregularities on the fitting surface of the metal. One problem with relatively large irregularities is that they will necessitate the metal to be relatively thick to allow for the porous surface and then to have adequate strength. In addition they were mainly produced by some sort of loss of wax casting technique and were technically sensitive as a consequence. The most effective means of preparing metal surfaces for conventional composite resin lutes is to etch the metal surface producing a micro porous surface analogous to etched enamel (the *Maryland* technique). This can only be achieved using non-precious metal casting alloys and relies on preferential destruction of metals at the grain boundaries within the alloy. Precise techniques are specific to the composition of the alloy concerned, but all rely on an electrolytic process under carefully controlled conditions in a highly acidic environment. The effectiveness of the process depends on a combination of the correct blend of acids and use of the correct current density for a specific metal alloy. As a consequence it is once again highly technique sensitive.

One final approach that has been developed depends on preparing the surface of the material with a specialized form of blasting sand. In this tribomechanical approach, silica coated corundum particles with a mean particle size of 30-μm are blasted against the surface to be bonded. The impacts of the corundum particles on the surface produce some roughening of the surface and also transfer of the silica from the surface of the corundum to the substrate. This *silicatized* surface can then be treated with a silane coupling agent before bonding with a conventional resin composite. This technique (Cojet®) can be used for all surfaces from composite resin through ceramics to metals.

Bonding of base metal alloys opened up the possibility of achieving union between dental amalgam and tooth substance. One specialist product based on 4-META and several of the materials referred to in Section 23.5 are now advocated by the manufacturers for this purpose. This has led to the *bonded amalgam* restoration. The potential advantages are that the cavity does not need to be so retentive and that the adhesive provides a means of reducing leakage. Other applications of these systems are in amalgam repairs (bonding amalgam to amalgam) and in amalgam core build-up (bonding amalgam to dentine).

Systems which bond to ceramics can be used to bond ceramic inlays, onlays, veneers and ceramic orthodontic brackets. The surface to be bonded may be initially prepared using a diamond bur, sand blasting or etching with hydrofluoric acid. The latter is an extremely caustic substance so the etching procedure is often performed in the laboratory rather than in the clinic. The priming agent comprises a solution of a silane–methacrylate coupling agent such as γ-methacryloxypropyltrimethoxysilane (as described in Section 22.3) in a

volatile solvent such as acetone. The solution is applied to the surface of the ceramic material and air drying rapidly removes the solvent to leave a layer of bound silane coupling agent. Very high values of bond strength (>20 MPa) to ceramic can be achieved using composite luting cements. In orthodontics concern has been expressed that ceramic brackets are bonded to enamel so strongly that debonding can result in fracture through the ceramic or, more seriously, fracture through the tooth. There is a suggestion that silane coupling becomes less effective with time as the silane may be subjected to hydrolysis (see also section 23.11).

Bonding in orthodontics

Bonding systems used to attach orthodontic brackets to teeth have distinctive requirements, which have led to the development of products used specifically for this purpose. During the bonding of brackets the adhesive is applied to the bracket base which is then located in the correct position on the tooth. The adhesive must possess ideal rheological properties which allow the positioning of the bracket on the tooth surface to
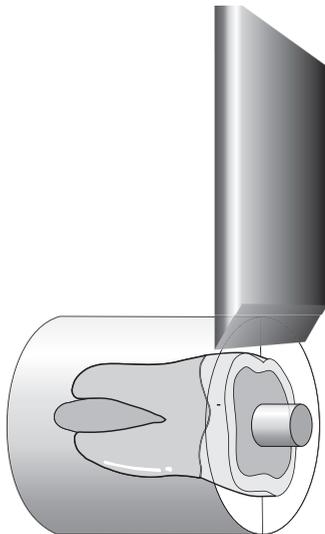
Fig. 23.20   Diagram illustrating the principle of a shear bond strength test. The tooth has been embedded in resin and ground to expose dentine. The adhesive and associated material has been bonded and is being sheared off using a test instrument. Measurement of the force to shear enables bond strength to be determined.

