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Review

Glass–ionomer cements as adhesives

Part I *Fundamental aspects and their clinical relevance*

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The literature on the clinical use of glass–ionomer cements is reviewed, and this shows that these materials are successful partly because of the good adhesion they exhibit towards a variety of substrates encountered in dentistry. The reasons for this good adhesion are identified as the good initial wetting of the surfaces met in clinical dentistry, the development of strong chemical bonding with the surface over time and the good mechanical properties of the cements themselves, which make them resistant to cohesive failure. In this review these features are described in detail and related to established mechanisms of adhesion from the wider field of adhesives technology.

1. Introduction

Since the invention of the zinc polycarboxylate cement by Smith in 1968 [1] and the glass–ionomer cements by Wilson and Kent in 1972 [2], adhesion has become an important consideration in the evaluation and selection of dental materials. In this review we are concerned with glass–ionomer cements as adhesives. Glass–ionomer cements are known to adhere well not only to both dentine and enamel [3], but also to stainless steel, so they can be used for the attachment of orthodontic devices.

Glass–ionomers, which are alternatively and more correctly known as glass–polyalkenoates, are a class of acid–base reaction cements that are formed from reactive glass powders and polymeric acids, typically homo- or copolymers of acrylic, itaconic or maleic acids [4]. The polyacid may be reacted as an aqueous solution, or the dried acid may be mixed with the glass to form a powder that undergoes reaction when water is added. Both of these systems are available commercially for use in dentistry.

In considering the adhesion of glass–ionomers it is useful to define the key terms: adhesive, adhesion and durability. An adhesive is a material, typically initially a liquid, that joins two substrates together, solidifies and is hence able to transfer a load from one of the substrates to the other. Adhesion or adhesive strength, on the other hand, is the measure of the load-bearing capability of an adhesive joint. The extent to which this capability is retained in service is referred to as the durability of the joint.

It is the aim of this paper to treat glass–ionomer cements as adhesives *per se*, and in so doing to review the literature covering the adhesion of these cements under conditions of clinical use. We start with a general overview of the phenomenon of adhesion.

2. Fundamental considerations

Basic or fundamental adhesion is a surface phenomenon, and in principle can be calculated as the sum of all interatomic or intermolecular forces [5], both bonded and non-bonded [6], at the interface between the adhesive and the substrate. The practical adhesion, on the other hand, is a reflection of the mode of failure of the joint. The actual value determined experimentally is the practical adhesion, and depends on the presence of readily fractured sites and the mode of application of the external stresses, i.e. whether tensile, shear, etc. This may be summarized as [5]

$$\text{practical adhesion} = f(\text{basic adhesion, other factors})$$

Failure of adhesive joints involves four possible mechanisms, although the actual failure may include a combination of two or more of these mechanisms. These are [7] cohesive failure in the substrate, interfacial failure at the interface between the adhesive and the substrate, cohesive failure within the adhesive and adhesive failure.

For heterogeneous adhesives, such as glass–ionomer cements, cohesive failure within the cement may take place by a mechanism that is essentially one of adhesive failure, i.e. because there is adhesive failure between the matrix and the particulate phase.

A term that has been widely used to characterize adhesive joints is the thermodynamic work of adhesion, W_A. Several workers have tried to correlate this with the adhesive strengths of materials, but with mixed success. The W_A term in an inert medium is the sum of the surface free energies of the solid and the liquid phases minus the interfacial free energy [8], i.e.

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

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Alternatively, W_A may be determined from the more accurate expression

$$W_A = \gamma_{lv}(1 + \cos\theta) + \pi_e$$

where θ is the contact angle and π_e is the equilibrium spreading pressure of the liquid vapour upon the solid and is zero for low-energy surfaces.

By employing the geometry-independent parameters obtained from fracture mechanics, this correlation can be made from a knowledge of the types of bonds in operation and the mode of failure [9]

$$G_c = G_0 + \psi$$

where G_c is the adhesive fracture energy or strain release energy rate, G_0 is the intrinsic adhesive fracture energy and ψ is the energy dissipated viscoelastically at the tip of a propagating crack.

