Effect of three surface conditioning methods to improve bond strength of particulate filler resin composites

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The use of resin-based composite materials in operative dentistry is increasing, including applications in stress-bearing areas. However, composite restorations, in common with all restorations, suffer from deterioration and degradation in clinical service. Durable repair alternatives by layering a new composite onto such failed composite restorations, will eliminate unnecessary loss of tooth tissue and repeated insults to the pulp. The objective of this study was to evaluate the effect of three surface conditioning methods on the repair bond strength of a particulate filler resin-composite (PFC) to 5 PFC substrates. The specimens were randomly assigned to one of the following surface conditioning methods: (1) Hydrofluoric (HF) acid gel (9.5%) etching, (2) Air-borne particle abrasion (50 μm Al_2O_3), (3) Silica coating (30 μm SiO_x, CoJet®-Sand). After each conditioning method, a silane coupling agent was applied. Adhesive resin was then applied in a thin layer and light polymerized. The low-viscosity diacrylate resin composite was bonded to the conditioned substrates in polyethylene molds. All specimens were tested in dry and thermocycled (6.000, 5–55 °C, 30 s) conditions. One-way ANOVA showed significant influence of the surface conditioning methods ($p < 0.001$), and the PFC types ($p < 0.0001$) on the shear bond strength values. Significant differences were observed in bond strength values between the acid etched specimens (5.7–14.3 MPa) and those treated with either air-borne particle abrasion (13.0–22.5 MPa) or silica coating (25.5–41.8 MPa) in dry conditions (ANOVA, $p < 0.001$). After thermocycling, the silica coating process resulted in the highest bond values in all material groups (17.2–30.3 MPa).
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1. Introduction

In dentistry today PFC materials, applied directly or indirectly, occupy an important position as they achieve acceptable longevity at a much lower cost than their ceramic counterparts. PFC restorations, especially when used as laminates, allow for minimally invasive preparations, or no preparations at all, for the replacement of missing tooth tissues by means of basic layering technique.

Novel dental composites today generally consist of a monomeric matrix resin, silanated inorganic fillers, a polymerization initiator system, inhibitors for storage stability, and pigmentation for shading. Although marked improvements have been noted in terms of physical and mechanical properties during the last 10–20 years, enzymes present in the oral cavity, for instance, can degrade the composite matrix [1–3].

Moreover composites are less stable in fluids and their degradation rate is higher in saliva simulating conditions, depending on the chemical nature of the monomers, amount of dimers and oligomers, the degree of cross-linking in the polymerized matrix, and other intraoral impact [4–6]. In addition, fatigue can accelerate the wear process in composite materials. All these factors result in discoloration, degradation, microleakage, wear, ditching at the margins, delamination or simply fracture being often experienced in clinical situations, which in turn, may require repair or replacement of the restoration [7–11].

Repair as an alternative to complete removal, would preserve the tooth as it is often difficult to remove an adhesive restoration without removing an integral part of the tooth [12, 13].

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A number of techniques have been proposed to improve bond strength of composite repair through roughening, etching the substrate surface with acidulated phosphate fluoride, HF acid gel, air-borne particle abrasion or using adhesive resins [14–21]. While several researchers found that the surface roughness of the composite was an important factor in developing high repair bond strength [21, 22], others reported that grinding or roughening of the bonding surface decreased the bond strength [15, 20, 23]. Despite the hazardous effects of HF acid gel, etching the surface of a composite restoration with this acid followed by the application of a silane coupling agent is a well-known and recommended method to increase bond strength. Although HF acid was found effective in roughening the composite surface for bonding resin composite [24, 25], neither etching with these solutions nor adding silane resulted in an adequate resin bond to some resin composites [26–29].

Recent developments in surface conditioning methods have resulted in improved resin-to-resin bond strengths. One alternative has been introduced with the use of silica coating and silanization [30]. Although comparative studies showing the advantages of various types of surface conditioning methods on different composites exist, there seems to be no consensus in the literature regarding the best conditioning method for individual PFCs.

Therefore, the objectives of this study were to evaluate the effect of three surface conditioning methods on the shear bond strength of a PFC to five PFC materials and to identify whether there exists an optimum method.