which the bracket is to be bonded, by 'sliding', but must then retain the positioned bracket without sliding until the adhesive is set. Furthermore, the adhesive must retain the bonded bracket in position throughout the course of orthodontic treatment but must allow the bracket to be removed at the end of the treatment without damaging the tooth enamel. It is advantageous if little or no adhesive is retained on the tooth surface after de-bonding as this may be difficult and time consuming to polish away and may discolour. Traditionally, two-paste, chemically activated or single-paste, light activated composites similar to those described in Chapter 22 have been used in which adhesion to enamel is achieved through bonding to acid-etched enamel, whilst bonding to stainless steel brackets is through mechanical engagement in undercuts created by a mesh on the bracket base. The required rheological properties are achieved through adjustment of the filler particle size and content. Contact adhesives have also been widely used in orthodontics. These materials consist of paste and liquid components. The composite paste is heavily loaded with initiator and the liquid contains dimethacrylate monomers and is heavily loaded with activators (see Chapter 12). The paste component is applied to the bracket base whilst the liquid component is applied to the etched tooth surface. Polymerisation is activated when the bracket is applied to the tooth and the initiator and activator are brought into contact.

A number of alternative materials are now available for orthodontic bonding including some which are based upon hybrids of glass ionomers and composites such as resin-modified glass ionomers and compomers. A potential advantage of materials having some glass-ionomer characteristic is that they may offer some protection to the teeth during orthodontic treatment by means of fluoride release. These issues will be discussed further in Chapters 24 and 25.

23.10 Bond strength and leakage measurements

It is recognized that the most meaningful test of a new adhesive system involves long-term clinical use as part of a formal clinical trial or as part of a prospective or retrospective audit procedure. *In vitro* testing of adhesives can be used as a means of ensuring that only relatively promising materials are subjected to clinical testing. The two

methods most widely used for assessing adhesives in the laboratory are bond strength and leakage. Bond strength testing involves the measurement of tensile or shear bond strength (the latter has been quoted in Table 23.1). These tests produce results which are notoriously variable, particularly for natural substrates such as enamel and dentine. Variations in the value of bond strength may result partly from imperfections in the testing equipment (e.g. imperfect alignment in a tensile bond test rig) or from variations in the substrate material. For example, bond strength to dentine varies with the type of tooth, age of patient, depth of dentine, time of storage after extraction, nature of the storage medium, etc. These variations can be dealt with in one of two ways – either by controlling the distribution of variables between test groups or by using teeth at random but using sufficiently large numbers of test specimens which will make biased distributions unlikely. The International Standards Organization has recognized these problems in its technical report on testing adhesion to tooth substance (ISO TR 11405). This report makes recommendations as to the nature of the teeth to be used in testing and to the method of storage, the method of forming and testing the bond. Even when the guidelines are followed a coefficient of variation of 50% is not unusual and this can cast some doubt over the reliability of some of the systems. The results of these tests suggest that there is always a reasonable probability of getting an unusually low value of bond strength and these examples when translated into clinical practice may account for some of the observed failures with otherwise 'good' materials.

In addition to the value of bond strength the mode of bond failure is normally quoted and this is often considered a more important parameter. The mode of failure may be adhesive, i.e. occurring at the adhesive/substrate interface, cohesive, i.e. occurring entirely within the substrate or adhesive or mixed, i.e. occurring partly at the interface and partly cohesively. A value of bond strength without any indication of the mode of failure is almost meaningless. Recently techniques have been developed to simulate dentine tubular fluid flow perfusion during bond strength testing. The surface of dentine that has been etched will be wet as a result of tubular fluid flow and it is important to simulate this if possible.