In an adhesive joint the crack may wander between the interface and the materials forming the interface. Assuming there is no adhesive failure, the intrinsic adhesive fracture energy will then be expressed as a weighted average of the various failure modes

$$G_0 = iG_0 + xG_0 + yG_0$$

where i, x and y are the area fractions for the crack as it passes through the interface, adhesive and substrate, respectively. The sum of these area fractions is unity, i.e.

$$i + x + y = 1$$

For adhesive joints that exhibit a solely interfacial locus of failure and in which only secondary bonds are in operation

$$G_0(\text{interfacial}) = W_A$$

This is not the case for glass–ionomer cements, which have been shown initially to develop hydrogen bonds that react to generate covalent bonds [10]. However, before considering in detail the specific case of glass–ionomers and their adhesion under clinical conditions, it is appropriate to outline the current theories of adhesion.

3. Theories of adhesion [11]

3.1. Mechanical interlocking

Perhaps the most widely cited example of this form of adhesion in dentistry is in the interlocking of mercury amalgam in drilled "ink-bottle" cavities of carious teeth.

3.2. Diffusion theory

The diffusion theory of adhesion relates to polymer–polymer interactions. The theory involves the diffusion of molecules across polymer substrate–adhesive interfaces and requires that macromolecules, or chain segments of the polymers possess sufficient mobility and are mutually soluble. This results in the concept of solubility parameter, which is discussed in Section 6. The adhesion of glass–ionomer cements to teeth conditioners or primers or to dental composite resins are examples of diffusion-based adhesion.

3.3. Adsorption theory

The adsorption theory of adhesion is the most widely applicable of the theories of adhesion. It states that intimate molecular contact between materials, leading to the development of intermolecular forces, is a precondition for adhesion to occur. These intermolecular forces vary in strength from primary chemical bonds (i.e. ionic, covalent and metallic; bond energies 60–1100 kJ mol^{-1}) to secondary and van der Waals' bonds (bond energies 0.08–40 kJ mol^{-1}) [12–14].

4. Surface chemistry

Since adhesion is a surface phenomenon, it is essential to understand the surfaces of both the adhesive and the substrate. At this point it is worth noting that, in this context, the surface of the acid-degradable glass of glass–ionomer cements can be regarded as a substrate in contact with the adhesive polyalkenoic acid. It is an approximation to regard the polymer as the acid and the glass as basic, since it is specifically the protons in the –COOH groups that are acidic and calcium-rich sites that are basic. Moreover, each component contains sites of opposite character, i.e. the oxygen in the C=O groups are actually basic and –SiOH groups on the surface of the glass are acidic. Indeed, the SiO_2: Al_2O_3 ratio is found to determine the acid degradability of the glass critically [15], a fact that may be related to the ratio of the acidic Si–OH to basic Al–OH groups in the surface [16].

This detailed consideration of the nature of the individual components of the polyacid and the glass surface shows that acid–base behaviour is a crucial aspect of the initial reaction in glass–ionomer cements. The cohesive strength of glass–ionomer cements is an approximate reflection of the adhesion between polyalkenoic acids and the glass. This point summarizes the essence of this review, that the study of adhesion is central to the study of this class of material. Indeed, a branch of adhesion science pioneered by Fowkes [17] is primarily concerned with this particular aspect. However, the rest of this review concerns the use of glass–ionomers as adhesives to attach various external substrates to each other.

Substrates can be categorized as being of high or low surface energy. Of those materials used in dentistry, stainless steel, hydroxyapatite and the glass in glass–ionomer cements are all high-energy substrates ($\gamma_c \geqslant 500$ kJ mol^{-1}). On the other hand, collagen, dental composite resin and tooth surface conditioners all have low-energy surfaces.

The above categorization begs the important question of whether enamel, dentine and glass–ionomer cements are high- or low-energy substrates. All are composed of at least two types of material, one of high and one of low surface energy. In each case the extent to which the constituents contribute to the final surface energy is uncertain.

