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"Mitään ei tapahdu jollemme ensin haaveile."

- Carl Sandburg

ABSTRACT

Milla Lahdenperä

Structural and interfacial adhesion elements of indirect fiber-reinforsed composite fixed dental prostheses

University of Turku, Faculty of Medicine, Institute of Dentistry, Department of Biomaterials Science, Finnish Doctoral Program in Oral Sciences (FINDOS-Turku) and Turku Clinical Biomaterials Centre (TCBC), Annales Universitatis Turkuensis, Turku, 2019

Crowns and fixed dental prostheses (FDP) of fiber-reinforced composite (FRC) have opened the potential for fabrication of metal-free dental restorations with direct and indirect techniques. Although direct FRC restorations are gaining popularity over indirect ones, however multiple unit restorations require fabrication in dental laboratories. FRC FDPs are composed of two types of resin composite materials: load-bearing FRC substructure and particulate filler resin composite (PFC) veneering. The objectives of this series of studies were to investigate some structural and interfacial adhesion elements of indirect FRC FPDs. In addition, incorporation of antimicrobial agent chlorhexidine digluconate (CHX) to the FRC and its release from the FRC was also evaluated.

In the first study, interfacial adhesion between E-glass FRC substructure and PFC was investigated by the shear bond strength test. Attempts to improve adhesion by intermediate resin (IMR) with different treatment times were made. Applying the IMR increased the bond strength values of PFC to FRC with multiphase polymer matrix (semi-interpenetrating polymer network of BisGMA and PMMA, IPN). It was also found that the polymer matrix of FRC can be polymerized to a high degree of monomer conversion without deteriorating the bond strength between FRC and PFC. A second study demonstrated that PFC can be better bonded to the FRC substructure with randomly oriented glass fibers than to the continuous unidirectional FRC substructure. A third study analysed the flexural properties and the release of CHX laced unidirectional FRC provisional FPD polymer. Flexural properties of provisional FPD polymer were increased by the addition of FRC, and the CHX was released into water by diffusion from the FRC during the first three weeks. The fourth study aimed to characterize water sorption, flexural properties, bonding properties, and elemental composition of two different photopolymerizable FRC materials (cross-linked and IPN polymer matrix FRC). Differences were found for the percentage of water sorption, but the flexural strength and veneering PFC bonding properties did not show a difference between the materials after 30 days of water storage.

These studies suggest that by using IMRs and randomly oriented glass fiber FRC the interfacial adhesion to PFC can be improved. Furthermore, it was found that FRC prepreg can be loaded with antimicrobial agent CHX, and the diffusion base released into water from the FRC lasted for three weeks.

Keywords: fiber-reinforced composite, short fiber-reinforced composite, fiber orientation, bonding, adhesion mechanism, intermediate resin, particulate filler resin composite, air inhibited layer, mechanical properties, water sorption, polymerization range, chlorhexidine digluconate.

TIIVISTELMÄ

Milla Lahdenperä

Epäsuoran kuitulujitteisen sillan valmistamisen rakenteelliset ja pintakiinnitteiset elementit.

Turun yliopisto, Lääketieteellinen tiedekunta, Hammaslääketieteen laitos, Biomateriaalitieteen oppiaine, Kansallinen suun terveystieteiden tohtoriohjelma (FINDOS-Turku) ja Turun Kliininen Biomateriaalikeskus (TCBC), Annales Universitatis Turkuensis, Turku, Suomi, 2019

Kuituvahvisteisella komposiitilla valmistetut yksittäiset kruunut ja kiinteät hammassillat ovat mahdollistaneet metallittoman ja esteettisen hammasta säästävän protetiikan. Suurin hyöty kuitukomposiittitekniikasta saadaan suoralla tekniikalla, mutta pidemmät siltarakenteet vaativat hammaslaboratoriovalmisteista epäsuoraa tekniikkaa. Kuitulujitteinen muoviproteesi koostuu kuiturungosta ja valokovetteisesta yhdistelmämuovista, joiden välinen kiinnittyminen on tärkeä rakenteen pitkäikäisen kliinisen toimivuuden kannalta. Tämän tutkimustyön tavoitteena oli tutkia epäsuorien kuitukomposiittirakenteiden mekaanisia ja adhesiivisiä ominaisuuksia sekä lisäksi tarkasteltiin antimikrobisen aineen, klooriheksidiinidiglukonaatin, sisällyttämistä kuitulujitteeseen ja sen vapautumista.

