Adhesion of resin composites to biomaterials in dentistry
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Chapter 1

General Introduction
stress intensity. Other factors like properties of resin adhesives, luting cements, design of the restoration, voids in cement layers, surface microdefects within the material, all may influence the fracture resistance of the restoration.

Failures related to debonding and difficulties in achieving durable adhesion required, have initiated this research in order to find the better methods for conditioning a number of dental biomaterials prior to cementation, recementation, lamination or repair actions. Although the body of research on dental adhesion is large, some basic principles and knowledge still seem to be neglected leading to shorter survival rate than would be expected from often expensive dental appliances. Some of the reported failure rates are listed below:

1-Clinical failure rates of adhesively luted ceramic restorations ranged between 0.6 to 5 % per year. By location of the pontic, failure rates were noted as 0 to 11 % for premolars and 24 % for molars. Mechanical problems accounted for 13 to 33 % of the failed units up to 3 years.5-7

2-Posts for endodontically treated teeth have received considerable attention in the dental scientific literature, but there is sparse in vivo research and certain information from in vitro investigations is contradictory about the adhesion of core materials to the metal posts. The retrospective studies indicated failure rate ranging between 1 to 7.5 % related to loss of adhesion of cores to metal posts.8

3-With the increased demand for adult orthodontics, the clinicians often lute brackets and retainer wires to the ceramic parts of fixed-partial-dentures. However, the failure rates are reported to be 9.8 % in 2 years. Even taking into account the short duration of bracket applications in orthodontics compared to other adhesive procedures in restorative dentistry, this failure rate is high.9

4-Clinical studies related to the survival rate of direct or indirect resin composite restorations revealed 30-60 % of all restorations had been replaced after 3-8 years mainly due to secondary caries followed by discoloration, degradation, microleakage, wear or ditching at the margins. It was reported that the clinicians spend the majority of their chair side time replacing restorations and the amount of time was found the highest for resin composite restorations10-14

5-Amalgam has served dentistry for more than a century. Longevity is reported up to 6 years with annual failure rates of 0.5-6.6 %.5 The results of recent surveys from cross-sectional studies indicate that complete cusp fracture of posterior teeth associated with amalgam restorations is a problem in dental practice. The failure rate range between 4.4 and 14 occasions per 100 subjects.
or 20.5 teeth per 1000 persons a year. Although only a few surveys exist in the literature, strictly speaking, the reported failure rates are not high. Nevertheless, any kind of failure is an unpleasant experience that poses aesthetic and functional dilemma and is costly both for the patients and the dentist.

Replacement of a failed restoration is not necessarily the most practical solution. Before making an attempt to restore failed restoration, clinicians should know the underlying reasons for the failure. Therefore, knowledge on the failure phenomena and the adhesion characteristics related to the underlying material should be well-recognized to receive the best possible adhesion.

A summary of the materials of particular concern in this study is listed in Tables 1a-c.

Background information

A good adhesion to the dental tissues has been achieved successfully over the few decades. Current research efforts are also aimed at the optimization of the adhesion between composites to metals (alloys), composites to ceramics and composites to other composites. A number of surface conditioning methods have been developed over the last few decades to produce adequate adhesion to the adherend for restorations. Advances in adhesive dentistry have resulted in the introduction of surface conditioning methods using chemical agents or air-borne particle abrasion of the adherend prior to bonding the adhesive in order to achieve optimum adhesion. A summary of conditioning techniques for restorative materials is presented in Table 2. These methods were initially based on macro or micromechanical retention either lying on the adherend like retention beads or located within the adherend such as grooves or undercuts. However, the methods based on mechanical retention mechanisms suffered from unreliable bonding strengths or gap formation between the adhesive and the adherend leading to microleakage. Also, while external retentions promoted overcontouring of the restoration, internal ones produced by drilling could introduce additional cracks or deformations and distortions in the adherend. Other surface conditioning methods used for alloys were based on creating micromechanical retention through electrochemical etching or electrolytic tin plating but unfortunately they were not applicable to all alloys.

Chemical conditioning methods rely on less invasive techniques via particle deposition on the adherend surface followed by coating the surface with a silane coupling agent and/or an intermediate monomer resin. One such system is tribochemical silica (SiO₂) coating. In this technique, surfaces are
air-abraded with aluminium trioxide (Al₂O₃) particles coated with silica. The blasting pressure results in the embedding of these silica coated alumina particles in the surface, rendering the silica-modified surface chemically more reactive to the adhesive through silane coupling agents.¹⁹-²³

The most popular chemical agent for conditioning dental ceramic or particulate filler composite surfaces prior to cementation is hydrofluoric (HF) acid gel. The greatest advantage of the use of HF acid gel is that it is very simple to apply in chair side procedures. Furthermore, restorations can be re-etched in case of failure without the need of laboratory procedures. It selectively dissolves the glassy matrix and causes physical alteration to promote adhesion of resin composite to the porous surface of the ceramic. Unfortunately, HF acid gel is a strong caustic agent that may create irritations of soft tissues.²⁴ Although intraoral use of this acid gel should be seriously questioned, most of the manufacturers still do recommend it particularly prior to cementation of adhesively luted restorations.

When two dissimilar materials are to be attached, whether micromechanical or chemical conditioning is chosen, the use of silane coupling agents could provide increased attachment.

**Silane coupling agents**

Silanes are hybrid organic-inorganic compounds that can function as mediators, coupling agents to promote adhesion between dissimilar, inorganic and organic materials.²⁵-²⁷ There are several explanations that describe what could happen at the interface during silane reactions. Briefly listed: a) Chemical bonding theory is the best known and its main idea is that silanes improve adhesion by formation of stable, covalent siloxane (Si-O-Si), bonds and metallo-siloxane bonds (Si-O-M); b) Deformable layer theory points to the plasticity of the interface region; c) Surface wettability theory suggests the improvement of adhesive strength by physical adsorption; d) The restrained layer theory states that some mechanical stress transfer between the phases take place; e) The reversible hydrolytic bond theory combines aspects of chemical bonding with the rigid interface of the restrained layer theory; f) An adhesion between silica and silane, made by two types of bonds, viz. siloxane bridges and hydrogen bonds; g) Consisting of ionomer bonding, interpenetration, both soft and rigid layer theories; h) The silane modifies the oxide layer on the substrate and forms a conversion layer. This layer is different with its electrochemical properties than those on the silanes and the metal oxide.
Silane coupling agents used in dentistry were at first vinyltrimethoxysilane and subsequently mainly 3-methacryloxypropyltrimethoxysilane, \( \gamma \)-MPS (also \( \gamma \)-MPTS) (3-methoxysilylpropylmethacrylate). These trialkoxyorganosilanes have an organic functional radical (R', e.g. vinyl- or methacryloxypropyl) that can co-polymerize with a resin composite. They have also three alkoxy groups (e.g. methoxy -O-CH\(_3\)) ready to hydrolyze in a water-alcohol solution, and then to react with surface hydroxyl group on an inorganic substrate (e.g. silica surface, oxide layer on a metal surface, ceramic, E-glass). In other words, surfaces to be silanated must contain OH-groups sufficiently. The functional alkoxy groups react as acid catalysed (usually in pH 4-5) in aqueous alcohol solution, to form at the first stage (i.e. hydrolysis) labile intermediate acidic silanol groups (-Si-OH):

\[
R'\text{-Si(OR)}_3 + 3 \text{H}_2\text{O} \rightarrow R'\text{-Si(OH)}_3 + 3 \text{R-OH} \tag{1}
\]