De Jong *et al.* [18] went some way towards answering this question by determining the *in vitro* contact angle of human enamel and dentine. The determination of the surface energies of solids using contact angle measurements is one of the easier methods of evaluating the surface energies, surface contamination, surface roughness and degree of wetting of solids. De Jong *et al.* [18] employed human

TABLE I Adhesive properties of a glass–ionomer cement on various substrates

Substrate	Treatment	Cohesive (%)	Cohesive/ adhesive (%)	Adhesive (%)	Mean ± SD adhesion (MPa)
Enamel	1	50	30	20	2.56 ± 1.13
Enamel	2	100			4.05 ± 0.51
Enamel	3	50	50		2.89 ± 0.36
Dentine	1			100	1.46 ± 0.47
Dentine	2		100		2.92 ± 0.90
Dentine	4	16.7		83.3	1.34 ± 0.59
Dentine	5			100	0.89 ± 0.41
Tinned Pt	6	90	10		3.84 ± 0.32
Tinned Pt	6	50	16.7	33.3	2.43 ± 2.72
Pure Pt	7			100	0.07 ± 0.11
Tinned Au	6	100			4.32 ± 0.29
Pure Au	7			100	0.05 ± 0.10
Porcelain	1			100	0

The glass–ionomer cement, ASPA, mixed at a powder : liquid ratio of 3 g ml^{-1}, was tested for adhesion to the above substrates with a centrifugal adhesion tester developed at the National Physical Laboratory. Treatments 1, 2 and 3 were 20 vol H_2O_2, 50% citric acid cleaner and 37% phosphoric acid etch, respectively. Treatments 4 and 5 were metal chelate and mineralizing conditioners, respectively, and treatments 6 and 7 were electroplating with tin and sand-blasting, respectively.

enamel: (i) with the acquired pellicle, (ii) with a thin layer (3–7 μm) of pellicle removed and (iii) with a thick layer (100–200 μm) of pellicle removed. With the aid of a camera, the contact angle of a drop of distilled water on these substrates was measured as a function of the storage time. De Jong *et al.* observed that $\theta_{\mathrm{i}} > \theta_{\mathrm{ii}} > \theta_{\mathrm{iii}}$, where θ is the contact angle and the subscripts refer to the notation given to the substrates above. The results imply that the magnitudes of the surface energies of the substrates are in the order i < ii < iii.

Hotz *et al.* [19] were among the first to study the adhesion of glass–ionomer cements with an appreciation of the relevance of the concept of surface energy. Platinum, gold, porcelain, enamel and dentine were considered for their adhesive properties to polyalkenoate cements. A summary of their results is given in Table I.

The conclusions arrived at by Hotz *et al.* [19] concerning the adhesion of glass–ionomer cements are the following.

1. A correlation exists between the adhesive strengths of the bonded joints and mode of failure of the joints.
2. The strength of the adhesive bond to enamel is significantly greater than that to dentine. In each case the bonding was by secondary intermolecular attractive forces of an ionic/polar character.
3. The glass–ionomer cements adhere only to reactive polar substrates: enamel, dentine, tinned platinum and tinned gold. They do not adhere to the inert surfaces of dental porcelain, platinum or gold.

In discussing the possible mechanisms of adhesion between glass–ionomer cements and substrates, Hotz *et al.* suggested that the prerequisite for adhesion was the presence of free pendant –COOH groups. These groups were assumed to establish hydrogen bonding with chemically reactive surfaces.

5. Wetting

In order to determine the ability of an adhesive to adhere to a substrate, it is necessary to consider the wetting equilibria; measure the surface free energies of the adhesive and the substrate, and the free energy of the adhesive–substrate interface; examine the kinetics and thermodynamics of the wetting process; and consider the details of the bonding operation [20].

The classical theory of wetting is that of Young [21], which dates from 1805. This theory deals with adhesion of liquids (adhesives) on an idealized smooth, homogeneous, isotropic, non-deformable solid surface, a scenario far removed from the situation existing when glass–ionomer cements are used clinically. Nevertheless, Young's equation remains a good starting point for the discussion of the adhesion of these materials.

Young's equation deals with the relationship between the surface free energies of a solid surface and the contact angle of the adhesive in contact with it, under equilibrium conditions

$$\gamma_{\mathrm{sv}} - \gamma_{\mathrm{sl}} = \gamma_{\mathrm{lv}} \cos\theta$$

where γ_{sv}, γ_{sl} and γ_{lv} are the surface free energies of the solid–vapour, solid–liquid and liquid–vapour interfaces, respectively, and θ is the equilibrium contact angle that the liquid adhesive makes with the solid surface. Depending on the relative values of the surface free energy terms, a liquid will wet, spontaneously spread or fail to wet the solid surface.

