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Review
Glass–ionomer cements as adhesives
Part II *Testing of adhesive joints*

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Although glass–ionomer cements are generally agreed to show very good adhesion to a variety of substrates encountered in clinical dentistry, laboratory testing of this property has not proved to be straightforward. In the current paper we review the published literature describing the testing of glass–ionomers as adhesives. We highlight the fact that these materials are employed under conditions of very high humidity and high moisture content that would impair the long-term bond durability of conventional adhesives. We conclude that further work is necessary to improve the understanding of the basic mechanism of adhesion in glass–ionomers and to extend the methods by which adhesion may be measured to include more-complex structures of greater clinical relevance.

1. Introduction

In Part I of this series we reviewed the literature concerning the adhesive properties of glass–ionomers [1]. The literature contains numerous reports of glass–ionomers showing good adhesion to both dentine and enamel [2, 3], and to stainless steel. Hence, in addition to their use as restorative materials, they are also widely used as adhesives in such applications as the adhesion of crowns to posts [3] and the attachment of orthodontic devices [1].

Part I of this review [1] showed that glass–ionomers are effective as adhesives for a number of reasons. These include good wetting of surfaces typically encountered in clinical dentistry, the formation of strong chemical bonds to the substrate and good mechanical properties of the cements themselves. In this paper we turn our attention to the question of testing joints that are bonded by glass–ionomers. As in Part I, the literature reviewed covers not only that which is immediately concerned with glass–ionomers, but also that which concerns the wider technology of adhesives testing.

The testing of bonded joints discussed here is confined to the destructive type, which is the prevalent mode of joint analysis that is used [4]. In selecting and using any test method it is important to identify the characteristics of both the adhesive and the substrate that form the joint [5]. This should include consideration of both the effect of pretreatment of the substrate and the influence of the service environment on adhesion. In this review the testing of adhesive joints is discussed under the following headings: the mechanical properties of the adhesive and substrates; laboratory testing of adhesive joints; *in vivo* testing of adhesives, and service environments.

2. The mechanical properties of adhesive and substrates

A number of factors affect the type and manner of failure of bonded joints. These include the stiffness of the substrate as manifested in the values of the shear modulus, G, and Young's modulus, E; Poisson's ratio of the substrate and the adhesive; the yield strength (σ_y) and yield behaviour, including analysis of elastic–plastic behaviour; the critical stress intensity factor (K_{Ic}) [6]; and the fracture energy, G_{Ic}. Several workers have determined these geometry-independent material properties of adhesives employing linear–elastic fracture mechanics (LEFM) [6–9].

The commonly encountered substrates for the adhesion of glass–ionomer cements are enamel, dentine, dental composites and stainless steel. The properties of stainless steel are well documented, in contrast to those of enamel, dentine and dental composites.

Quite often the *in vitro* testing of the adhesion of glass–ionomer cements to enamel and dentine is carried out on bovine as opposed to human teeth. Nakamichi *et al.* [10] investigated the validity of this and found that the adhesive strength to enamel showed no statistically significant difference between bovine and human teeth, although the mean values were always slightly lower with bovine teeth. Renson and Braden [11] determined the rigidity modulus, Poisson's ratio and elastic limit in shear of human dentine, and these results are presented in Table I.

The material properties presented in Table I are relevant only for adhesive joints in which the substrate is wholly dentine. However, such joints represent only a fraction of those encountered by glass–ionomers in clinical use. Others involve adhesion either to enamel

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TABLE I Mechanical properties of human dentine

Specimen	Young's modulus, E, (GN m^{-2})	Rigidity modulus, G, (GN m^{-2})	Poisson's ratio, ν
Molar (1)	11.4	4.67	0.12
Molar (2)	17.7	6.15	0.14
Molar (3)	18.1		
Premolar-root		5.93	
Molar (4)-crown	17.6	6.99	0.26
Molar (5)-crown		5.15	
Molar (6)-crown	19.3	6.55	0.15
Canine-root	17.5	7.05	0.12
Canine-root	11.1	5.54	0.0
Canine-root	15.3	7.69	− 0.025