2. Materials and methods

Thirty-six specimens were made from five brands of PFC materials, namely Gradia (GRA), Sculpture (SCU), Sinfony (SIN), Targis (TAR), Tetric Ceram (TET) (total number of specimens = 180). The composites were packed into cylindrical (diameter: 6 mm, thickness: 2 mm) undercut cavities prepared in auto-polymerized poly(methylmethacrylate) (Palapress, Vario, Heraeus Kulzer) with a hand instrument and polymerized incrementally according to each manufacturers' recomendations. Tables I and II summarize the composition of PFC types with codes and

manufacturing company names. The exposed surface of each specimen was ground finished to 1200 grit silicon carbide abrasive (Struers RotoPol 11, Struers A/S) and cleaned for 10 min in an ultrasonic bath (Quantrex 90 WT, L&R Manufacturing Inc.) containing distilled water and air-dried. Subsequently, the substrates in each PFC group ($n = 6$) were randomly assigned to one of the three conditioning methods:

2.1. Surface conditioning methods

Method 1: The substrates were etched with 9.5% HF acid gel (Ultradent® Porcelain Etch) for 90 s in accordance with the manufacturer's recommendations.

Method 2: Air-borne particle abrasion with 50 μm Al_2O_3 (Korox®, Bego) was applied using an intraoral air abrasion device (Dento-Prep™, RØNVIG A/S) from a distance of approximately 10 mm at a pressure of 2.5 bars for 4 s.

Method 3 was a silica coating process that was achieved using the same device under the same conditions as method 2 but this time 30 μm SiO_2 (CoJet®-Sand, 3M ESPE AG) was used.

The conditioned substrates were then coated with a 3-methacryloxypropyltrimethoxysilane coupling agent, γ-MPS (ESPE®-Sil, 3M ESPE AG) and waited for its reaction for 5 min. An intermediate monomer resin (IMR) (Scotchbond Multipurpose Adhesive, 3 M Dental Products) was applied a thin layer and it was light-polymerized (Optilux 501, Kerr) for 10 s.

In an additional experiment, ($n = 15$, 1/group) the conditioned surfaces of the five substrates were first gold sputtered and then examined using a scanning electron microscopy, SEM, (JSM-5500, Jeol Instruments).

2.2. Bonding procedures

The bonding procedures were carried out in accordance with the manufacturers' instructions by the same operator throughout the experiments. The low-viscosity diacrylate resin composite (Sinfony Dentin, Shade A2, 3M ESPE) was bonded to the conditioned PFC substrates in translucent polyethylene molds with inner diameter of 3.6 mm and height of 5 mm. The Sinfony Dentin was packed against the substrate with a composite-filling instrument and polymerized in a

TABLE I Monomer types and percentages of particulate filler composites with codes, and manufacturing company names

Trade name	Abbreviation	Matrix type	Manufacturer
Gradia	GRA	UEDMA/ ethylene dimethacrylate[1]	GC, USA
Sculpture	SCU	dimethacrylate[2]	Jeneric Pentron, USA
Sinfony	SIN	HEMA/diacrylate[3]	3M ESPE, Germany
Targis	TAR	Bis-GMA, DDDMA, UEDMA, TEGDMA[4]	Ivoclar Vivadent AG, Liechtenstein
Tetric Ceram	TET	Bis-GMA, UEDMA, TEGDMA[5]	Ivoclar Vivadent AG, Liechtenstein

Bis-GMA = Bis-phenol-A-glycidylmethacrylate, UEDMA = Urethane dimethacrylate, TEGDMA = Triethyleneglycol dimethacrylate, DDDMA = Decandiol dimethacrylate, and HEMA = 2-hydroxyethyl methacrylate.
[1]UDMA (10–25%) and ethylene dimethacrylate (5–10%).
[2]Dimethacrylate.
[3]10–30% (octahydro-4,7-methano-1H-indenediyl) bis(methylene)diacrylate).
[4]Bis-GMA (9%), DDMA (4,8%), UEDMA (9.3%).
[5]Bis-GMA (<9%), TEGDMA (<5%), UEDMA (<8%).