Glass–ionomer cements do not spread spontaneously, but instead can be forcibly spread by the application of pressure in bonding operations. The contact angle that they exhibit in the making of an adhesive joint will therefore be a dynamic one, as presented in the Fritz equation

$$\tan\theta_{\mathrm{d}} = m(\eta v_{\mathrm{s}})^{n}/\gamma_{\mathrm{lv}}$$

where η is the viscosity of the adhesive moving at a velocity v_{s}, and m and n are constants.

This takes into account the time–temperature dependence of wetting and contact angle measurements. It also takes account of the changes in the adhesive as it hardens, and hence can be applied to glass–ionomer cements as they set.

Conventional glass–ionomer cements are formed via the cross-linking of polyalkenoic acids by di- and trivalent cations from acid-degradable glass powders [4]. The viscosity of the cements increases with time and temperature. The reptation hypothesis of thermoplastics predicts high cohesive strengths for materials with increasing viscosity [22]. Against this, for glass–ionomer cements, increasing viscosity leads to a reduction in interaction, resulting from the unavailability of –COOH groups and restricted motion of polymer molecules. This time–temperature dependence can be expressed by [23]

$$\cos\theta_t = \cos\theta_\infty[1 - k_1\exp(-k_2 t)]$$

where k_1 and k_2 are constants. k_2 is known as the wetting constant and is given by $k_2 = \gamma_{lv}/\eta L$. L is a constant with the dimensions of length, and is independent of temperature but related to the adhesive–substrate interfacial interactions [23–25]. The compromise alluded to in the relationship between the viscosity and adhesive strength of glass–ionomer cements is implicit in the above equation. Good wetting of the substrate by the adhesive requires the adhesive to possess a low contact angle, high surface tension and low viscosity, but the last two terms are mutually exclusive.

An alternative approach taken by Vrbanac and Berg [26] was to investigate the effect of temperature on the conversion factor, f, in the expression

$$W_A = fN(-\Delta H_{abs})$$

where N is the number of accessible functional groups taking part in an acid–base reaction and ΔH_{abs} is the enthalpy change of this acid–base reaction.

Vrbanac and Berg showed that f increases with temperature for copolymers of ethylene and acrylic acid, a finding which suggests that adhesive bonds between glass and polymer in glass–ionomer cements will be more numerous in cements formed at higher temperatures.

Holmes-Farley *et al.* [27] studied the acid–base behaviour of carboxylic acid groups, and with the aid of some assumptions came up with a correlation between the degree of ionization α, pH (as reaction proceeds), contact angle θ, of the material in contact with water and the surface energies γ_{ls} and γ_{sv}.

In all of this work, the contentious issue of the measurement of contact angles arises. There are four stable contact angles that can be obtained for a system: the equilibrium advanced and receded and the advancing and receding contact angles. Added to this is the hysteresis in contact angles resulting from short-range rotational mobility around the C–C bonds of the polymer subgroups. This will be particularly relevant to freshly prepared cements with a large number of free –COOH groups. All of these factors combine to make the determination of contact angles, and the interpretation of adhesive strength based on them, extremely difficult. Nevertheless, it remains clear that one essential attribute of a good adhesive is the capability to wet the substrate, and this feature is shown by glass–ionomers on a number of clinically important substrates.

6. Solubility parameter

The concept of the solubility parameter [28] is relevant to substrates including a significant organic component, such as dental composite resins, and to surfaces treated with adhesion promoters or other conditioners. The basic premise of the concept of solubility parameter is that for the development of a strong bond between the adhesive and the substrate, there must be an attendant decrease in the free energy, ΔF, of the system, given by

$$\Delta F = \Delta H - T\Delta S$$

where ΔH is the heat of mixing, T is the absolute temperature and ΔS is the entropy change.

There is generally an increase in entropy upon mixing, so the ΔS term is usually negative. Materials will tend to combine when ΔH_{mixing} is negative. This heat of mixing depends on the attractive forces between the adhesive and the substrate surface. As in the case of glass–ionomer cements in their adhesion to stainless steel and other suitable substrates, the development of chemical interactions such as hydrogen bonds tends to give the heat of mixing a negative value, so the cement wets the substrate and adheres.