TABLE II Factors affecting the strength of adhesive joints

1. Joint design
   Geometrical configuration, bondline thickness
2. Adherends
   Susceptibility to deterioration, linear coefficient of thermal expansion and permeability, nature of adhesive and substrate, mechanical properties
3. Adherend surface
   Surface chemistry, cleanliness, surface topography
4. Nature of primer
   Viscosity, chemical composition, mechanical properties
5. Nature of adhesive
   Viscosity, chemical composition, reactivity, mechanical properties, linear coefficient of thermal expansion, permeability
6. Bonding conditions
   Temperature of substrate, ambient temperature, humidity, working time, airborne contamination, applied pressure
7. Internal stress
   Cure shrinkage, environmental conditions
8. Service conditions
   Stress, moisture, temperature
9. Testing conditions
   Strain rate, cyclic frequency, temperature

alone or to both enamel and dentine within the same restoration.

Due to the diversity of dentine having different biological origins and to the difficulty in obtaining sufficiently large specimens, the use of either resins coated with hydroxyapatite or thin slices of dentine embedded in resin is increasing. In such systems it is the mechanical properties of the resin that need to be determined.

3. Laboratory testing of adhesive joints

In Part I of this review [1] we discussed how the physical and chemical properties of glass–ionomer cements such as wetting, chemical bonding and mechanical strength influenced the adhesive strength of joints bonded with these cements. Other factors that affect the strength of adhesive joints are listed in Table II. They highlight where more and better information is needed on the subject of adhesion in dentistry.

There are a number of different designs of test pieces for studying adhesion. The American Society for Testing and Materials (ASTM) has produced a standard that is an extremely comprehensive evaluation of adhesive testing, and some of the standard test pieces described in this document are illustrated in Fig. 1.

The history of adhesive joint testing started with the simple pull-off test [4]. In its simplest form this test employs the so-called poker chip test piece. Examples of results using these particular test pieces are abundant in the early literature of the analysis of glass–ionomer cements [3]. Results show considerable scatter and a careful consideration of the test piece reveals why. The greatest problem when using this test piece is the alignment. A very slight misalignment of the test piece in the jaws of the test apparatus will result in the nominally tensile mode of testing developing an appreciable cleavage or shear component. The extent to which a test regime departs from the purely tensile will determine the extent of the scatter.

Even with improvements in the assembly, such as the inclusion of self-aligning joint components, it is difficult to ensure purely tensile loading [12]. Hence, despite the apparent simplicity, the usefulness of tensile testing for adhesives is limited.

The single metal-to-metal lap joint loaded in tension is a test piece that has probably received the most attention from stress analysts. This test piece measures the strength of materials predominantly under shear conditions, although there is an element of peel fracture in the observed adhesive strength [13]. The widespread use of the single lap joint is a result of the ease of manufacture and assembly, and approximates to commonly occurring joint designs used in practice.

There are two basically complementary tools necessary for the evaluation of adhesive strengths of bonded joints.

1. Stress analysis, which involves detailed knowledge of the stress distribution in a bonded joint and is particularly valuable in the study of the integrity of a bonded joint and for the interpretation of the effects of