The silanol groups then condense to form dimeric (and then oligomeric) molecules:

\[
\text{R-Si(OH)}_3 + \text{R-Si(OH)}_3 \rightarrow \text{R-Si(OH)}_2\text{-O-Si-(R)(OH)}_2 + \text{H}_2\text{O} \tag{2}
\]

In the next fast step, they form a three dimensional highly cross-linked polysiloxane (-Si-O-Si-) layer with covalent bonds, and also -Si-O-M (M = metal) bonds with hydroxyl groups on the substrate surface. Water is eliminated in this reaction and methanol is released but in minute amounts.

\[
...\text{R-Si(OH)}_2\text{-O-Si-(R)(OH)}_2... + 2\text{OH-M} \rightarrow \text{R-Si-O-Si-O...} + \rightarrow \text{etc.} \tag{3}
\]

Commercial dental silanes are typically pre-hydrolyzed or in other words, ready to use. The advantage of silane coupling agents appear to enhance bond strength by promoting a chemical bond between the adhesive and the adherend. Although early commercial silane solutions suffered from instability, they have been steadily improved demonstrating higher bond strengths.\(^{28,29}\)
Relevance and objectives of this thesis

The work described in this thesis was initiated as a result of the recognition of failures experienced in clinical dentistry. It aims to elucidate the relations between the material properties and the adhesion principles. Moreover, the large variations of new dental biomaterials needed to be studied from the perspective of their adhesive behaviour in order to find the optimal combination. Therefore, the overall aim of this thesis was to increase our knowledge on the interactions between surface conditioning methods used for different dental restorative, prosthetic and orthodontic materials, and the adhesives, with a particular emphasis on ceramics, amalgam, titanium metal and particulate filler resin composites and to choose the most suitable method for the specific substrate. Such knowledge would help the clinicians to prolong the service life of the restorations. This allows minimally invasive and cost effective manner of treatment.

References:

The phenomenon of adhesion, here meaning the physico-chemical adhesion of two dental materials rather than the adhesion of biological substances existing in the oral cavity, is involved in almost all disciplines of dentistry. Basically, adhesion is the force that causes two substances to attach when they are brought into intimate contact with each other. The molecules of one substance adhere or are attracted to molecules of another. This force is called adhesion when unlike molecules are attracted and cohesion when molecules of the same kind are attracted. The material or film added to produce adhesion is known as the adhesive and the material to which it is applied is called the adherend or substrate.\(^1\) Adhesion in dental applications can be considered to include two categories: one to the dental tissues like enamel, dentin or cement and the other to artificial materials. Artificial materials used in dentistry are, in general terms, biomaterials. By definition, any material or substance (other than a drug) or combination of materials, synthetic or natural in origin, which can be used as a whole or as a part of a system which treats, augments, or replaces any tissue, organ, or function of the body are called biomaterials.\(^2\)

A plethora of dental biomaterials is being introduced in dentistry for various indications that require attachment to the tooth substance or to substrates using adhesive means. Despite the increased effort to improve the adhesion between various restorative and prosthetic materials in dental applications, adhesive and/or cohesive failures are still being experienced either in the form of debonding, delamination or fractures.\(^3,4\)

Many factors play a role in the failure of dental restorations such as the inherent physical features of the materials, external factors or insufficient adhesion. In fact, even if the restorations were made at ideal conditions, experiencing failures is not surprising. The differences between the elastic properties and thermal expansion coefficients of the dental materials that the clinicians try to adhere to are sometimes large. They function in a moist and aggressive oral environment and they are exposed to thermal and mechanical fatigue, static and impact forces caused by the occluding teeth. The result is catastrophic failure of the restoration either at the interface or within the material itself.

The presence of minute flaws contributes to failure in many ways, primarily where the restoration or restoration-tooth system flexes under loading, causing deflection and resulting in loss of adhesion or debonding between materials. The failures may also be simply experienced due to technical mistakes during the preparation of the restorations and occasional presence of flaws. Mechanical fatigue of restorative materials is mainly governed by mechanisms that are related to material properties including microstructure, crack length and fracture toughness, as well as to applied...
### Table 1a. Trade names, types of ceramics, titanium, amalgam used as substrates and the manufacturing company names.

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Type</th>
<th>Manufacturers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Finesse</td>
<td>leucite reinforced</td>
<td>Ceramco, Burlington, NJ, USA</td>
</tr>
<tr>
<td>In-Ceram</td>
<td>glass-infiltrated alumina (70%)</td>
<td>Vita Zahnfabrik, Bad Säckingen, Germany</td>
</tr>
<tr>
<td>Zirkonia Blank for Celay</td>
<td>glass-infiltrated zirconia</td>
<td>Vita Zahnfabrik, Bad Säckingen, Germany</td>
</tr>
<tr>
<td>IPS Empress 2</td>
<td>lithium disilicate</td>
<td>Ivoclar, Vivadent AG, Schaan, Liechtenstein</td>
</tr>
<tr>
<td>Procera AllCeram</td>
<td>high alumina (99.9%)</td>
<td>Nobel Biocare AB, Göteborg, Sweden</td>
</tr>
<tr>
<td>Experimental alumina</td>
<td>high alumina (99.7%)</td>
<td>Tampere University of Technology, Tampere, Finland</td>
</tr>
<tr>
<td>VMK68</td>
<td>feldspathic ceramic</td>
<td>Vita Zahnfabrik, Bad Säckingen, Germany</td>
</tr>
<tr>
<td>Titanium</td>
<td>DIN 17850-T4/3.70651</td>
<td></td>
</tr>
<tr>
<td>Amalgam</td>
<td>non-gamma 2, lathe-cut, high-copper alloy</td>
<td>ANA 2000 Duet, Nordiska Dental AB, Ängelholm, Sweden</td>
</tr>
</tbody>
</table>

### Table 1b. Monomer matrix types of particulate filler composites used as substrates and the manufacturing company names.

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Matrix type</th>
<th>Manufacturer</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gradia</td>
<td>UEDMA/ethylene dimethacrylate(^1)</td>
<td>GC, Alsip, IL, USA</td>
</tr>
<tr>
<td>Sculpture</td>
<td>dimethacrylate(^2)</td>
<td>Jeneric Pentron, Wallingford, CT, USA</td>
</tr>
<tr>
<td>Sinfony</td>
<td>HEMA/diacrylate(^3)</td>
<td>3M ESPE, Seefeld, Germany</td>
</tr>
<tr>
<td>Targis</td>
<td>Bis-GMA, DDMMA, UEDMA, TEGDMA(^4)</td>
<td>Ivoclar Vivadent AG, Schaan, Liechtenstein</td>
</tr>
<tr>
<td>Tetric Ceram</td>
<td>Bis-GMA, UEDMA, TEGDMA(^5)</td>
<td>Ivoclar Vivadent AG, Schaan, Liechtenstein</td>
</tr>
</tbody>
</table>

\(^1\) UDMA (10-25 %) and ethylene dimethacrylate (5-10 %)
\(^2\) dimethacrylate
\(^3\) 10-30- % (octahydro-4,7-methano-1H-indenediyl) bis(methylene-diacylate)
\(^4\) Bis-GMA (9 %), DDMMA (4.8 %), UEDMA (9.3 %)
\(^5\) Bis-GMA (< 9 %), TEGDMA (< 5 %), UEDMA (< 8 %)
Table 1c. Filler types and percentages of particulate filler composites.