Ensimmäisessä tutkimusosassa selvitettiin valokovetteisen yhdistelmämuovin kiinnittymistä yhdensuuntaiseen jatkuvaan E-lasikuitulujitteeseen erilaisen väliresiinin käsittelyajan jälkeen. Todettiin monifaasisen kuitumatriisin ja yhdistelmämuovin välille siveltävän väliresiinin kasvattavan sidoslujuutta sekä mahdollistavan hyvän adheesion myös jo polymeroituun kuitukomposiitti-rakenteeseen. Toinen tutkimusosa osoitti, että yhdistelmämuovi kiinnittyy jatkuvaa yhdensuuntaista kuitukomposiittia paremmin satunnaisesti suuntautuneeseen, hieman lyhyempiä kuitupätkiä sisältävään kuitumatriisiin. Kolmannessa osatyössä analysoitiin klooriheksidiinillä (CHX) käsiteltyjen yksisuuntaisten kuitukomposiittien taivutuskestävyyttä sekä CHX:n vapautumista kuitukomposiitin sisältä. Väliaikaisen muovisiltamateriaalin taivutusominaisuuksien todettiin kasvavan CHX kuitukomposiittilisäyksen myötä ja taivutuslujuudet olivat verrattavissa yhdensuuntaisen kuitulujitteen vahvistusvaikutukseen. CHX:ä vapautui kuitukomposiitista kolmen viikon ajan vesisäilytyksen aloittamisesta. Neljäs osatyö vertaili kahden erilaisen valokovetteisen kuitukomposiitin vesisorptiota, taivutus- ja sidosominaisuuksia sekä alkuainekoostumusta. Kuitulujitteiden välillä havaittiin pieniä eroja ainoastaan vesisorptiotuloksissa.

Saadut tulokset viittaavat siihen, että käyttämällä väliresiiniä ja satunnaisesti suuntautunutta lasikuitukomposiittia voidaan parantaa kerrostettavan yhdistelmämuovin ja kuiturungon välistä sidosta. Lisäksi havaittiin, että kuitukomposiittiin sisällytetty antimikrobinen CHX vapautuu kolme viikkoa.

Avainsanat: kuitukomposiitti, lyhyitä kuituja sisältävä komposiitti, kuituorientaatio, sidostuminen, sidosmekanismi, väliresiini, filleripitoinen komposiitti, inhibiitiokerros, mekaaniset ominaisuudet, vesisorptio, polymerointiaste, klorheksidiinidigluconaatti.

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ABBREVIATIONS

ANOVA	Analysis of variance
ATR	Attenuated total reflectance
Bis-GMA	Bisphenol-A-glycidyl dimethacrylate
Bis-PMA	Bismetakryloksipropoksifenyylipropaani
BPO	Benzoyl peroxide
CHX	Chlorhexidine digluconate
CQ	Camphorquinone
DC%	Degree of conversion
df	Fiber diameter
EDS	Energy dispersive spectrometer
E-glass	Electrical glass
FDP	Fixed dental prostheses
FRC	Fiber-reinforced composite
FTIR	Fourtier transform infrared spectrometry
GPa	Gigapascal
HEMA	Hydroxyethylmethacrylate
HPLC	High performance liquid chromatography
IMR	Intermediate resin
ISO	International organization for standardization
IPN	Interpenetrating polymer network
kPa	Kilopascal
MDP	10-Methacryloyloxydecyl dihydrogen phosphate
MMA	Methylmethacrylate
MPa	Mecapascal
MPTS	3-Methacryloxypropyl trimethoxy silane
NDT	N, N´- Diethanol-p-toluidine
PFC	Particulate filler composite
PBMA	Poly (butyl methacrylate)
PEMA	Poly (ethyl methacrylate)
PMMA	Poly (methyl methacrylate)
SEM	Scanning electron microscopy
TEGDMA	Triethylenglycoldimethacrylate
UDMA	Urethane dimethacrylate
UHMWPE	Ultra-high-molecular-weight polyethylene
UTMA	Urethane tetramethacrylate