As the development of new adhesives has accelerated, particular emphasis has been placed upon the comparative values of bond strength to different substrates and this in turn has produced greater scrutiny of the tests themselves. Problems which have been highlighted include:

(1) Questions over the value of bond strength testing using specimens produced in a non-clinical environment.
(2) Questions arising out of the wide variability of test results and the lack of agreement between results from different test centres.
(3) Questions over the values of bond strength arising from studies in which many fractures occur by cohesive failure.
(4) Difficulties in obtaining sufficient numbers of suitable test teeth to be used as substrates for bond strength testing.

In order to address some of these issues, new tests have been developed and of these the micro-tensile test has achieved the greatest level of acceptance. This involves bonding a restorative material to an extracted tooth using an adhesive, to form a monolithic block which is then sectioned by cutting into 'sticks' or 'slabs' enabling multiple specimens to be prepared from one test tooth. The sticks or slabs are then bonded to two adjacent metal platens using a cyanoacrylate cement so that when the platens are driven apart the bond is broken and the bond strength can be measured. (Fig 23.21) The nature of the test is such that fracture at the tooth–adhesive interface is encouraged (adhesive failure). Values of bond strength
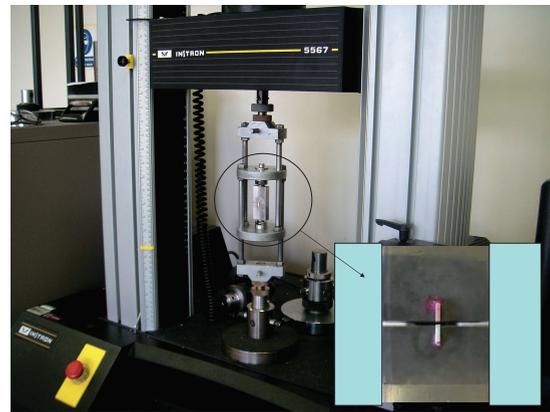
Fig. 23.21   Stick specimen for microtensile bond strength testing in which half the stick is tooth substance and half is composite filling material.

tend to be greater than those measured using more conventional methods.

Problems with the test can be a concern over stress development during sectioning of specimens which can lead to premature failures and uncertainties over the interpretation of results since several test specimens may be derived from a relatively small number of teeth.

Leakage studies are designed to give an indication of the ability of a material to form an effective seal against fluids and bacteria at the tooth/adhesive interface. Tests are normally performed by placing restorations in restored teeth and then subjecting them to storage, normally with an element of thermal cycling, in a solution of dyestuff or other marker (e.g. radioisotope). At the end of the prescribed period of testing the restoration and tooth are sectioned and the effectiveness of the seal is judged by how far the dye (or other marker) has penetrated down the margin towards the cavity floor. Guidelines for leakage testing are also included in ISO TR 11405.

23.11 Polymerizable luting agents

Resin-based luting agents are being used increasingly in association with adhesive dentine bonding agents to enhance the retention of prostheses to tooth tissue. These lutes tend to be chemically setting unless they are being used with porcelain veneers, as light penetration through either all ceramic crowns or ceramic or resin inlays is poor and for obvious reasons light activated materials cannot be used with metallic restorations. They can be used for all forms of restoration but to achieve maximum benefits there must be mechanisms for attachment between the fitting surface of the restoration and the surface of the preparation on the tooth. The latter is relatively straightforward when the preparation is wholly on tooth tissue (either dentine or enamel) when contemporary dentine bonding agents can be used. The lightly-filled diacrylate resin luting agents must be used with total-etch dentine bonding agents rather than self-etching systems. The residual acidity of the latter interferes with the polymerisation of chemically curing resin systems. However when the surface of the 'tooth' preparation is predominantly on some form of core material there are greater problems achieving a bond between a resin lute and the surface of the prepared tooth. Amalgam is difficult to bond to with anything

other than the chemically active lute. A gold post and core is even more difficult in terms of adhesion, whereas a composite resin is more receptive to bonding with a resin lute. However all of the difficulties that are discussed in Section 22.7 concerning bonding between 'old' prepared composite and newly polymerised resin remain.