<table>
<thead>
<tr>
<th>Trade name</th>
<th>Filler type and content</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gradia</td>
<td>Alumina silicate glass (40-50 w-%), amorphous precipitated silica (5-10 w-%)</td>
</tr>
<tr>
<td>Sculpture</td>
<td>Glass-infiltrated alumina (70 w-%)</td>
</tr>
<tr>
<td>Sintony</td>
<td>Strontium-aluminium borosilicate glass, silicon dioxide (50 w-%)</td>
</tr>
<tr>
<td>Targis</td>
<td>Silanized Ba-glass fillers (46.2 w-%), highly dispersed silica (11.8 w-%), mixed oxides (18.2 w-%), catalyst and stabilizers (0.6 w-%), pigments (≤0.1 w-%)</td>
</tr>
<tr>
<td>Tetric Ceram</td>
<td>Silanized Ba-glass, ytterbium trifluoride, silanized unknown metal oxide, silanated barium-aluminium-fluoro-silicate glass, silanated silica glass (79 w-%)</td>
</tr>
</tbody>
</table>

Table 2. Characteristics of conditioning principles with some details, brand names and the manufacturers of surface conditioning methods assessed.

<table>
<thead>
<tr>
<th>Conditioning principle</th>
<th>Details</th>
<th>Brand names and manufacturers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Orthophosphoric acid</td>
<td>(37 %, 60 s)</td>
<td>Ultradent® Ultraetch, South Jordan, UT, USA</td>
</tr>
<tr>
<td>Hydrofluoric acid</td>
<td>(9.5 %, 90 s)</td>
<td>Ultradent Porcelain Etch®, South Jordan, UT, USA</td>
</tr>
<tr>
<td></td>
<td>(5 % , 20 s)</td>
<td>IPS Empress Ceramic Etch, Vivadent AG, Schaan, Liechtenstein</td>
</tr>
<tr>
<td>Air-particle abrasion</td>
<td>(110 µm aluminium trioxide, 380 kPa, 10 mm, 13 s)</td>
<td>Korox®, Bego, Bremen, Germany</td>
</tr>
<tr>
<td>Chair side air-particle abrasion</td>
<td>(30 µm aluminium trioxide, 250 kPa, 10 mm, 4 s)</td>
<td>Korox®, Bego, Bremen, Germany</td>
</tr>
<tr>
<td>Tribochemical silica coating</td>
<td>Rocatec® Pre, Rocatec® Plus (280 kPa, 10 mm, 13 s)</td>
<td>Rocatec™, 3M ESPE AG, Seefeld, Germany</td>
</tr>
<tr>
<td>Chair side silica coating</td>
<td>(CoJet®-Sand, 30 µm SiO2 coated Al2O3, so called SiOx, 250 kPa, 10 mm, 4 s)</td>
<td>CoJet®, 3M ESPE AG, Seefeld, Germany</td>
</tr>
<tr>
<td>Silica coating-silanization</td>
<td>Silicoater® Classical, Silicoater® MD, Silico®, Heraeus-Kulzer GmbH, Wehrheim, Germany</td>
<td></td>
</tr>
<tr>
<td>Acrylization</td>
<td>5 min</td>
<td>Kevloc®, Heraeus-Kulzer GmbH, Wehrheim, Germany</td>
</tr>
<tr>
<td>Silane coupling agent</td>
<td>5 min</td>
<td>ESPE®-SI, 3M ESPE AG, Seefeld, Germany</td>
</tr>
<tr>
<td>Alloy primer</td>
<td>Alloy Primer™, Kuraray Medical Co. Ltd, Tokyo, Japan</td>
<td></td>
</tr>
<tr>
<td>Pre-impregnated bidirectional</td>
<td>everNET™, StickTech, Turku, Finland</td>
<td></td>
</tr>
<tr>
<td>E-glass fiber sheets</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Outline of this thesis

In Chapter II the effect of three surface conditioning methods on the bond strength of a Bis-GMA based luting cement to six dental ceramics were assessed by shear bond test.

In Chapter III the resistance of six core materials on titanium posts after using five surface conditioning methods and two types of opaquers were evaluated by means of electronic rotational torque device.

In Chapter IV the effect of five surface conditioning methods on the bond strength of polycarbonate brackets to feldspathic ceramic surfaces were evaluated by shear bond test. Furthermore after debonding, the adhesive remnant index was used for classifying failure modes and the fracture surfaces were analyzed using scanning electron microscope.

In Chapter V the effect of three surface conditioning methods on the bond strength of a diacrylate resin to five particulate filler resin composites were assessed by shear bond test and the surfaces were analyzed using scanning electron microscope after the conditioning methods.

In Chapter VI the effect of seven conditions on the bond strength of a resin composite to amalgam surfaces were evaluated using shear bond test and the correlation between surface roughness and bond strength was assessed.

In Chapter VII the results are discussed and ongoing or further planned studies are mentioned and in Chapter VIII these studies together with the discussion and future research ideas are summarized.
This thesis is based on the following papers:


Fracture Reasons in Ceramic-fused-to-metal Restorations

Fracture Reasons in Ceramic-fused-to-metal Restorations

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SUMMARY
Ceramic-fused-to-metal restorations are widely used in dentistry with a high degree of general success. Fracture of the ceramic veneers as a result of oral function or trauma is not an uncommon problem in clinical practice. Although fractures of such restorations do not necessarily mean the failure of the restoration, the renewal process is both costly and time consuming and therefore remains a clinical problem. Fractures in the anterior region pose an aesthetic problem but when they are in the posterior, chewing function could also be affected. The published literature reveals that reasons for failures cover a wide spectrum from iatrogenic factors to laboratory mistakes or due to factors related to the inherent structure of the ceramics or simply to trauma.

Introduction
Because of their excellent biocompatibility and superior aesthetic qualities, ceramic-fused-to-metal crowns and bridges are commonly applied in fixed prosthodontics. Despite the increased effort to improve the bond strength between the ceramic and the metal substrate, on occasion, fractures of ceramic veneers still occur under clinical conditions. The reasons for such failures are frequently repeated stresses and strains during chewing function or trauma. Clinical studies indicated that the prevalence of ceramic fractures ranged between 5-10% over 10 years of use (Coornaert, Adrians & de Boever, 1984).

Ceramic fractures are serious and costly problems in dentistry. Moreover, they pose an aesthetic and functional dilemma both for the patient and the dentist. Therefore the intent of this paper is to review the published literature on the reasons for fractures, concentrating on the data obtained both from in vitro and in vivo studies.
Failure rates

Many patients are still in need of fixed restoration replacements due to some failures in those restorations. Only a few studies in the literature have dealt with the survival rates of metal-ceramic restorations.

In a clinical follow up study by Coornaert et al. (1984), the prevalence of fractures in metal-ceramic crowns was found to be approximately 5% over 10 years of function. Strub, Stiffler & Schärer (1988) observed a failure rate of metal-ceramic restorations of only between 1% to 3% over 5 years. Studies by Karlsson (1986) revealed a 93% success rate for fixed bridge restorations during a 10-year period, while Palmqvist & Schwartz (1993) reported a 79% success rate over a 18 to 23 year period. The survival rates obtained by Glantz et al. (1993) as a function of time between 1979 and 1994 indicated that most of the debondings occurred over 15 years and almost all recorded dislodgements were observed within 5 years of placement. Subsequent clinical results from Hankinson & Cappetta (1994) and Kelsey et al. (1995) exhibited 2 to 4% failure rates after two years of function, rising from 20 to 25% after 4 to 5 years due to consistent repeating occlusal contacts.