Vol%	Volume percentage
Wt%	Weight percentage

LIST OF ORIGINAL PUBLICATIONS

I. Keski-Nikkola MS., Alander PM., Lassila LVJ., Vallittu PK. Bond strength of Gradia veneering composite to fibre-reinforced composite. Journal of Oral Rehabilitation. 2004, 31: 1178-1183.

II. Keski-Nikkola MS., Lassila LV., Vallittu PK. Bond strength of veneering composite resin to glass fibre veil reinforced composite substrate. European Journal of Prosthodontics and Restorative Dentistry. 2004, 12 (2): 80-86.

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IV. Lassila LVJ., Tezvergil A, **Lahdenperä M**, Alander P, Shinya A, Shinya A., Vallittu PK. Evaluation of some properties of two fiber-reinforced composite materials. Acta Odontologica Scandinavica. 2005, 63: 196-204.

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1 INTRODUCTION

Fiber-reinforced composite (FRC) technology is one of the material technologies which has opened the potential for fabrication of metal-free dental restorations with high material durability and natural looking appearance (Vallittu & Sevelius 2000, Freilich *et al.* 1998a, 1998b, Goldberg and Freilich 1999a, 1999b, Meiers *et al.* 2002). The laboratory procedure for FRC appliance fabrication is simple because processes of casting / milling / laser sintering of metal alloys, and milling and sintering of ceramics are not needed and the FRC framework of the restoration can be hand-laminated and cured on model.

Despite suitable mechanical properties, especially fracture toughness of FRCs, designing the FRC-particulate filler resin composite (PFC) structure has proven a critical factor for the long-term success and survival of the restoration and treatment outcome. In addition, adhesion of veneering PFC and resin composite luting cements to the FRC framework of the fixed dental prostheses (FDP) plays a significant role for the long-term survival and success. Adhesive interface between FRC and PFC is meant to transfer loads by the masticatory system to be carried by the restored tooth and periodontal ligament. However, problems in interfacial adhesion (so called bonding) of PFC to FRC substructure have been reported, especially with cross-linked polymer matrix FRCs. The optimal bonding of new resin composite to already cured resin composite substrate, e.g. to the substructure of the FRC was suggested to be achieved with a combination of mechanical roughening, chemical conditioning and with primers conditioning before addition of a new resin composite on the FRC substructure (Crumpler *et al*. 1989, Rosentritt *et al.* 1998). As an alternative bonding mechanism, so called secondary-interpenetrating polymer network (secondary-IPN) bonding has been introduced (Vallittu 2009).

The load-bearing capacity of FRC crown and FPD depends on the FRC material which has been used, its cohesive strength and toughness, and on the interfacial adhesion of the composite layers within the device and to the tooth. Consequently, adequate adhesion of veneering PFC and luting cement to the substructure material of the retaining crown or inlay unit is essential. The FRC-PFC restoration can fracture at the interface of the FRC substructure and PFC, or in the veneering PFC itself (Behr 2001, Coker *et al.* 2003, Samadzadeh *et al.* 1997). Like in other multiphase dental restorations of several other materials, such as metal-ceramic and zirconia-porcelain restorations, the framework needs to provide good support for the veneering material. Therefore, in the case of FRC-PFC restorations, so-called high-volume FRC substructure is recommended to be used. In addition, the importance of the suitable monomer composition of veneering composite system

has been highlighted, i.e. primer, adhesive resin and PFC. In practice, several compositions of veneering PFC systems and FRCs have been used in pontics and FRC substructure of FDPs, and use of high-volume fraction substructure or other means to toughen the framework structure has become a standard in fabrication of FRC restorations (Meiers and Freilich 2001, Freilich *et al.* 2002a, 2002b).