Polymerisable lutes are available based on both composite resins and resin-modified glass ionomer cement (RMGIC) technology (see Chapter 25). Obviously the latter offer the theoretical benefit of fluoride release at the margin but there is no clinical evidence to substantiate any benefit for their use. The RMGIC lutes tend to be used with relatively retentive tooth preparations unlike the composite-based materials which are now often used to attach onlays and overlays with minimal if any retentive capacity, as well as ceramic veneers, all ceramic crowns and adhesive bridgework.

The composite based lutes come in two forms; those that are essentially dilute or lightly filled composite resins and those that have some form of intrinsic adhesive capacity due to the resin molecules in the lute itself (see also section 23.9). The technology required to retain restorations with these differing materials is separate and distinct.

Lightly-filled diacrylate resins

These materials can be regarded as lightly filled composite resins with both low filler loading and small particle size fillers to facilitate the formation of thin films of lute. They are available in both chemical and light initiated versions, but the most common form are so-called 'dual-cure' materials. These products can either be activated by light alone or when the light-activated paste is mixed with a second paste containing a chemical catalyst where there is a dual cure mechanism. This approach is intended to give the benefits of command set at the periphery of translucent restorations (for example a porcelain veneer) whilst ensuring that some degree of cure occurs when a translucent restoration is sufficiently thick that it attenuates the light from a curing source sufficiently to prevent light initiated activation of the setting reaction. This approach is necessary, for example, when luting a ceramic or composite resin inlay or onlay, when either the thickness of the inlay/onlay is sufficiently great or there may be shadowing effects from the residual tooth

structure or from adjacent teeth to prevent effective light activation. Such resins have a limited ability to form adhesive bonds to restorations.

Attachment strengths to prefabricated composite resin structures (for example a composite resin inlay, see section 22.8) are surprisingly low. This has been attributed to the relatively high conversion rate that can be achieved in resin materials in a laboratory setting where curing can be undertaken either at increased temperature or under pressure, or both.

They have no intrinsic capacity to bond to ceramics. The fitting surface of the ceramic has to be roughened, usually by etching with hydrofluoric acid and then coated with a silane coupling agent before an adequate bond strength can be achieved. There is some controversy in the literature whether the silane is best applied in the production laboratory or at the chairside. In practical terms it is easiest to apply the silane at the chairside having ensured that the ceramic restoration has an appropriate quality of fit to the underlying prepared tooth. This approach can only be used when the fitting surface of the ceramic is susceptible to etching with hydrofluoric acid. Some of the high strength ceramics used for crowns cannot

be treated in this way, particularly the glass infused material InCeram® (section 11.6).

These resins have no intrinsic capacity to bond to metals, but once again a coupling agent can be used or the metal surface roughened in some way to provide mechanical interlocking of the resin to metal (see also section 23.9).

Chemically active resins (see also section 23.9)

Chemically active resin lutes contain organic groups which have intrinsic adhesive activity. This chemical activity principally works with metal substrates and application of some form of ceramic primer is required for use with porcelain. There are two types of chemically active materials:

(1) *Phosphorylated materials:* (see Fig. 23.5 and Fig. 23.11) these materials contain phosphorylated resins, for example phenyl P (2-methacryloxyethyl phenyl hydrogen phosphate) and MDP (10-methacryloxydecyl dihydrogen phosphate), which are intrinsically acidic and have the potential to provide some chemical interaction with both tooth substance and with metal surfaces, particularly those

(b)

(a)