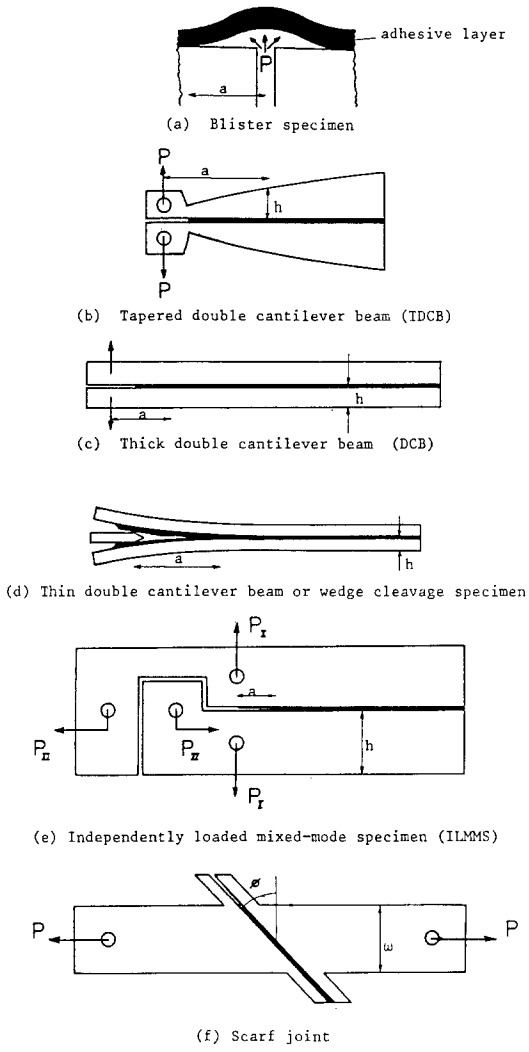

Figure 1 Standard test-pieces for adhesion testing.

geometrical parameters such as the effect of the adhesive layer thickness and substrate overlap length on the bond joint strength. Finite-element analysis is a numerical method developed specifically to deal with the real joints of irregular shapes and in non-linear joints [14].

2. Fracture mechanics, which deals with the strength of real solids and is governed by the presence of flaws in materials. Fracture mechanics has proved to be particularly useful for such aspects as characterizing the fracture toughness, G_c, or stress intensity factor, K_I, of adhesives. The most important aspect of this approach is the geometry-independence of the parameters defined above.

A recent preoccupation of both approaches is the explanation of the increase in bond strength of cements with decreasing adhesive layer thickness. Several workers who have measured the adhesive strength of glass–ionomer cements have neglected to determine the adhesive layer thickness, and this may help to explain the large scatter in the results reported for such experiments. Previous work with non-dental adhesives has shown that the bond thickness can affect the measured fracture energy, although not in any regular way [15–17].

The experimental observation that the bond strength varies inversely with the adhesive layer thickness is not readily accounted for by the early theories of stress analysis. This has prompted the use of finite-element analysis, most notably by Crocombe and co-workers [18–20]. However, they did not study glass–ionomer cements. Recently, Akinmade and Hill [21], employing linear–elastic fracture mechanics, investigated the effect of the adhesive layer thickness on the shear bond strength of glass–ionomer cements.

Matsui [22] gave the failure initiation conditions in a bonded joint as follows. Taking d as the thickness of the adhesive layer, d_m as the thickness of the adhesive layer when $d_m\,(=d)_{\alpha=1}$ and α is the stress concentration factor for interfacial failure, l as the length of the overlap in the single lap joint, τ_u is the average ultimate shear stress (USS_{av}) needed to produce failure, with τ_{ud}, τ_{ui}, τ_{us} and τ_{ut} being the USS_{av} for the failures of cohesive-in-substrate, interface, cohesive-in-adhesive and adhesive, respectively. Then:

1. Cohesive failure in the substrate occurs when $l > l_{opt}$, $d_{opt} < d < d_m$, $\tau_{ud} < \tau_{ui}$, $\tau_{ud} < \tau_{us}\tau_{ud} < \tau_{ut}$ and $\tau_u = \tau_{ud}$.
2. Interfacial failure in the bimaterial interface occurs when $l < l_{opt}$, $d < d_{opt}$, $\tau_{ui} < \tau_{ud}$, $\tau_{ui} < \tau_{us}$, $\tau_{ui} < \tau_{ut}$ and $\tau_u = \tau_{ui}$.
3. Cohesive failure in the adhesive layer occurs when $d > d_m$, $\tau_{us} < \tau_{ud}$, $\tau_{us} < \tau_{ui}\tau_{us} < \tau_{ut}$ and $\tau_u = \tau_{us}$.
4. Adhesive failure occurs when $d_{opt} > d > d_m$, $\tau_{ut} < \tau_{ud}$, $\tau_{ut} < \tau_{ui}$, $\tau_{ut} < \tau_{us}$ and $\tau_u = \tau_{ut}$.