FRCs clinical applicability and success relates also to microbial adhesion to the surface of FRC restoration (Tanner 2003). Attempts to develop self-cleaning surfaces of dental restorations have been made (Karthikeyan *et al.* 2013). Chlorhexidine digluconate (CHX) has been widely used as an antimicrobial agent in clinical dentistry. It is an effective antimicrobial agent in direct exposure, and it has an ability to adhere to various substrates resulting in a long-term widespectrum antimicrobial efficacy (Gjermo *et al.* 1974, Bonesvoll 1977). CHX confounds microbial adhesion to polymer surfaces. Earlier in vitro studies have shown that the number of adherents of yeast cells decreases when the denture base polymer has incubated with CHX (McCourtie *et al.* 1985, Waltimo *et al*. 2004). It has been shown also that pretreating the porous polymer-preimpregnated glass fiber reinforcement with CHX results in reduction in the number of adherent yeast cells on the surface FRC material (Waltimo *et al*. 2004). However, to our knowledge there is no information available concerning the influence of CHX to mechanical properties of FRC. Furthermore, the release rate of CHX from such material is not known. Release of substructure from medical and dental composites occurs typically by diffusion in a water containing environment. Absorbed water acts as a plasticizer of resin composites and causes reduction in mechanical properties. Simultaneously with the release of substances from the resin composite, water is absorbed into the system by diffusion (Behr *et al.* 2000, Lassila *et al*. 2002, Vallittu *et al.* 1998). This is affected by chemical composition and hydrophilicity of the polymer matrix.

In this series of studies, the interfacial adhesion aspects of FRC-PFC systems as well as release of CHX from a modified FRC were studied and discussed.

2 REVIEW OF LITERATURE

2.1 FRC materials in dental technology

FRC restorations can be fabricated directly at chairside or indirectly via the dental laboratory. The indirect method of fabrication should be chosen in cases of multiple teeth replacement where intraoral fabrication is difficult. Laboratory build-up of resin composite parts of a long span FRC restoration offer better depth of cure by a light initiated curing system, elimination of porosities, better contour, surface gloss, and proper coverage of the FRC layers (Husein and Berekally 2005, van Heumen *et al.* 2010). Indirect FRC- restoration is light-polymerized and often post- polymerized by increased temperature. A high degree of polymer curing (degree of monomer conversion, DC%) increases mechanical properties and improves biocompatibility of the material (Park 1996).

FRCs were developed for the first time for engineering applications over sixty years ago with several different types of fiber reinforcement materials. Since 1990, carbon, aramide, glass, ultra-high-molecular-weight polyethylene (UHMWPE) and glass fibers have been tested and used on a larger scale to provide fiber reinforcement for dental polymers (Smith 1962, Ladizesky 1990, Goldberg and Burstone 1992, Vallittu 1993, 1998, Vallittu *et al.* 1994b, Powell *et al.* 1994, Amin 1995, Samadzadeh *et al.* 1997, Freilich *et al.* 1998a, 1998b, Saygili *et al.* 2003, Gopichander *et al*. 2015). Out the several fiber types which were tested, glass fibers and UHWMP fibers were stated to be clinically used (Vallittu 1997a, 1997b, 1997c, 1999, Freilich *et al.* 1998b, Behr *et al.* 2001, Bae *et al.* 2001, Kangasniemi *et al*. 2003).

2.1.1 Type of fibers

Carbon fibers are a generic name for carbon/graphite fibers containing various ratios of graphite in the fiber which influences the modulus of elasticity and tensile strength of fibers. Carbon fibers exhibit high strength on compression and tension, and they are light weight. For this reason, carbon FRC, for example, has been the most commonly used material to replace metal parts of airplanes. In dental use, the carbon fibers´ main unfavourable property is the black color (Buckley and Edie 1993, Preethi and Kala 2008, Brocks *et al.* 2013).