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Trade name	Abbreviation	Filler type and content
Gradia	GRA	alumina silicate glass (40–50 wt%), Amorphous precipitated silica (5–10 wt%)
Sculpture	SCU	Glass-infiltrated alumina (70 wt%)
Sinfony	SIN	Strontium-aluminium borosilicate glass, silicon oxide (50 wt%)
Targis	TAR	Silanized barium glass fillers (46.2 wt%), highly dispersed silica (11.8 wt%), mixed oxides (18.2 wt%), catalyst and stabilizers (0.6 wt%), pigments ($\leq$0.1 wt%)
Tetric ceram	TET	Silanated Ba-glass, ytterbium trifluoride, silanated metal oxide, silanated barium-aluminum-fluoro-silicate glass, silanated silica glass (79 wt%)

Figure 1 (a)–(c). Shear bond strengths after (a) Hydrofluoric acid etching, (b) Air-borne particle abrasion and (c) Silica coating at dry and thermocycled conditions. Vertical lines represent the standard deviations. For abbreviations, see Table I.

light-curing oven (Visio Beta Vario, 3M ESPE) for 40 s. Polyethylene molds were gently removed from the test specimens.

All groups of PFC/conditioning method combinations were randomly divided into 2 groups ($n = 6$) for dry and thermocycled storing conditions. While dry samples were kept in a dessicator at room temperature for 24 h prior to testing, the other groups were subjected to thermocycling (Thermocycler 2000, Heto-Holten A/S) for 6.000 cycles between 5 °C and 55 °C in deionised grade 3 water. The dwelling time at each temperature was 30 s. The transfer time from one bath to the other was 2 s.

Specimens were mounted in a jig (Bencor Multi-T shear assembly, Danville Engineering Inc.) of the universal testing machine (Lyold LRX, Lloyd Instruments Ltd.) and the shear force was applied to the adhesive interface until failure occurred. The specimens were loaded at a crosshead speed of 1.0 mm/min and the stress-strain curve was analyzed with Nexygen 2.0 software (Lyold LRX, Lloyd Instruments Ltd).

Statistical analysis was performed using SAS System for Windows, release 8.02/2001 (SAS Institute Inc). *P* values less than 0.05 were considered to be statistically significant in all tests. The differences in means of each group were analysed by analysis of variance (ANOVA) with shear bond strength as the dependent variable, the surface conditioning methods and the PFC types as the independent factors. Since the interaction between surface conditioning methods and PFC types were statistically significant (two-way ANOVA, $p < 0.0001$) in dry and thermocycled conditions, one-way ANOVA with multiple comparisons using Tukey-Kramer adjustment test was used for further analyses. Furthermore, two-sample *t*-test was used to determine the significant differences between dry and thermocycled conditions.

3. Results

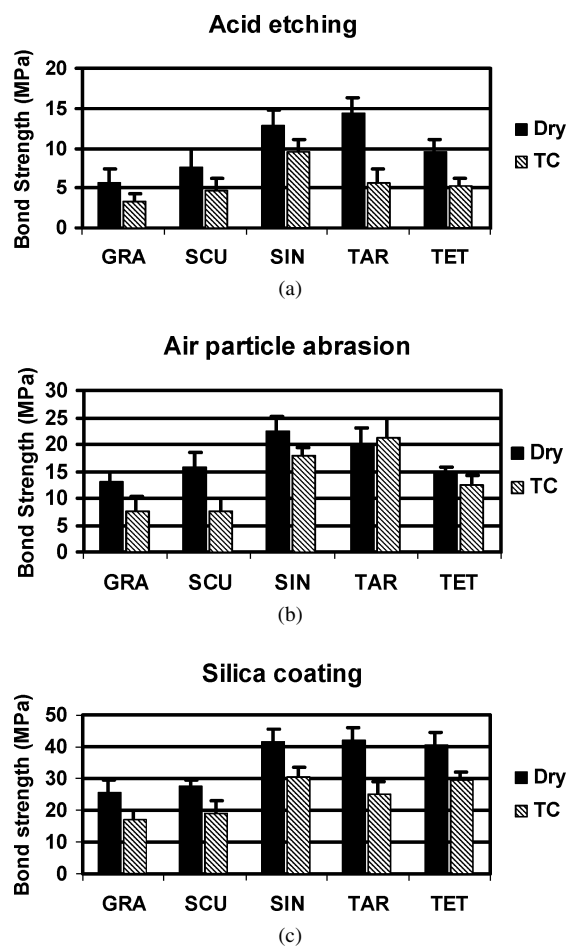The results of the shear bond strength test for HF acid etching, airborne particle abrasion and silica coating are presented in Fig. 1(a)–(c). One-way analysis of variance (ANOVA) showed significant influence of the surface conditioning methods ($p < 0.0001$), and PFC type on the bond strength values ($p < 0.001$). The differences in bond strength between storage conditions were significant except for TAR after air-borne particle abrasion (two-sample *t*-test, $p < 0.05$).