What these four criteria of failure amount to is that fracture of a bonded joint will take place at the weakest link, with the adhesive layer thickness critically determining the stresses present in the joint.

In the case of a "thin" adhesive layer, $d < d_{opt}$, and the stress concentration factor α (interfacial failure) increases until a point when its product with the τ_{ui} becomes equal to the shear stress of the adhesive joint, τ_B. At this point the joint fractures in an interfacial mode. In the case of a "thick" adhesive layer, $d > d_m$, the adhesive is deflected by a bending moment. When the maximum bending stress in the adhesive layer equals the strength of the adhesive, cohesive failure in the adhesive results in fracture of the joint.

The above analysis is of limited use because fracture in an adhesive joint can actually take place via a combination of more than one failure mode. Also, the analysis utilizes the concept of average shear stresses. It has been established that the stresses in single lap joints are not uniform [23], and this has prompted the use of finite-element analysis to investigate the stress profit of this test piece. Crocombe [18] employed the concept of global yielding to predict the strengths of adhesive joints. This is based on the premise that adhesive failure in a joint will occur when the adhesive can no longer sustain the applied load. Using finite-element analyses on single lap joints, he was able to predict increases in bond strength with decreasing adhesive layer thickness. The main finding of his work is that thicker adhesive joints yielded completely at loads at which thinner joints still had an inner level of unyielded material capable of sustaining further load increases.

Two possible reasons were given by Crocombe for the more rapid spread of yielding in the thicker joint.

1. His analysis showed that the level of stress in a thicker joint, although lower, was spread more uniformly than in a thinner joint. Thus, when yielding did occur there was less elastic reserve to sustain further loading, hence yielding spread more quickly.
2. When yielded, the adhesive shear stress will be greatest when the direct stresses are in pure hydrostatic tension or compression. This is more likely to be the case in highly constrained thinner joints, so for such joints an increase in load can be sustained with a smaller degree of yielding because the shear stress is higher.

The approach taken by Crocombe was based on using a value of maximum adhesive strain (or stress) to estimate the point of failure in a joint. A complementary approach is to use values of maximum stresses (and hence strain) in the critical region of the adhesive joint. Such an approach was taken by Akinmade [24] using linear elastic fracture mechanics as a tool. His treatment of a glass–ionomer adhesive joint was based on the work of Williams [25], which relates the adhesive layer thickness to the plastic zone size of the cement (a material property) to predict the type of failure in a bonded joint.

Brittle fracture of bonded joint occurs when the adhesive layer thickness $> 2\sigma$ (the plastic zone diameter), and ductile fracture of the bonded joint prevails when the adhesive layer thickness $< 2\sigma$.

The brittleness or ductility of fracture of a bonded joint affects the observed adhesive strength of the joint. This is because the fracture energy of a cement is determined mainly by the energy dissipated in the formation of a plastic zone at the tip of a crack propagating in the bulk of a cement. Therefore, if the plastic zone in an adhesive in a joint is constrained by an adhesive layer thinner than the potential size of an adhesive plastic zone, the fracture energy will be reduced, and hence, so will the adhesive strength. This effect is opposed by the increase in the plastic zone size in thin adhesive layers due to the increase in the level of the out-of-plane transverse tensile stress, σ_{11} [26].

As Kinloch described [27], the combination of these two factors produces a maximum in the relationship between adhesive fracture energy and adhesive layer thickness,

$$h_{am} = 2\sigma = 1/\pi\,(k_{1c}/\sigma_y)^2$$

The plastic zone size is determined by the expression:

$$2\sigma_p = 1/\pi(K_{1c}/\sigma_y)^2$$

where K_{1c} is the critical stress intensity factor.