Aramid fibers (aromatic polyamid fibers), are best known by the trade name of Kevlar^{R} by DuPont. Composite-grade aramid fiber is light weight, has good impact, abrasion, and heat resistance, and has good strength properties. However, in dental applications the aramid fiber reinforced materials have showed low

flexural modulus and strength and improper adhesion between the fibers and polymer matrix. The distinct yellow color and poor polishability of exposed FRC surface also limit their use in dentistry (Goldberg *et al.* 1994, Tanner 2003, Baker *et al.* 2004). Aramid fibers have been used with the epoxy, vinyl or polyester resins, and their common applications are kayaks, canoes, boats, and wind turbines.

Ultra-high-molecular-weight polyethylene (UHMWPE) fibers are strong and have high impact resistant, they are chemically inert, and have low density. Oral microbe adhesion and proteins adsorb to the surface of UHMWPE FRC, which limits its use as dental material (Tanner 2003). UHMWPE fibers has shown difficulties in creating a good interfacial adhesion between fibers and the polymer matrix (Bae *et al.* 2001, Vallittu 1997c, Beloica *et al.* 2010, Mangoush *et al.* 2017).

The most widely used reinforcing material in dental and industrial applications are the glass fibers that have high tensile strength, low elongation at break and transluency. The glass fibers are classified into A, C, D, E, R and S-glass according to the chemical compositions of the glass mass (Mallic 1997). The most suitable used glass fiber in dental applications is E-glass (Electrical glass) (Vallittu 1993, 1998, Freilich *et al.* 2002a), with a typical oxide composition of SiO_2 55 wt%, Al_2O_3 14.5 wt%, CaO 17 wt%, MgO 4.5 wt%, B_2O_3 8.5 wt% and Na_2O 0.2w% (Wallenberger *et al.* 2001, Zhang & Matinlinna 2012). E-glass has good tensile and compression strength and stiffness, but relatively low impact resistance. Flexural strength of E-glass FRC varies between 420-1240 MPa and it depends on the storage and testing conditions, type of the polymer matrix, and fiber geometry in the test specimen (Lassila *et al.* 2002, Alander *et al.* 2004, Alander *et al.* 2005, Göhring *et al.* 2005).

2.1.2 Polymer matrix and fiber orientation

Reinforcing efficiency of fibers in the polymer matrix depends on the type, length, volume fraction, and orientation of fibers (Mallick 1997). Continuous and discontinuous unidirectional fibers or two dimensionally orientred fibers (woven) and three dimensionally oritented fibers are the most commonly used fiber geometries in FRCs. The polymer matrix holds the fibers together in the FRC structure and protects the fibers (Zhang and Matinlinna 2012). Interfacial adhesion between the reinforcing fibers and the polymer matrix is required to transfer stress from the weaker polymer matrix to fibers (Mallick 1997).

Fiber orientation influences the physical and the mechanical properties of FRC; continuous unidirectional fibers give the highest strength and stiffness in the direction of the fibers (anisotropic) and the Krenchel´s factor is 100% (Murphy 1998). Continuous bidirectional (woven) fibers have reinforcing fibres in two

orientation which gives a reinforcing effect equally in the two directions (orthotropic). The theoretical reinforcing efficiency of such fibres is 50 or 25%. Randomly orientated discontinuous (chopped/mat) short fibers, provide the mechanical properties which are the same in all directions. The theoretical reinforcing efficiency of Krenchel´s factor is 20% in three dimensions (isotropic) and 38% in two dimensions (Murphy 1998). *Figure 1* provides examples of continuous and discontinuous reinforcements (Campbell 2010).