Conditioning the PFC substrates with the HF acid etching resulted in the lowest bond strength values amongst all conditioning methods ranging between 5.7 MPa and 14.3 MPa in dry conditions and between 3.3 MPa and 9.5 MPa after thermocycling. In dry conditions after HF acid etching, there were significant differences between SIN vs TET ($p = 0.047$), TAR vs TET ($p = 0.002$). After thermocycling, there were significant differences between SIN vs TAR ($p = 0.0007$), SIN vs TET ($p = 0.0002$) in the HF acid etched groups.

In the air particle treated group, bond strengths increased significantly compared to HF acid etching for GRA (13.0 MPa, $p = 0.0007$), SCU (15.7 MPa, $P = 0.0001$), SIN (22.5 MPa, $p = 0.0001$), TAR (20.0 MPa, $p = 0.02$) and TET (14.8 MPa, $p = 0.009$) in dry conditions and for SIN (18.0 MPa, $p = 0.01$), TAR (21.2 MPa, $p < 0.0001$) and TET (12.5 MPa, $p < 0.0001$ MPa) after thermocycling.

Significantly higher ($p < 0.0001$), bond strengths were achieved after silica coating and silanization amongst all the conditioning methods for all types of

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PFCs ranging between 25.5 MPa and 41.8 MPa except for TAR after air-borne particle abrasion vs silica coating ($p = 0.17$) in dry conditions.

SEM analysis, complementary to the shear bond strength tests, revealed that HF acid gel dissolves the filler components of the PFCs and produces porous irregular surfaces (Fig. 2(a)–(e)). On the other hand, airborne particle treated groups either with Al_2O_3 or SiO_x exhibited similar rough surfaces covered with abundant sand particles on the substrate surfaces (Fig. 3(a) and (b)).

4. Discussion

The results of this study indicated that conditioning the substrates with HF acid gel adversely affected the morphological features of PFC substrates thereby resulting in poor repair strength when compared with other methods tested.