(c)
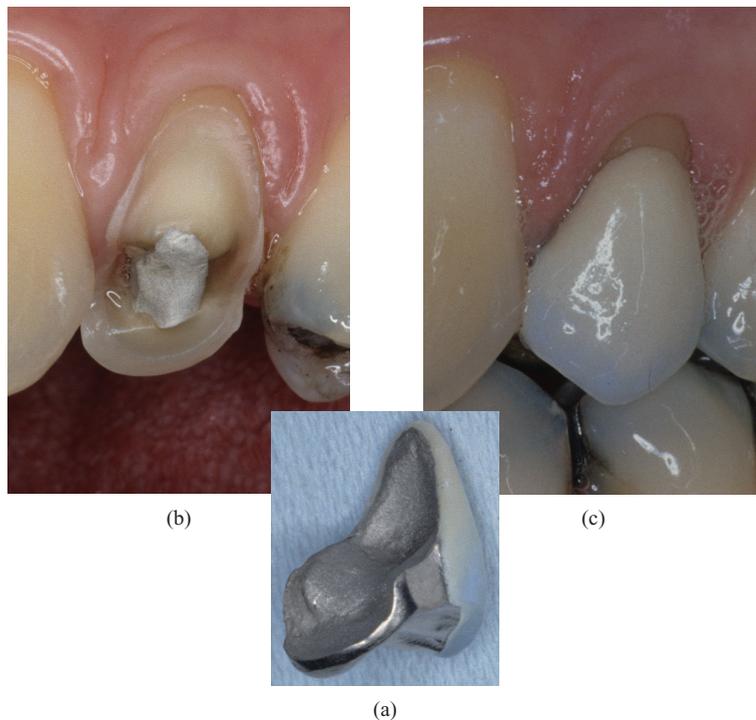
Fig. 23.22   Adhesive techniques for the management of fractured and worn teeth. A metal ceramic addition (a) bonded to a non-retentive cavity (b) using an adhesive luting agent to restore the tooth (c). From Walls, A.W.G. (2001) in *Advances in Operative Dentistry*, eds Roulet, J.-F., Wilson, N.H.F. & Fuzzi, M., pp. 229–239. Quintessence Publishing.

with a stable oxide layer on the surface (for example stainless steel and non-precious metal casting alloys). Bonding to metals may be enhanced by roughening the surface by sandblasting and by applying proprietary priming agents. The Panavia range of materials is particularly susceptible to oxygen inhibition and is provided with a gel barrier to facilitate full curing of the material. These materials are available as chemical set alone or in dual cured forms and some also require the use of a dentine bonding system to optimize attachment to tooth tissue. However they also have some activity as self-etching primers to enamel and dentine.

(2) *4-META products:* The resin 4-methacryloloxyethyl trimellitate anhydride (4-META) also exhibits chemical reactivity with tooth and with metal oxide layers. Its incorporation into a resin lute again facilitates bonding but there are some concerns about the chemical reactivity of this agent (see Fig. 23.10).

It is undoubted that these resin lutes can result in substantial bonds being developed between the lute and both tooth surface and a restoration being bonded in place. Their development has allowed a new era of restorative dentistry where mechanical retention is not necessarily a pre-requisite for long-term success (Fig. 23.22) and conservation of tooth tissue becomes the overriding feature of preparation design and clinical practice. They are not however a panacea for all problems.

There must be surfaces that can be bonded on both the 'tooth' and the crown/restoration and it must be possible to achieve an adequate standard of moisture control for adhesively retained restorations to be a predictable part of clinical care. Contamination of an etched tooth surface with saliva or crevicular fluid will prevent bond formation and facilitate marginal leakage as a consequence. Furthermore they are methacrylate-based products and undergo substantial shrinkage during setting. Whilst the lute space should be relatively small in most circumstances the C factor is very large as the only free surface is at the margin of the restoration. This may not be a problem for extra-coronal restorations and those with limited mechanical retention. It is however a problem with inlay type restorations where considerable strain continues to be applied in tensile mode to the remaining tooth structure.

23.12 Suggested further reading

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Jordan, R.E. (ed.) (1991) Eight articles on bonding to various substrates. *J. Esthet. Dent*. **3**, 117.

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Van Meerbeck, B. *et al*. (1998) The clinical performance of adhesives. *J. Dent*. **26**, 1.