The solubility parameter, δ, is related to the heat of mixing by

$$\delta = (E/V)^{1/2}$$

$$H = \mathrm{V}(\delta_1 - \delta_2)^2\phi_1\phi_2$$

where E is the energy of vaporization, V is the molar volume and V is the total volume. ϕ_1 and ϕ_2 are the volume fractions of the respective components.

The smaller the difference between the two solubility parameters is, the more negative the value of the heat of mixing. Hence, a strong interaction is most likely when the adhesive and the substrate have similar solubility parameters [29]. It is therefore not surprising that a 25% solution of high-molecular weight poly(acrylic acid) is an effective conditioning agent for the promotion of good adhesive strength. The resultant high bond strengths obtained are due to primary bond formation between the adsorbing species of the adhesive and the substrate.

In order to understand adhesion in terms of the solubility parameter, it is important to know which species are present on the surfaces commonly encountered in dentistry. Table II lists the actual absorbing species claimed to be present on the surfaces of a number of substrates of clinical importance.

The etched composite resin referred to in Table II is that prepared by the technique pioneered by Buonocore [30]. This acid-etch technique has become widely used in dentistry and involves roughening the substrate surfaces before placement of a restorative material with solutions of acid, typically phosphoric acid. The technique is employed in the laminate restoration of cavity class III, IV and V carious lesions pioneered by McLean *et al.* [31]. In this procedure the surfaces of glass–ionomer cement liners are etched and a composite inlay fixed in place, with or without the use of bonding agents [32].

The purpose of etching the substrate is to improve

TABLE II Substrates encountered in dentistry and their adsorbing species

Bulk substrate	Surface character
Stainless steel	Interbatch variation in roughness with stripwise grooves along the rolling direction of the steel. Non-deformable and homogeneous
Enamel	Heterogeneous (patchwise) 98% apatite mineral and 2% collagen
Dentine	Heterogeneous (patchwise) 70% apatite mineral and 30% collagen. Non-uniform roughness arising from variations in angle and depth of dentinal tubules
Etched composite resin	Pitted non-uniform surface resulting from excessive porosity with glass and matrix dissolution

adhesion, and this improvement comes about by one or more of the following mechanisms.

1. Removal of a weak boundary layer on the surface, or prevention of its formation.
2. Maximization of the degree of intimate molecular contact between the adhesive and the substrate during the bonding operation.
3. Ensuring that the level of intrinsic adhesion forces established across the interface(s) is sufficient for the attainment of both the initial joint strength and good bond durability.
4. The generation of a specifically beneficial topography on the adhesive.
5. Assistance in the hardening of the adhesive.
6. Protection of the surface of the substrate before the bonding operation.

7. Effect of surface topography

As outlined in the preceding section, the substrates encountered by glass–ionomer cements are of various chemical compositions and roughnesses. Topography is a term used to describe the overall physical nature of the surface of a solid, and encompasses the roughness. The extent of contact between the surfaces of an adhesive and a substrate is affected critically by the topography of the solid surface. This is even more relevant in the case of commercially available acid–base glass–ionomer cements, since they have a finite working time. The contoured surface of stainless steel orthodontic brackets serves to increase the adhesive strengths of glass–ionomer cement-bonded joints by increasing the area of contact between the materials and by subtly changing the stress distributions within the joint. It may well be that increases in the bond strengths can also be attributed to the inhibition of cracks propagating close to or at the bimaterial interface [33].

In laboratory tests, stainless steel test pieces are roughened by grit-blasting or emery paper abrasion. The former produces irregular pits and the latter results in stripwise grooves in the stainless steel. The adhesion processes of cements on these two topographies are different. A liquid adhesive in a groove will tend to elongate in the direction of the groove, the direction representing the minimum energy. The energy barrier preventing the spreading of the adhesive will be higher across the grooves than along them. Also, the shape and depth of these grooves also affects the adsorption of liquid adhesives on the substrate [34]. This preferential adsorption of cements could be responsible for the observation by several workers of less-reproducible adhesive strength results obtained for emery-abraded surfaces compared with grit-blasted ones [35, 36].

The grit-blasted stainless steel surface is more akin to those of enamel and dentine from the standpoint of the topography of the surfaces. These are considered next.