Usually inorganic fillers are integrated into the polymer matrix by silane coupling agents, that form an interface between the hydrophobic resin matrix and the hydrophilic filler particles. Commonly, hydrolyzed γ-MPS is used as a coupling agent for the fillers. When
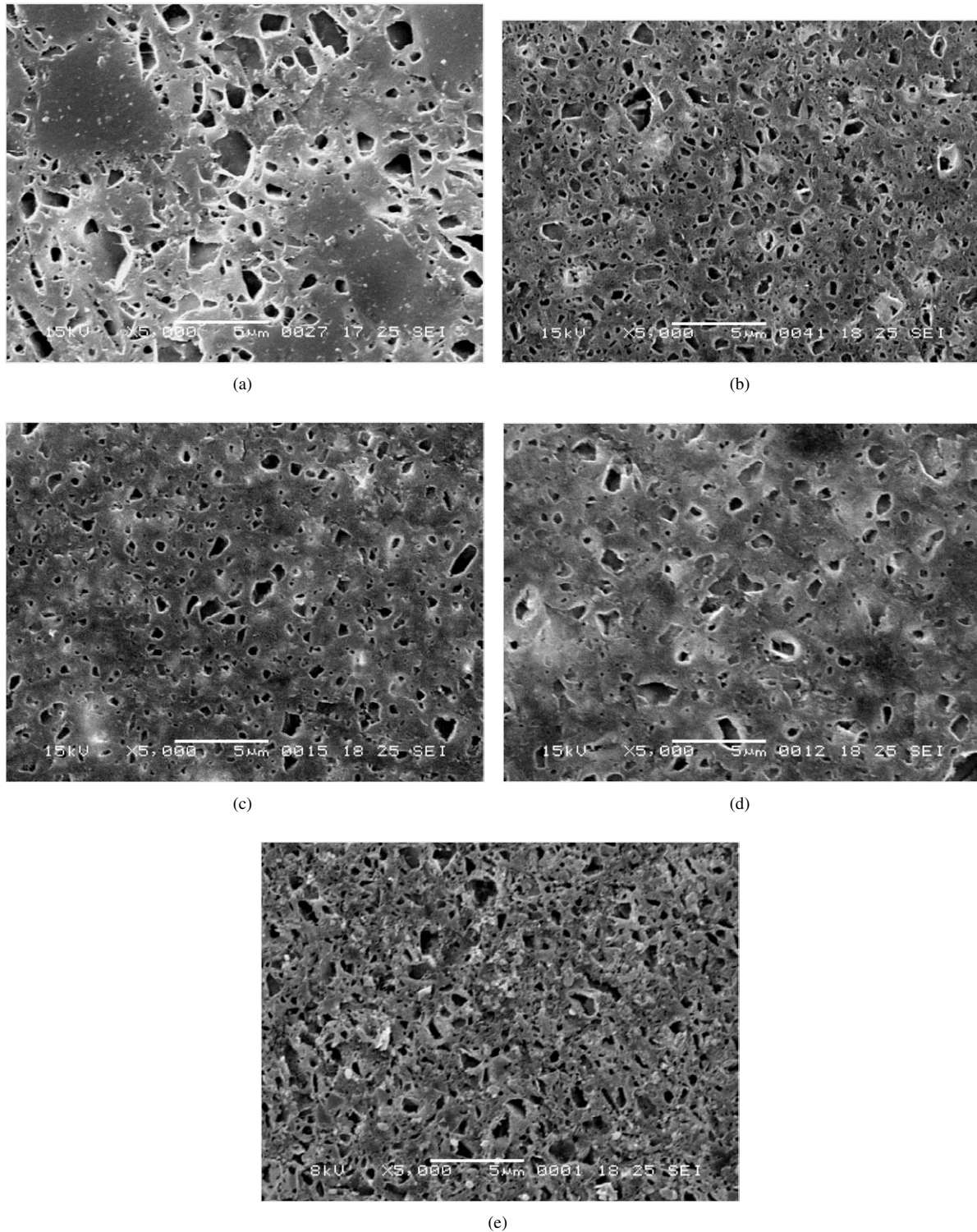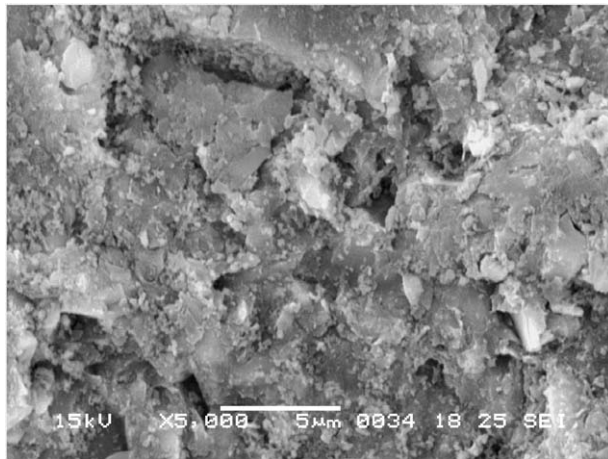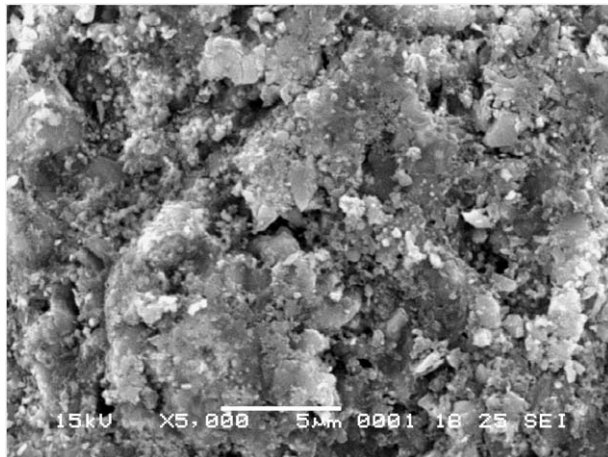

(a)

(b)

(c)

(d)

(e)

Figure 2 (a)–(e). Typical SEM view of (a) GRA, (b) SCU, (c) SIN, (d) TAR, (e) TET PFC substrates exposed to 9.5% HF acid gel application for 90 s and rinsing. Note that the acid treatment dissolved the filler components of the substrates (original magnification ×5000).