With this approach Akinmade and Hill [21] were able to show that the shear bond strength of the glass–ionomer cements was not affected by the thickness of the adhesive layer due to the very small ($< 12\,\mu m$) plastic zone size of these cements. On the other hand, the zinc polycarboxylate cements with significantly large plastic zone sizes showed a great dependence of adhesive layer thickness on shear bond strength.

As mentioned earlier, finite element analysis is particularly useful for irregularly shaped joints. These are the most relevant to real service life joints since such joints are invariably of irregular shape.

One application of finite element analysis was performed by Hickman *et al.* [28] on a minimal class II cavity in a premolar restored with a composite resin. The main aim of the work was the determination of internal stresses arising as a result of polymerization shrinkage of the composite resin. The actual adhesive joint included enamel, dentine, a glass-ionomer liner and a composite resin, while the formation of a progressively larger crack in the system represented failure of dentine bonding. Hickman *et al.* [28] concluded that the deformation occuring in the dentine may explain the high incidence of post-operative sensitivity observed following the placement of direct composite restorations. This has a bearing on the development of a toughened glass-ionomer cement, with high K_{1c}, for the posterior teeth since glass-ionomer cements exhibit no polymerization shrinkage [3].

4. *In vivo* testing of adhesives

Although much information can be obtained from laboratory tests there is still no substitute for *in vivo* (clinical) studies of the efficacy of the bond integrity in service life. Such an analysis has recently been carried out by Welbury *et al.* [29]. They undertook a five-year clinical trial to compare a commercial glass-ionomer with an amalgam in deciduous tooth restorations. In all, 119 restorations were placed in a total of 76 patients between 1982 and 1987 in Class I and Class II cavities.

The performance of these two types of material was assessed for anatomical form, marginal integrity and the presence or otherwise of recurrent caries. Welbury *et al.* [29] came to the conclusion that the amalgam was more durable in terms of all three parameters when placed in a conventional cavity. However, they highlighted the fact that glass–ionomers had a median survival time of about 39 months for cements placed in a relatively atraumatic fashion and with less cavity preparation. This was perhaps the reason for their commercial success in specialized applications in restorative dentistry.

It is instructive to probe the criteria Welbury *et al.* [29] employed in evaluating the performance of restorative marginal integrity and anatomical form. These phenomena in restorative materials are well recognized and the British Standards Institution (BSI) guidelines for testing adhesion of dental materials to tooth substrate includes test methods for microleakage (marginal integrity) and gap formation (anatomical form). The possible causes of microleakage in dental restorations are: stresses in the cement as a result of polymerization shrinkage [30]; attack of the interface between the tooth substrate and the cement by oral fluids; the mismatch of the coefficients of thermal expansion between the joint components; diffusion of water through the cement itself; adhesion to

cavity walls, i.e. dissimilar adhesive strengths exhibited to substrates in contact with an adhesive; and flexibility of the cavity walls [31, 32].

Glass–ionomers owe some of their success to the fact that, for two of these, i.e. absence of polymerization shrinkage and very similar coefficient of thermal expansion to dentine and enamel, their properties are excellent. That such properties are specified in standards, with maximum stipulated values linked to the use of these materials in various applications, is significant. It marks the coming of age of these materials in terms of our understanding of their performance characteristics.

5. Service environment

Where possible it is desirable that test conditions should simulate the service environment as closely as possible. For glass–ionomer cements the service environment contains oral fluids, which consist largely of water, but with a variety of solutes dissolved in it. The mechanical properties (strength, E, G and T_g) of bonded joints generally deteriorate with exposure to service environments containing water. This is because the hydrophilic character responsible for the adhesive properties of a material also make the adhesive–substrate interface susceptible to attack by water. This is especially true for high-energy substrates. The main processes involved in the hydrolytic deterioration of a joint are: adsorption of water by the adhesive; adsorption of water at the interface through displacement of the adhesive; and corrosion or deterioration of the substrate surface.