In another clinical retrospective analysis, 1219 three-unit fixed bridges and 1618 single crowns in the anterior region were evaluated between 1969 and 1989 (Kerschbaum, Seth & Teeuwen, 1997). The results of the study supported the superiority of metal-ceramic systems over acrylic-veneered crowns with 2 to 4% failure rates after 2 years of function. Statistical analysis however, showed that after 10 years, 88.7% of the metal-ceramic crowns and 80.2% of the metal-ceramic bridges were still in function.

Overall survival rate of metal-ceramic restorations demonstrate a paradox in the different survival rate values in the literature. It is well recognized that many factors are involved in the success rate assessments of fixed partial dentures limiting the longevity of the restorations.

Factors affecting failure

Failure of the restorations is in fact a multifactorial problem which could be related to a combination of different reasons. Optimization of the metal-ceramic restorations requires knowledge of the failure phenomena. Numerous studies over the years have focused on reasons for failure.

Mechanical failures of metal-ceramic systems are not surprising considering the vast differences in modulus between the metal and ceramic materials. When feldspathic dental porcelain is cooled, the leucite crystals
contract more than the surrounding glass matrix leading to the development of tangential compressive stresses around the leucite particles as well as to microcracks within and around the crystals (Hasselman & Fulathy, 1966; Mackert, 1988; Anusavice & Zhang, 1998; Denry, Hollowey & Rosentiel, 1998).

Twenty to 30% reduction in metal-ceramic strength was found in a moist environment (Sherill & O’Brein, 1974). Michalske & Freiman (1982) indicated that silicate bonds in the glassy ceramic matrix are susceptible to hydrolysis by environmental moisture in the presence of mechanical stress. The porcelain restoration functions in a moist environment, which may allow static fatigue to cause the propagation of fractures along the microcracks resulting in failure of the restoration. The environment of the oral cavity was found to aggravate the strength of dental ceramics. The silicon-oxygen bond was found to become weaker between the metal and ceramic in the presence of moisture which abet failure in many ways primarily because of the water propagation at the crack tip (Dauskardt, Marshall & Ritchie, 1990).

The minute scratches present on the surfaces of nearly all materials sometimes behave as sharp notches whose tips are as narrow as the spacing between atoms in the materials. Thus, the stress concentration at the tips of these minute scratches causes the stress to reach the theoretical strength of the material at relatively low average stress. When the theoretical strength of the material is exceeded at the tip of the notch, the bond at the notch tip breaks. As the crack propagates through the material, the stress concentration is maintained at the crack tip until the crack moves completely through the material (Lamon & Evans, 1983). Long anterio-posterior metal substructure also flexes under heavy or complex loading causing porcelain fracture (Reuter & Brose, 1984).

It was also noted that other reasons for the ceramic fractures are technical mistakes during the preparation of the restorations and claimed that occasional presence of pores inside the ceramic could account for their weakness and eventual fracture at that site (Oram & Cruicshank-Boyd, 1984). The same results were also found by Øilo (1988) who agreed that such mistakes markedly increase the failures.

Microcracks in ceramic could also be caused by the condensation, melting, and sintering process of the ceramics on metal due to thermal coefficient differences (Yamamato, 1985). Faulty design of the metal substructure, incompatible thermal coefficients of expansion between the metal substructure and ceramic, excessive porcelain thickness with inadequate metal support, technical flaws in the porcelain application, occlusal forces or trauma were also included as the failure reasons (Diaz-Arnold, Schneider & Aquilino, 1989). Due to the heterogeneous nature of many dental
materials, they are likely to contain defects or flaws in various amounts and sizes. Such flaws remain at fixed length unless under load but then they become unstable and propagate, catastrophically culminating in fracture. Small changes in microstructure or surface treatment can lead to drastic alterations in service life of fixed restorations and repeated stresses and strains can cause slow crack growth and mechanical fatigue. Even a single load cycle can produce measurable cracking at the contact area and damage accumulation during load cycling (Chadwick, Mason & Sharp, 1993; White et al., 1995).

Wiederhorn (1968, 1974) stressed that during actual masticatory conditions, restorations are subject to repeated loading over long periods, with superposed tangential motion and further claimed that, especially in chemically active aqueous environments, this could greatly exacerbate damage build up. He stated that the ceramic fracture process might be accelerated by the environment. It was reported that facings may crack, be fractured or damaged as a result of trauma, parafunctional occlusion or inadequate retention between the veneer and the metal (Farah & Craig, 1975). Mechanical fatigue of ceramics on the other hand, is probably governed by several mechanisms which are related to material properties including microstructure, crack length and fracture toughness, as well as to applied stress intensity (Ban & Anusavice, 1990). Evans et al. (1990) indicated that every effort should be made to minimize air entrapment between ceramic particles since porosity does occur during ceramic application and can impair aesthetics as well as promote fracture. Properties of resin adhesives, cementation agents, preparation designs, voids in cement layers, and thickness of the ceramic restorations were reported to affect the fracture resistance as well (Tsai et al., 1998). In a finite element analysis however, it was found that the presence of a void in the ceramic structure did have a significant effect on the fracture (Abu-hassan, Abu-hammad & Harrison, 1998). Another reason for porcelain fracture was attributed to inadequate tooth preparation, which results in too little interocclusal space for the metal substructure and porcelain. It was concluded that the improper design of the restoration for the occlusion is the major cause of failure (Creugers, Snoek & Käyser, 1992).

Llobell et al. (1992) described the reasons for intraoral ceramic fracture as impact load, fatigue load, improper design, microdefects within the material, and added that clinically, mastication, parafunction and intraoral occlusal forces create repetetive dynamic loading. The fatigue failure is preceded by a combination of crack initiation and crack propagation. Finally catastrophic failure occurs in the form of fracture. It was emphasized that fatigue is of
considerable importance for metal-ceramic restorations which are subjected to small alternating forces during mastication.

In order to minimize the formation of microcracks a fairly uniform thickness was recommended, which may occur during the firing of the ceramic. Avoidance of acute line angled preparations was advised since they enhance the formation of microcracks within the porcelain during the firing procedures (Burke, 1996). Bertolotti (1997) described the reasons in detail why ceramic materials do not yield in the same manner as metals. It is noted that amorphous materials like glasses or glassy materials do not possess an ordered crystalline structure as do metals. Dislocations of a crystalline lattice do not exist in glassy materials and they have no mechanism for yielding without fracture. Dislocations exist in crystalline ceramic materials, but their mobility is severely limited. The energy required to do this is so large that dislocations are essentially immobile in crystalline ceramic materials.

Stress direction is another contributory factor for failure as sometimes failure occurs at sites of relatively low local stress merely because there is a particularly large flaw oriented in a stress field which is ideal for causing fractures. The possible sites from which failure may start were found to be highly unpredictable, since this depends on flaw size and is related to the stress distribution (White et al., 1997). High biting forces, destructive premature contacts and common beverages with low pH ranges were reported to cause glass-containing dental restorations to break down (Anusavice & Zhang, 1998).

The possible failure of ceramics were sometimes attributed to inadequately registered occlusion, material type, spanning of the restoration or inadequate marginal adaptation (Niedermeier et al., 1998).

Özcan (1999) observed that the majority of the ceramic fractures occur during normal chewing function followed by either trauma or some kinds of accidents. Since complications involving fixed partial dentures can also occur during the preprosthetic preparation phase, Raustia et al. (1998) noted that the clinical skill of the dentist or dental student is extremely important.