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(a)

(b)

Figure 3 (a) and (b). Typical SEM view of (a) GRA and (b) TET after airborne particle abrasion with alumina and SiO_x, respectively. Note that the surfaces were covered with abundant sand particles (original magnification ×5000).

PFC substrates are exposed to HF acid gel, a water monolayer may penetrate via voids to the filler, that in turn, may disorganize the silane layer which is responsible for stabilizing the filler-resin interface [31]. All these mechanisms may weaken the particle-matrix interface that leads to filler dissolution. This phenomenon was observed in the SEM analysis where a great portion of the fillers were lost from the matrix after they were exposed to HF acid etching (Fig. 2(a)–(e)).

The extent of filler erosion after HF acid gel treatment is dependent on the filler type. It has been reported that barium, boroaluminosilicate, silicate, strontium glass, and zinc glasses exhibited extended degradation on acid attack, whereas quartz, silica, lithium aluminosilicates and their mixtures showed less involvement [32, 33]. The SEM picture in Fig. 2(e) revealed that more fillers were dissolved from the highly filled TET (79 wt%) that is composed of silica and barium fillers. A high filler content adversely affects processing and results in too much cross-linking of the resins which could embrittle the material in a similar way to what was observed with TET. The morphologic and compositional changes obtained for the materials after etching will also be dependent on the type of acid used

as well as the composition of the restorative material. Although flourides with lower concentrations like 1.23% APF were used, similar findings were reported in a previous study where APF was found to dissolve the fillers and caused degradation [34]. In this study, etching the PFCs with a 9.5% HF gel for 90 s resulted in variations in repair strength dependent on the composite material. This is in line with the study of Swift *et al.* [24] where they found that etching with 9.5% HF acid gel for 30 s either increased or decreased the repair strengths of composites. This finding together with ours could be explained on the grounds of variations in matrix composition. All the monomers used in current composite techniques are organic esters of methyl methacrylate derivatives and generally, organic esters in low pH undergo hydrolytic cleavage of the ester group. Increased filler dissolution after HF acid conditioning might result in increased surface area exposure of the resin matrix and consequently an accelerated hydrolytic effect. This phenomenon was very evident in high filled PFCs with similar filler types (TAR, TET) when compared to a relatively low filled one (SIN).

Bond strength is dependent on unconverted C=C double bonds on the resin, which may be attributed either to a low conversion rate or a high level of matrix resin. The bond between the substrate and new resin is also based on unreacted C=C double bonds of the functional groups on the surface of polymer matrix. A high degree of conversion that resulted from the use of heat and light used for polymerization causes improvement in mechanical strength and hardness and therefore makes the attachment of the new composite more difficult. Controversy still exists regarding whether the degree of conversion is compromised when PFCs are photo-activated [33]. However, it was also assumed that a certain percentage of unconverted C=C double bonds are available even after laboratory processing [35]. In this study, in dry conditions satisfactory bond strengths were obtained according to ISO standards [36]. Although the substrate surfaces were only finished by grinding, there might be some unreacted carbon bonds available on the surface. However to what extent those types of unreacted bonding sites existed in the PFC materials, needs further clarification, namely using e.g. infrared spectroscopy for the surface charecterization.

In general, the strength, stiffness and stability of a given polymer are increased with the presence of long, individual polymer chains. This is because of the nature of the interactions between the chains. The length of the molecules or chains in a polymer is usually described in one of the following ways: (a) as the average of the molecular weight of each chain or (b) as the degree of polymerization. A third way to describe the extent to which the polymerization reaction has taken place would be to count the percentage of C=C bonds that disappear during the reaction. This can be done with infrared spectroscopic techniques and provides a value for the degree of conversion of the polymer system. Because the polymerization reaction is also referred as curing reaction, degree of conversion is synonymous with degree of cure. This is an important method for expressing the extent of the polymerisation

reaction in cross-linked network polymers such as dental composites, adhesives and sealants. In FTIR (Fourier transformation infrared spectroscopic) evaluations that have already been published, it was found that the UEDMA/TEGDMA phase had a conversion of 70% and exhibited superior wear resistance, while the Bis-GMA/TEGDMA had a degree of conversion of 55% [37]. The lowest bond strength results obtained with GRA could be attributed to its high UEDMA matrix content. In PFCs with such matrix content, the possibility to obtain free radical polymerization bonding is low because of relatively small number of unreacted C=C double bonds on the polymer surface [38]. Monomer mixtures of Bis-GMA and TEGDMA give rise to polymers in which the quantity of remaining double bonds increases with the content of Bis-GMA, without the mechanical properties being significantly effected [39].