Pores and pits in stainless steel, enamel, dentine or dental composite resins can be approximated by cylindrical and "ink-bottle" pits. In either case, for maximum adhesion it is essential that the pits be filled by the adhesive. The penetration of the pores by the adhesive is governed by the time–temperature dependence of the viscosity of the cements. In other words, the kinetics of pore penetration must be considered. Penetration of cylindrical pores has been shown by de Bruyne to differ from penetration of "ink-bottle" pits [37]. He modelled the penetration of closed cylindrical pores using

$$l_p = l\left(1 - \frac{P_a r_0}{2\gamma_{lv}\cos\theta + P_a r_0}\right)$$

where P_a is the atmospheric pressure and l is the length of a cylindrical pore of radius r_0. The smaller the pore radius is, the greater the proportion of the pore length that will be filled at equilibrium.

Starting with Poiseille's law for the flow of a Newtonian liquid of viscosity η in a tube of radius r_0 under the influence of a pressure P [38],

$$l_p \frac{dl_p}{dt} = \frac{r_0^2 P}{8\eta}$$

If the driving pressure is taken to be the capillary pressure

$$2\gamma_{lv}\cos\theta/r_0$$

Integrating the previous equation, assuming θ and η to be constants,

$$l_p^2 = r_0\gamma_{lv}\cos\theta\, t/2\eta$$

This shows that the penetration l_p is proportional to the square root of time. This implies that low-viscosity cements with long working times will penetrate into pores more readily than high-viscosity cements with shorter working times. However, because of the presence of air voids and other discontinuities in low-viscosity cements, the best cement formulations for use as adhesives are those of intermediate viscosity. These are the so-called luting cements [3, 4].

Alternatively, de Bruyne [37] determined the change in viscosity of a cold-setting thermoset adhesive as the setting process takes place as

$$\eta = \eta_0 e^{bt}$$

where b is a constant.

De Bruyne thus modified Poiseille's equation to describe the penetration of such a liquid into a closed pore of length L as

$$l_{\mathrm{p}}\frac{\mathrm{d}l}{\mathrm{d}t} = \frac{r^{2}\mathrm{e}^{-bt}}{8}\left(P_{1} - \frac{P_{0}L}{L - \mathrm{x}}\right)$$

where P_1 is the driving pressure and the second term in the parentheses represents the back-pressure of trapped air. For an appreciable driving pressure this term can be neglected and

$$l_{\mathrm{p,\,max}} = rP_{1}/2\eta_{0}b$$

where η_0 is in P and b in s^{-1}.

This expression is very significant. If the application of an adhesive on a substrate is delayed, η_0 will take a higher value and the penetration of the adhesive into the crevices on the substrate surface will be reduced. This results in unsatisfactory adhesive strength due to the presence of moisture-laden air voids which act as stress-raisers in the joint.

Adhesion to dentine is a special case, however, because of the presence of the dentinal tubules. The assumption of a back-pressure of trapped air in closed pores, as in the analysis by de Bruyne, does not hold in the case of dentine. Indeed, the adhesive in contact with dentine is rather like the blister test piece for the determination of stressed durability. This may account for the findings of Powis *et al.* [39]. They found that etching of dentine did not improve the adhesive strengths of polyalkenoate-bonded joints, using a technique based on pulling stainless steel lingual buttons off conditioned dentine surfaces. If dentinal fluids were continually ingressing and displacing the surface layer of the cement, in a manner analogous to the blister test, then no amount of prior surface treatment would improve the adhesion of the resultant restoration.

8. Conclusions

In this paper we have reviewed the literature covering glass–ionomer cements as adhesives. This shows that these materials are effective for a number of reasons. First, they show good wetting of the surfaces typically encountered in clinical dentistry; secondly, the initial relatively weak interaction based on hydrogen bonding gradually gives way to a stronger interaction based on chemical bonding of a polar/ionic kind; and thirdly, the mechanical properties of the cements themselves are such that they show good resistance to cohesive failure. This last effect itself owes its origin to adhesion, since the glass–ionomer cements themselves involve strong adhesive bonding between the polymer matrix and the powdered glass filler. Given this excellent adhesion, we believe that the potential for further exploitation of glass–ionomer cements in clinical dentistry is considerable.

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