Conclusions

Fracture of porcelain is often considered an emergency treatment and the restoration process can present a difficult challenge to the dentist. Clinical studies indicated that the prevalence of ceramic fractures ranged between 5-10% over 10 years of use (Coornaert et al., 1984).

Because of the nature of the porcelain processing, new porcelain cannot
be added to an existing restoration intraorally. The manual fabrication of metal frameworks and the porcelain veneers is time consuming and requires a high level of skill (Freilich et al., 1998). It is an unpleasant experience for the patient and arduous for the dentist to remove these restorations from the mouth. Replacement of a failed restoration is not necessarily the most practical solution because of the obviously substantial costs and the complex nature of the restoration (Fan, 1991).

The complexities of the oral environment and varied surface topography of dental restorations make it difficult to precisely define the magnitude and mode of stresses precipitating clinical fracture. The laboratory cannot reproduce intraoral variables and the complexities of the oral environment. When the crowns are cemented intraorally, factors other than inherent mechanical strength of the materials come into play. Under continuous application of the mechanical environmental loads, progressive degradation may lead to crack initiation and growth and ultimately to a catastrophic failure of the restoration. Although failures of ceramic-fused-metal restorations can be overcome by either some repair techniques or renewal of the restoration, it is beneficial to know the reasons for the failures, especially those due to iatrogenic or technical mistakes, which would help to increase the service time of such restorations.

References


Evaluation of Alternative Intraoral Repair Techniques for Fractured Ceramic-fused-to-metal Restorations

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SUMMARY Ceramic fractures are serious and costly problems in dentistry. Moreover, they pose an aesthetic and functional dilemma both for the patient and the dentist. This problem has created demand for the development of practical repair options which do not necessitate the removal and remake of the entire restoration. Published literature on repair techniques for fractured fixed partial dentures, concentrating on the data obtained both from in vitro and in vivo studies, reveals that the repair techniques based on sandblasting and silanization are the most durable in terms of adhesive and cohesive failures compared to those using different etching agents.

Introduction

Despite the increased effort to improve the bond strength between the ceramic and the metal substrate, on occasion, fractures of ceramic veneers still occur under clinical conditions. Clinical studies indicated that the prevalence of ceramic fractures ranged from between 5-10% over 10 years of use (Coornaert, Adrians & de Boever, 1984).

Although fractures of such restorations do not necessarily mean the failure of the restoration, the renewal process is both costly and time consuming and therefore remains a clinical problem. Fractures in the anterior region pose an aesthetic problem but when they are in the posterior region, chewing function could also be affected. The published literature reveals that the reasons for failures cover a wide spectrum from iatrogenic causes to laboratory mistakes, or related to the inherent structure of the ceramics or simply due to trauma.

It is well recognized that many factors are involved in the success rate assessments of fixed partial dentures limiting the longevity of the restorations.
Need for an intra-oral repair technique

Fracture of porcelain is often considered an emergency treatment and the restoration process can present difficult challenges to the dentist. Because of the nature of the porcelain processing, new porcelain cannot be added to an existing restoration intraorally. The manual fabrication of metal frameworks and porcelain veneers is time consuming and requires a high level of skill (Freilich et al., 1998). It is an unpleasant experience for the patient and arduous for the dentist to remove these restorations from the mouth. Replacement of a failed restoration is not necessarily the most practical solution because of the obviously substantial costs and the complex nature of the restoration (Fan, 1991).

Besides some economic and technical reasons, it was reported that the cracks or crazing in the fractured area might become a haven for microorganisms and plaque accompanied by staining (Walton, Gardner & Agar, 1986). On the basis of previous studies, a consensus was reached that the repeated firing cycles cause distortion of the ceramic restorations. Deformation or most of the distortion was found to occur especially during the initial oxidation of the alloys but small changes from 30 to 99.6 µm were also examined at the margins of the restoration during the subsequent heating and ceramic applications (Van Rensburg & Strating, 1984; Richter-Snapp et al., 1988).

Intra-oral repair options provide the possibility of repairing the veneer in the patient’s mouth preventing replacement of the complete restoration. Aesthetic and functional repair, wherever possible, has many advantages over time-consuming and expensive remakes of crowns or bridges. Given these problems and concerns, it is desirable to repair the fixed restorations in the mouth so that the service time can be increased in a more conservative approach. Various intraoral repair alternatives for metal-ceramic restorations have been the subject of numerous studies.

Previous intraoral repair trials

The clinical success of the ceramic repair system is almost entirely dependent on the integrity of the bond between the ceramic and the composite resin. This integrity is achieved either by chemical or mechanical bonds. Many of the previously advocated techniques were dependent on mechanical retention but the results of these earlier repairs were unsatisfactory because of aesthetic and mechanical limitations. Various repair techniques have been suggested in
the literature, many of which are considered interim but are still preferable as it is important to salvage an extensive restoration for even a few years. 3 conditions for the repair of ceramic fractures were suggested (Chung & Hwang, 1997):
1. Fracture in ceramic only
2. Fracture with both ceramic and metal exposed
3. Fracture with substantial metal exposure.

Hydrofluoric acid

Intraoral repair systems based on topical acid application have become very popular in bonding resin to ceramic. The greatest advantage of these systems is that chair-side application is very simple. Furthermore the restoration can be re-etched in the case of failure without the need for sophisticated laboratory procedures. The most often cited etching agent for the ceramic surface has been hydrofluoric acid.

It has been postulated that acid concentrations and etching times should be adjusted with specific ceramics to optimize bond strength (Calamia & Simonsen, 1984). Furthermore, the bond strength of composite resin to aluminous porcelain was found to be inferior to that of feldspathic porcelain. In principle, chemical etching agents dissolve the glass matrix selectively and cause physical alteration to promote adhesion of composite-resin to the porous surface of fractured ceramic (Calamia et al., 1985; Sheth, Jensen & Tolliver, 1988; Thurmond, Barkmeier & Wilwerding, 1994).

Ceramics etched with hydrofluoric acid demonstrate a microstructure that appeared most conducive to the development of high strength as a function of the number of large porosities within its amorphous surface. Resin penetration of these spaces enhance micro-mechanical retention (Stangel, Nathanson & Hsu, 1987) and produces greater roughness on the ceramic surface than other acid agents (Aida, Hayakawa & Mizukawa, 1995).

Alumina content of the ceramic materials plays a significant role on the effect of hydrofluoric acid. It was stated that reducing the etching time to less than three minutes dissolved less of the glass matrix (Tjan & Nemetz, 1988). Sorenson et al. (1991) observed that etching feldspathic porcelain with 20% hydrofluoric acid for 3 min significantly increased its bond strength to composite resin. Although many commercially available, porcelains are similar in chemical formula, there are distinct differences in constituents, crystalline structure, particle size, sintering behaviour and microtopography which effect the etched surface. Alumina increases the strength of the ceramic but it is
highly resistant to chemical attack and therefore does not etch well. Higher bond strength after etching and a high percentage of cohesive failures in Vita ceramics containing 10% alumina has been observed.

Lacy et al. (1988) observed that etching the ceramic surface without using a silane coupling agent did not provide greater bond strength to the composite resin than mechanical roughening with a fine diamond bur. Llobell et al. (1992) found significantly higher bond strengths with hydrofluoric acid compared with phosphoric acid and advised use of hydrofluoric acid for mechanical retention and silane coupling agents for chemical retention. While some studies showed enhanced bond strength with the application of silane to the etched ceramic surface (Lacy et al. 1988), others exhibited significant variation in bond strengths between proprietary brands of silane. On the other hand, especially after hydrofluoric acid treatment, the use of silane coupling solutions promoted good results (O’Kray, Suchak & Stanford, 1987; Nicholls, 1988; Bailey, 1989).