An interesting result was achieved with the SIN composite, with octahydro-4,7-mathano-1H-indenediyl) bis(methylene)-diacrylate, in its monomer matrix. It showed high bond strengths, similar to those of Bis-GMA/TEGDMA PFCs, with also less decrease after thermocycling. One reason for this may be related to the function of IMR that may bond covalently to the pendant, unreacted methacrylate groups. It has been reported earlier that swelling of the composite substrate surface with different solvents and the use of low-viscosity IMR influence the bond between two composites [20, 38, 40]. The functions of IMR are to achieve better wetting of the substrate surface and to some degree dissolve and swell the polymer surface of the substrate. The hydrophilic adhesive joint in GRA, SCU, TAR, TET may be less rigid than the adhesive joint made by hydrophobic monomer resin such as the main monomer of SIN.

After air-particle abrasion, either with Al_2O_3 or SiO_x followed by silanization, significant increase in bond strengths was noted for all materials. When comparing the results of the acid etched groups with those of air-abraded ones, the function of silane coupling agent should not be disregarded. In this study, γ-MPS was chosen because of the compatibility of the methacrylate moiety for copolymerization with the PFC. Silane treatment also improves the wettability of the filler, affects its surface energy, hence its dispersion in the matrix. However when little or no filler remains after HF conditioning, this effect of silane could obviously not profited from. One can anticipate that alumina or silica on the surface of the substrate could form strong enough chemical bonds, covalent bridges, through its surface hydroxyl groups with hydrolyzed silanol groups of the silane:- Al—O—Si— or —Si—O—Si. The methacrylate groups of the organosilane γ-MPS compound form covalent bonds with the resin when polymerized.

It is difficult to compare our results with previous studies as storage conditions are not the same but our findings after thermocycling with the use of air-particle abrasion with either alumina or silica followed by silane coupling agent and IMR application were higher than those reports where specimens were tested either after short term water storage [34] or lower number of thermocycles [28]. After thermocycling, the bond strengths

provided were well above the recommended ISO standards [36]. While some studies reported that the type and chemical structure of repair resin have no influence on the strength of the repair [35], others proved that the use of silica coating provided a significant improvement in the repair strength [28, 30]. Boyer *et al.* [40] found that highly filled resin composites provided higher bond strengths which contradicts with our findings and warrants further research.

Water uptake has an important role in the chemical degradation of composite materials. It takes place in the resin matrix and is a diffusion-controlled process where the diffusion coefficient decreases with the concentration of water in the matrix. Many resin composite bonding studies have addressed the effect of storage time in water on bond strength of repairs. Söderholm and Roberts [41] found that the repair resin had a tendency to weaken when they were stored in water for 3 and 12 months. The variation in coefficient of thermal expansion of the materials, especially the intermediate resin, could be a factor in the reduction of bond strength after thermocycling.

5. Conclusions
Within the limitations of this study, the following conclusions were made:

1. Composite-to-composite adhesion strengths varied with the PFC types and surface conditioning methods tested.

2. HF acid gel dissolved the filler particles but resulted in lower bond strengths than alumina particle abrasion and silica coating.

3. Air-particle abrasion with silica particles followed by silanization increased the bond strengths regardless of the PFC type.

4. When compared to dry testing conditions, bond strengths decreased after thermocycling in all HF acid gel treated substrates but no significant change was noted after alumina particle abrasion or silica coating followed by silanization.