The most important factor in joint durability is the environmental stability of the adhesive–substrate interface. This is dictated by the type of adhesive and the nature of the substrate, and is influenced by the substrate surface pretreatment. Generally, the presence of water or moisture (for example, in environments with relative humidity $> 80\%$) leads to failure of adhesive joints at the bimaterial interface.

Considering the reversible work of adhesion, W_A, in the presence of water

$$W_A = \gamma_{sv} + \gamma_{lv} - \gamma_{sl}$$

where γ_{sv}, γ_{lv} and γ_{sl} are the surface free energies of the solid/vapour, liquid/vapour and solid/liquid interfaces respectively. This term reduces in value and, under certain circumstances, may become negative. When a negative value is obtained, this indicates that the adhesive–substrate interface is metastable.

Such an analysis could equally well apply to a glass–ionomer cement itself where, as mentioned previously [1], the polyalkenoic acid can be considered to be the adhesive and the glass powder the substrate. Hill *et al.* [6] determined the fracture toughness of glass–ionomer cements and observed a decrease in the value of this property for cements stored in water. Whether water will actually penetrate the interface, resulting in interfacial failure in the adhesive joint, depends on the kinetics of the process of diffusion of water through the cement. Work such as this was done by Watts and Castle [33] on polybutadiene bonded in single lap joints. They were able to show that the incidence of interfacial failure in this type of joint is controlled by the diffusion of water through the polymer. By plotting the rate of interfacial failure as a function of the immersion time against the inverse of the test temperature, the activation energy for the diffusion of water through the polymer was found to approximate the diffusion coefficient of water through the polymer.

The experimental study of glass–ionomers as adhesives in realistic structures has received very little attention to date. This deficiency has recently been addressed in a study by Mitchell *et al.* [34]. They were studying post-crown failures in an attempt to develop a theoretical model of the failure processes. They used a glass–ionomer luting cement (Aqua-Cem; Dentsply Ltd, De Trey Division, Weybridge, Surrey, UK) in order to retain crowns on posts, the posts being smooth-sided rather than serrated, in order to prevent mechanical interlocking. Specimens were stored at 100% humidity for 24 h before testing. The study concluded that the glass–ionomer cement was a brittle material whose failure was due to defects in the structure causing stress concentrations.

Mitchell *et al.* [34] went on to consider the limitations inherent in testing in the laboratory. Despite using a complex apparatus designed to give a loading on the bonded tooth structure that should be similar to that met *in vivo*, there were a number of features that were excluded from the model. For example, in the clinical situation the post-crown assembly is subject to variations in temperature, humidity and position. These were not considered in the model apparatus used. Other features occurring clinically, such as the variation in frequency, duration and velocity of loading, were impossible to simulate fully. However, it was recognized by Mitchell *et al.* that these variations would impose more-complex forces in actual clinical use than could be applied in the laboratory. Further studies are planned with this system to determine the behaviour of post-retained crown under simulated clinical conditions [34].

6. Conclusions

As we have shown, glass–ionomer cements owe much of their success to their adhesive nature. However, for a number of reasons, testing of this property is far from straightforward. First, there is the problem of relating results from relatively simple laboratory tests to the clinical situation. Next there is the fact that evaluation of durability is difficult. Glass–ionomers were developed for use in an environment of high humidity and high moisture content, conditions under which conventional adhesives are rarely employed because it is so difficult to maintain performance. Finally, in clinical use glass–ionomers are used to bond complex structures; simulating these for the purposes of testing is only just beginning.

This review has highlighted the need for considerable improvements in two related areas: first, in our understanding of the phenomenon of adhesion as exhibited by glass–ionomer cements; and secondly, in

the methods available for measuring the adhesive strength of glass–ionomers in clinically realistic bonded joints.

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