From a clinical point of view, hydrofluoric acid application alone was considered inadequate when preparing a ceramic surface for composite resin bonding (Pameijer, Louw & Fischer 1996). Matsumara et al. (1989) concluded that acid treatment might only be useful, in practice, to remove the smears from the ceramic. In another study, increased incidence of cohesive failures were observed in samples pretreated with 9.5% hydrofluoric acid due to deep acid penetration but 5 minutes of hydrofluoric acid application to be too long (Wolf, Powers & O’Keefe, 1992). Durability of bonding between composite resin and ceramic formed with chemical agents was markedly inferior to alteration of the ceramic surface with either aluminum oxide air abrasion, hydrofluoric acid or a combination of both (Thurmond, Barkmeier & Wilwerding, 1994).

Although new chemical etching systems claimed to provide adequate retention, the study by Tylka & Stewart (1994) indicated that these chemical etchants unfortunately produce a shallower etch pattern on metal. They also reported that even though an optimal bond could be achieved with either etchant or in conjunction with an organosilane, the intraoral use of dangerous hydrofluoric acid should be seriously questioned.

The hazards of hydrofluoric acid are well recognized. Despite its effectiveness, hydrofluoric acid presents severe hazards to human tissue and advised more reasonable repair alternatives (Chung & Hwang, 1997). Practitioners were warned, indicating that the problem is particularly acute when adequate rubber dam isolation is not possible, such as repair cases of fixed partial dentures where a tight cervical seal cannot be attained.

There has been only one clinical study conducted using etching gel for the repair process (Creugers, Snoek & Käyser, 1992). In this study, in order to
study the effect of 37% phosphoric acid application, the surfaces of 20 ceramic crowns were fractured on purpose. 12 of them included metal exposure, and 8 of them had fractures with no metal exposure. Crowns were cemented and the patients were recalled at 2 weeks, 3, 6 and 12 months after the repair. The failure rate was found to be 50% after 12 months. Failures were mostly observed at the bonding interface between the crown and the repair resin with no cohesive failures. The survival rate was noted to be 59% at the end of 12 months of the evaluation period. Because of the low survival rate, this method was not recommended for use, especially in occlusal repair of metal-ceramic crowns.

Although hydrofluoric acid is considered to be a dangerous, harmful, irritating compound and categorized as a poisonous reagent (Llobell et al. 1992), both laboratory evaluations and clinical procedures concerning its use for intraoral porcelain repair have been reported. Etching with hydrofluoric acid may not be practicable due to the biological risks in vivo. It still seems intraoral repair options with acid agents are effective on an interim basis. Moreover, acid etching is a method which could be used in ceramic fractures with no metal exposure.

The studies on the use of hydrofluoric acid have significant findings. Concentration of the acid and the application period are apparently important factors to note. Considering the vast range of ceramics in today's dental practice, the choice of suitable acid etching process clearly needs further research in order to avoid misleading information for the practitioners.

**Acidulated Phosphate Fluoride**

The hazards, extreme caustic effects to soft tissues and the danger for clinical use of hydrofluoric acids are well known. For this reason some studies questioned whether 1.23% acidulated phosphate fluoride gels might serve as a safe and effective substitute for etching ceramic surfaces to bond composite resin because of the reduced risk it presents. Some studies demonstrated that the bond strength of composite resin to silanized ceramic after being etched by acidulated phosphate fluoride was comparable to that of hydrofluoric acid etching (Sposetti, Shen & Levin, 1986; Wunderich & Yaman, 1986; Abbasi et al., 1988).

Lacy et al. (1988) reported that ceramic surfaces could be etched with 1.23% acidulated phosphate fluoride gels in relatively short periods of time. It was concluded that 1.23% acidulated phosphate fluoride gels can be substituted for 9.5% hydrofluoric gels as prolonged etching times were...
required with the lower concentrations of hydrofluoric acid.

Remarkable differences in the etched ceramic surface morphology were observed in visual comparisons. Application 1.23% acidulated phosphate fluoride gel was found to create smooth, homogenous surfaces on the exposed ceramic, whereas hydrofluoric acid produced a porous, amorphous surface. The widely accepted theory that hydrofluoric acid enhances the composite resin bond to ceramic more than an acidulated phosphate fluoride was not substantiated (Senda, Suzuki & Jordan, 1989; Tylka & Stewart, 1994). The SEM findings showed that etching by acidulated phosphate fluoride gel might not be adequate (Nelson & Barghi, 1989).

No significant difference was found between the tensile bond strengths for specimens etched with 9.6% hydrofluoric acid and those of specimens etched with 4% acidulated phosphate fluoride gel in the data obtained by Della Bona & van Noort (1995). However, the group etched with 4% acidulated phosphate fluoride gel, showed a wider statistical spread than the one etched with 9.6% hydrofluoric acid. This suggested that hydrofluoric acid etching might well produce a more reliable and consistent result but this has not been confirmed since the sample size was too small.

This literature review led to the conclusion that intraoral use of acid agents appears to be unwarranted.

**Micromechanical roughening**

Some practitioners have relied on mechanical retention such as grooves or undercuts to retain the composite resin to ceramic or metal. Owing to microleakage and humid intraoral conditions, this type of repair was considered as an interim procedure. It was reported that the use of fine and coarse diamond burs increases crack initiation and propagation through the ceramic which could result in failure (Wood et al., 1992). These trials did not give long lasting, predictable results in ceramic repair.

**Air abrasion with Al₂O₃**

One easy method for intraoral repair is roughening the surface by air abrasion with Al₂O₃, thereby increasing the surface area for bonding and decreasing the surface tension. This technique was based on direct sandblasting of the surfaces by an intra-oral device. Air abrasion (or sandblasting) promotes micromechanical retention. Physical alteration of the ceramic surface with
$\text{Al}_2\text{O}_3$ was mostly achieved using a particle size of 50 µm. Air abrasion improves the retention between the metal and resin by cleaning oxides or any greasy materials from metal surfaces, creating very fine roughness enhancing mechanical and chemical bonding between some resins and metals. When $\text{Al}_2\text{O}_3$ treatment was performed on the alloy, microscopically cleaned and roughened surfaces were observed which allowed efficient wetting by resins and stronger composite-alloy bonds (Schneider, Powers & Pierpoint, 1992).

Higher bond values with $\text{Al}_2\text{O}_3$ were obtained than those with typical silane application on etched ceramic surface and advised its use in lieu of fluoride etching (Lacy et al., 1988).

A variety of treatment regimens including medium diamond bur, air abrasion with 50 µm $\text{Al}_2\text{O}_3$, hydrofluoric acid, phosphoric acid, silane and bonding agent were compared. The shear test results revealed that the most durable bond values were obtained with physical alteration of the ceramic using $\text{Al}_2\text{O}_3$ air abrasion followed by hydrofluoric acid (Thurmond, Barkmeier & Wilwerding, 1994).

Sandblasting was described as the most effective surface treatment for the fractured metal-ceramic restorations no matter whether the surface was simplified with metal, porcelain, or a combination of the two. Sufficient bond strength was obtained with $\text{Al}_2\text{O}_3$, eliminating the use of caustic and potentially harmful acid agents (Chung & Hwang, 1997). However the compulsory use of silane together with $\text{Al}_2\text{O}_3$ was advised in order to avoid changes in retention (Shahverdi et al., 1998).