References
1. I. B. LARSEN, M. FREUNF and E. C. MUNKSGAARD, *J. Dent. Res.* (1992) 1851.
2. K.-J. SÖDERHOLM, R. MUKHERJEE and J. LONGMATE, *ibid.* (1996) 1692.
3. D. C. SARRETT, D. P. COLETTI and A. R. PELUSO, *Dent. Mater.* (2000) 62.
4. J.-F. ROULET, in "Degradation of Dental Polymers" (Basel, Karger, 1987) p. 60.
5. J. L. FERRACANE and J. R. CONDON, *Dent. Mater.* (1990) 282.
6. U. ØSTENGREN, H. WELLENDORF, S. KARLSSON and I. E. RUYTER, *J. Oral Rehabil.* (2001) 1106.
7. I. A. MJÖR and F. TOFFENETTI, *Oper. Dent.* (1992) 82.
8. I. A. MJÖR and C. M. UM *Int. Dent. J.* (1993) 311.
9. W. D. BROWNING and J. B. DENNISON *Oper. Dent.* (1996) 160.
10. F. J. BURKE, S. W. CHEUNG, I. A. MJÖR and N. H. WILSON, *Prim. Dent. Care.* (1999) 17.
11. A. R. AL-NEGRISH, *Int. Dent. J.* (2002) 461.

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12. I. A. MJØR and V. V. GORDAN, *Oper. Dent.* (2002) 528.
13. M. ÖZCAN and W. NIEDERMEIER, *Int. J. Prosthodont.* (2002) 299.
14. C. H. LLOYD, D. A. BAIGRIE and I. W. JEFFREY, *J. Dent.* (1980) 171.
15. K. C. CHAN and D. B. BOYER, *J. Prosthet. Dent.* (1983) 345.
16. D. B. BOYER, K. C. CHAN and J. W. REINHARDT, *J. Dent. Res.* (1984) 1241.
17. P. AZARBAL, D. B. BOYER and K. C. CHAN, *Dent. Mater.* (1986) 153.
18. E. C. KAO, H. G. PRYOR and W. M. JOHNSTON, *J. Prosthet. Dent.* (1988) 328.
19. A. D. PUCKETT, R. HOLDER and J. W. O'HARA, *Oper. Dent.* (1991) 136.
20. T. T. KALLIO, T. M. LASTUMAKI and P. K. VALLITTU, *Dent. Mater.* (2001) 80.
21. K. A. KUPIEC and W. W. BARKMEIER, *Oper. Dent.* (1996) 59.
22. S. A. SHAHDAD and J. G. KENNEDY, *J. Dent.* (1998) 685.
23. H. MITSAKI-MATSOU, A. KARANIKA-KOUMA, Y. PAOADOYIANNIS and S. THEODRIDOU-PAHINE, *Quintessence Int.* (1991) 475.
24. E. J. SWIFT JR. B. D. LEVALLEY and D. B. BOYER, *Dent. Mater.* (1992) 362.
25. C. W. TURNER and J. C. MEIERS, *Oper. Dent.* (1993) 187.
26. G. M. IMAMURA, J. W. REINHARDT, D. B. BOYER and E. J. SWIFT JR. *ibid.* (1996) 249.
27. E. J. SWIFT JR. B. C. CLOE and D. B. BOYER, *Am. J. Dent.* (1994) 200.
28. M. R. BOUSCHLICHER, J. W. REINHARDT and M. A. VARGAS, *ibid.* (1997) 279.
29. P. F. CESAR, P. M. MEYER FAARA, R. MIWA CALDART, R. GASTALDONI JAEGER, *et al.*, *ibid.*, (2001) 373.
30. M. ÖZCAN, *J. Prosthet. Dent.* (2002) 469.
31. E. P. PLUDDEMANN, *J. Adhesion.* (1970) 184.
32. K. KULA, S. NELSON and V. J. THOMPSON, *J. Dent. Res.* (1983) 846.
33. K. KULA, S. NELSON, T. KULA and V. J. THOMPSON, *J. Prosthet. Dent.* (1986) 161.
34. L. PAPAGIANNOULIS, J. TZOUTZAS and G. ELIADES, *ibid.* (1997) 405.
35. W. A. GREGORY, B. POUNDER and E. J. BAKUS, *ibid.* (1990) 664.
36. International Organization for Standardization, Amendment ISO 10477 (1996).
37. J. L. FERRACANE and E. H. GREENER, *J. Biomed. Mater. Res.* (1986) 121.
38. I. E. RUYTER and S. A. SVENDSEN, *Acta Odontol. Scand.* (1978) 75.
39. E. ASMUSSEN and A. PEUTZFELDT, *J. Dent. Res.* (2001) 1570.
40. D. B. BOYER, K. C. CHAN and J. W. REINHARDT, *ibid.* (1984) 1241.
41. K.-J. SÖDERHOLM, M. J. ROBERTS, *Scand. J. Dent. Res.* (1991) 173.