Combined data from the literature revealed that sandblasting with $\text{Al}_2\text{O}_3$, is an effective surface treatment regardless of whether the fracture was metal, porcelain, or a combined exposure. It was also stressed that air abrasion does not expose patients to the risk of severe acid burns. Controversial reports on the effect of whether $\text{Al}_2\text{O}_3$ should be used alone, followed by silane application or together with hydrofluoric acid, needs to be identified. Furthermore, concerns on the mechanism of each treatment regimen should also be clarified.

### Combined surface treatments

Some trials combined the above-mentioned methods in order to obtain better bond strengths.

Combined use of silane with hydrofluoric acid or air abrasion demonstrated better results with $\text{Al}_2\text{O}_3$ air abrasion than those with etched ceramic surfaces (Bertolotti, Lacy & Watanabe, 1989). Llobell et al. (1992)
observed that silane and hydrofluoric acid combinations did not affect the bond strengths positively.

Various surface treatments including air abrasion with Al$_2$O$_3$ of 50 µm, roughening with a diamond, etching with 9.6% hydrofluoric acid and a combination of the latter two methods were evaluated (Suliman, Swift & Perdigao, 1993). Shear tests revealed that the most effective surface treatment combinations were: mechanical roughening with diamond burs and then chemical etching with hydrofluoric. In another study, it was advised to acidify the surface with 32% phosphoric acid in combination with Al$_2$O$_3$ air abrasion or roughen with a diamond instrument to alter the ceramic surface. It was also found that the durability of bonds between composite and ceramic formed with chemical agents was markedly inferior to alteration of the ceramic surface with either Al$_2$O$_3$ air abrasion and hydrofluoric acid or a combination of both (Thurmond et al., 1994).

Castellani et al. (1994) roughened the exposed metal and ceramic surfaces with a diamond bur and created mechanically retentive areas on the metal surface. The best results were observed with the use of 50 µm Al$_2$O$_3$ sandblasting on the etched surface of the metal. Pameijer, Louw & Fischer (1996) obtained the best results in their study with the combined use of sandblasting and hydrofluoric acid application. Shahverdi et al. (1998) found that the combination of chemical and mechanical retention techniques seem promising for improved bond strength. In their study, the samples treated first with air abrasion, then with hydrofluoric acid and silane exhibited the highest shear bond values compared to those of the air abraded and silanized or hydrofluoric acid etched and silanized groups.

Although the data appear to document the efficacy of air abrasion, it appears that optimum protocol for the treatment of either ceramic or metal using these methods is yet to be defined.

**Air abrasion with SiO$_x$**

Although satisfactory bonding between ceramic and metal is achieved in current dental practice, many attempts have been made to develop better techniques for bonding composite resin materials to dental alloys. The nature of the metal-resin junction is critical; therefore, the strength of the bonding system, its resistance to microleakage, and the minimum space required for the system are very important. As an alternative to the conventional mechanical retention systems, chemical retention systems aim to develop a bond between metal and resin. This has led to the development of various
surface conditioning techniques.

Guggenberger (1989) introduced the Rocatec® System*, which presented a new kind of acrylic-metal bonding system. The principle is tribochemical application of a silica layer by means of sandblasting. According to the extraoral use of the Rocatec® System, samples are blasted with 110 µm grain size aluminum oxide particles modified with silicic acid, so called, Rocatec® Plus*. The blasting pressure results in the embedding of silica particles on the metal surface rendering the surface chemically more reactive to resin via silane. The Rocatec® System was proclaimed to be a novel acrylic/metal bonding system. Shear, compression and tensile tests revealed increased bond strength values with this system compared to those obtained from mechanical bead retention, even after thermocycling and storage in water for one year.

Edelhoff & Marx (1995) conducted a study in which different surface conditioning methods were used for ceramic surfaces including diamond roughening, sandblasting, silica coating, and acid etching. The results obtained by silica coating showed significantly higher bond strengths of resin on ceramic surfaces compared with other systems. Best results were obtained when the nozzle of the intraoral sandblaster was held perpendicular to the surface at a distance of approximately 10 mm. Depending on the size of the fracture, it was advised that the surface be sandblasted for approximately 13 s (Proano et al., 1998).

In another study which was performed on disc samples, removing the debris layer with SiOx of 30 µm particle size resulted in higher bond strengths of resins to ceramic surfaces with no metal exposures. Mostly cohesive failures were observed and use of particles of 110 µm grain size was found to decrease the bond strengths compared to the etching technique after 24 h of water storage at 37°C (Sindel, Gehrlicher & Petschelt, 1996). The same research group compared 5% hydrofluoric acid etching with use of SiOx of 30 and 110 µm particle size. In that study, 30µm silica coating showed significantly higher bond strength values with cohesive failure modes than those obtained with acid etching after 24 h of storage in distilled water without thermocycling (Sindel, Gehrlicher & Petschelt, 1997). This study has significant findings but it could be criticized on the grounds that storage period was too short.

In a subsequent study, bond strengths using two different coating methods were evaluated. After storage in distilled water at 37°C for 30, 90, 150, 360 days without thermocycling, the test samples were subjected to tensile loads until they fractured. Significant differences in bond strength were obtained especially after an interval of 360-day-period. The tensile bond

* ESPE, Seefeld, Germany
strength for the intraoral silica coating technique using SiO$_x$ of 110 µm grain size showed better results than that of 30 µm SiO$_x$ and Al$_2$O$_3$ after 60 sec of application on NiCr alloys (Edelhoff, Marx & Spiekermann, 1998). The outcome of this study is in contrast with the findings of Sindel et al. (1997).

**Some aspects of silane pre-treatment**

The system of bonding composite resin to dental porcelain using silane solutions produced reliable bonds. It was thought to be an effective method for intraoral repair of fractured or chipped ceramic restorations. However, this method, reported in the 1970s by Newburg & Pameijer, suffered from difficulties at first because of the instability of the silane solutions used to prepare the ceramic surface. Silane coupling agents have been steadily improved, producing higher bond strengths. For an effective bond of resin to feldspathic porcelain and metal, the use of silane in combination with a surface treatment is compulsory. Silane promotes adhesion between the fractured ceramic and the repair resin. Recent advances in silane coupling agents appear to enhance bond strength by promoting a chemical bond between the composite resin and the porcelain (Calamia et al., 1985; Tjan & Nemetz, 1988; Hayakawa et al., 1992; Mueller, Olsson & Söderholm, 1997).

Eames et al. (1977) evaluated various organosilanes to establish their bonding to ceramic or metal and observed that they did not bond to the metal surface as they had with the ceramic. In other studies, silane coupling agents were found to improve the bonding of composite resin to ceramic by approximately 25%. These studies demonstrated the use of silane or its degraded solutions to be completely ineffective when used on a glazed ceramic surface (Newburg & Pameijer, 1978; Diaz-Arnold, Schneider & Aquilino, 1989; Lacy et al., 1988).

Rapid increase in the amount of water absorbed by the composite material causes hydrolysis and degradation of the silane. Water storage and thermocycling were described as detrimental for the silane-ceramic bond (Roulet, 1987). Reuter & Brose (1987) reported that silanized interfaces appear to be unstable in humid conditions and the silane bond was found to deteriorate under atmospheric moisture. Since the resins are permeable to water, the bond between silane and composite resin was expected to deteriorate by hydrolysis over time. It was concluded that in humid conditions this may lead to stress corrosion and subcritical crack growth.

In other studies, it was indicated that the use of silane is a must but different composite systems yield different values. It was noted that there is
little information on the bond strength between organosilane and ceramic repair materials (O’Kray, Suchak & Stanford, 1987; Bailey, 1989).

The use of the Rocatec® System (SiO_x) increased the bond strength effectively because of the increase in silica content, which provided a basis for the silanes to enhance the bonding with the resin. For a better clinical success, Guggenberger (1989) advised the use of silane coupling agents as crucial ingredients in creating long-term bonds of resin to ceramic or metal.

A study conducted by Shahverdi et al. (1998) concluded that although silane coupling agents are capable of forming bonds with both inorganic and organic surfaces, silane itself was not found to help in bonding. Therefore, its use in combination with silica coating was recommended. In this study, in the cases where silane was not used, the bond strengths were less after water storage for 30 days. The data showed that when only silane was applied on the ceramic surfaces, the bond strength did not improve because of insufficient mechanical retention.

Studies indicated that silane coupling agents are important in the adhesion of composite resin to ceramic. The main contribution to the obtained values was made, not by the mechanical interlocking of the composite resin, but by the formation of siloxane bonds via silane (Söderholm et al., 1984).

The implication found in these studies was that silane coupling agents improves wettability and contributes to covalent bond formation between the ceramic and the resin composite. Literature supports silanization of ceramics, which provides a more reliable bond than etching with hydrofluoric acid only but little is known about the hydrolytic stability of the silanes especially in humid conditions.

**Repair composite-resins**

Composite resins are commonly used for the repair of ceramic fractures. If there is a small part missing, composite resins of appropriate shade have been the material of choice for aesthetic appearance and ease of manipulation.

In order to withstand the functional loads, the bond between the repair material and the restoration must be sufficiently strong. The repair material which ensures this bond should have a minimal coefficient of thermal expansion and minimal polymerization shrinkage. The type of composite resin also affects its bond strength to ceramic. Larger particle size composite resins or hybrid type resins at the ceramic interface result in higher bond strength than those of microfilled composite resins (Gregory & Moss, 1990). For repair purposes, use of the hybrid composite resins was advised as the most suitable
ones (Lutz & Phillips, 1983). Bond strengths are also dependent on the type of the composite resin used. Hybrid composite resin was found to increase strength and decrease stress compared with a microfilled one (Simonsen & Calamia, 1983; Stangel, Nathanson & Hsu, 1987). The problems of wear and surface changes are not related to the repair system but to the use of the microfilled composite resin which could be minimized if a hybrid composite resin is used. It is also recommended to be used where fatigue loading is of consideration (Creugers, Snoek & Käyser, 1992; Llobell et al., 1992).

A large number of studies investigated the effect of surface treatment regimens on the bond strength of composite resins to ceramic surfaces. The data from these studies should be interpreted cautiously as the type of the repair resins used in these studies exhibit different structures.

**Effect of thermocycling**

The durability of the bond values under the stresses of the oral environment is important for clinical predictability of dental materials. Usually, dental materials are subject to mechanical, thermal, and chemical stresses in the mouth during oral functions. Thermocycling and water storage *in vitro* is a common way of testing dental materials to establish their suitability for *in vivo* use. Exposing the specimens to thermocycling speeds up the diffusion of water in between the composite resin and the metal or ceramic. Changing the temperature creates stress at the interface of the two materials because of different coefficients of thermal expansion. Most of the studies with repair process involved different thermocycling times but the common consensus was that the thermocycling decreased the bond strength as it weakens the resin structure (Cochran et al. 1988).

Water storage and thermocycling are detrimental to the silane-ceramic bond as well. However, it was not clarified whether the silane was broken down by the water storage or thermocycling (Cochran et al., 1988; Pratt et al., 1989).

With the use of silica coating, Peutzfeld & Asmussen (1988) found no statistical decline in the adhesive strength from the initial bonding results obtained after 20 h of water storage at 36°C plus 6 h thermocycling repeated 180 times between 15-70°C and those after one year water storage and repeated 900 times thermocycling between 15°C to 70°C. However in another study, thermocycling caused decreased bond strength values for samples sandblasted with 50 µm Al₂O₃ (Wolf, Powers & O’Keefe, 1992).

A comparative study was performed by Kern & Thompson (1993) between 5 different resin-bonding systems to cobalt-chromium alloys. The samples
were stored in artificial saliva for 150 days at 37°C and every second day they were subjected to 1000 thermocycles in a temperature range of 5 to 55°C for 75000 cycles. Samples were tested after 24 h, 10, 30, 90 days and after 150 days of water storage. The results indicated that, in contrast to the micromechanical bonding systems, silica coating showed no significant change in the tensile bond strength during this observation period. The system was recommended as suitable for cobalt-chromium alloys used in resin-bonded restorations.

The relevance of the studies in which thermocycling was applied for a shorter period of time should be questioned. There seems to be a lack of agreement that water storage and thermocycling have decreasing effects on the resin-ceramic bond. The main reason for this could be attributed to various thermocycling times in the experiments.

Conclusion

Successful intraoral repair of fixed partial dentures has been a great problem especially when the metal substructure is exposed (Chung & Hwang, 1997).

From the previously introduced intraoral repair techniques, organosilane coupling agents are not able to bond to metal surfaces as they do to dental ceramics (Bailey 1989). Hydrofluoric acid and acidulated phosphate fluoride facilitate micromechanical retention but these chemical agents are not applicable to the fractures where metal is exposed and they are also hazardous to soft tissues. Mechanical roughening of the metal or ceramic with fine and coarse diamond burs however, are reported to provoke crack initiation and propagation through the ceramic. Both experimental and clinical reports provided evidence of significant differences between the repair techniques but the results were not uniform and therefore they were considered to be interim procedures.

For the repaired restoration to withstand functional loads, the bond between the repair resin and the remaining restoration must be strong and durable. Recently, the advantages of extraoral silica coating (tribochemical coating) using the Rocatec® System were combined with the practical use of an intraoral sandblaster in order to get a better bond strength in repairing fractured veneers in vivo. Although the intraoral sandblasters had already been designed to be used with Al₂O₃, because of their superior advantages, SiOₓ (aluminium oxide coated SiOₓ particles) was used instead of Al₂O₃, together with silane application (Proano et al., 1998, Özcan 1999).

At present, the minimum bond strength for retention of an adhesive to a
metal-ceramic restoration in the oral environment is not known. Maximum bite force capability of each patient, the estimated biting force on specific teeth, the presence or absence of surface damage may reduce the success rate. There is however, insufficient clinical data available at this time to predict the clinical performance from *in vitro* studies and the performance of ceramic repairs *in vivo* (Özcan, Schulz & Niedermeier, 1999).

From the available literature, it could be interpreted that the innovative air abrasion technique with SiO$_x$, recently called the CoJet$^\circledR$-System*, does not expose the patients to the risk of severe acid burns with the advantage of repairing fractures with both ceramic and metal exposure. Owing to the increasing number of composite resin materials on the market, it is still not easy to choose the best one. When the composites are used in the anterior region, more aesthetic expectations should be fulfilled and the clinician must meet both aesthetic and functional challenges. They should behave similarly to dentin and enamel with respect to the properties of reflection, refraction, scattering and transmission of light to give the illusion of natural teeth.

Before any attempt at a repair, the underlying metal substructure should first be found to be sound and that it is not the real cause of the failure. If this is the reason, instead of attempting the repair process, the restoration should be renewed.

When evaluating the current literature on ceramic repair techniques, the variables of composite resin, storage conditions and silane application should be taken into consideration.

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