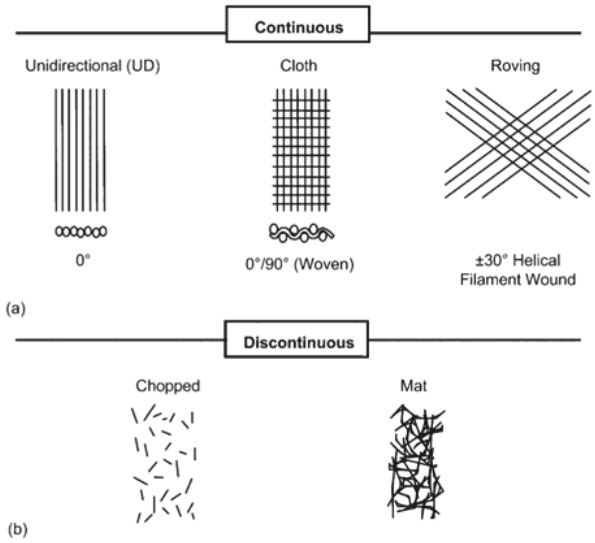


Figure 1. Examples of fiber orientations in the FRC (Campbell 2010).

The matrix which binds and protects the fibers of FRC can be a polymer, metal or ceramic. Polymers are the most commonly used matrix materials in FRCs. Both thermoplastic and thermoset polymers are used: thermoplastic polymer is commonly used in bulk production of injection molded FRC products and thermoset polymer in more advanced FRC products. Dental and medical FRCs are typically made of thermoset polymer. In dental applications of FRC, where the dimensions of the construct are small, all factors which are responsible for durability are important to be considered. Therefore, for instance, the polymer matrix-fiber interface had to be optimized for good chemical and mechanical adhesion, which should also be hydrolytically stable (Vallittu 1995). Interfacial adhesion is crucial for strength and toughness of the composite. The interphase between fiber and the polymer matrix is a system where compounds of adhesion primers and sizing agents form a multimolecular layer which binds the components

together. An example is glass fiber polymer matrix interface where there is acid cleaned glass fibers primed with silane coupling agent specifically matched to the composition of the polymer matrix. At the interface there are also other sizing compounds, such as antistatic compounds which allows easy technical processing of the fibers (Lung and Matinlinna 2012, Vallittu and Matinlinna 2017, Matinlinna *et al.* 2018).

One of the key technical process to produce FRC is resin impregnation of fibers which is made by thermal plasticization means with thermoplastic resins and by monomer resin impregnation with thermoset resins. With thermoset resin impregnation of fibers, vacuum chambers and packages are used to ensure penetration of resin into the spaces between the fibers and elimination of air bubbles. In the context of dental FRC, it should be noted that although the most common denture base polymer, (poly)methyl methacrylate (PMMA), is a thermoplastic, its use in dental laboratory processes follows the principles of using resin monomer systems of thermosets, i.e. PMMA is cured from the monomers (Baker *et al.* 2004).

The resin impregnation method of continuous and discontinuous glass fibers with resin systems used in dental laboratories is typically based on manual wetting of fibers with the resin monomers although some other preimpregnation methods have also been tested (Goldberg and Burstone 1992). The manual impregnation process varies up to the application: denture base PMMA-glass fiber system is impregnate differently than dimethacrylate resin-glass fiber system of crown FDP. In the denture base PMMA-glass fiber system the fibers have been preimpregnated with solid but porous PMMA, and during manufacturing of FRC reinforced denture, free space in the porous PMMA is infiltrated with monomer of methylmethacrylate (MMA) and MMA dissolves the porous PMMA (Vallittu 1995). The process results in a homogeneous polymer matrix of the FRC-rich part of the denture compared to the rest of the denture base polymer. Free radical polymerization is undertaken by thermal initiation or autopolymerization (Vallittu and Shinya 2017). If there are poorly impregnated regions in the FRC water sorption is increased and that decreases mechanical properties (Miettinen and Vallittu 1997). Poorly impregnated areas in the FRC can act as an oxygen reservoir and cause internal oxygen inhibition of the free radical polymerization (Vallittu 1997d).

Impregnation of glass fibers with resins in the production of FDP is more straightforward: silanated glass fibers are manually wetted with dimethacrylate monomers. High viscosity of most commonly used monomers of bisphenol-A-glycidyldimethacrylate (Bis-GMA) can hinder impregnation, and therefore diluting monomer of triethyleneglycol dimethacrylate (TEGDMA) is commonly

used as a co-monomer. Other dimethacrylate monomers which have been used in laboratory-made dental constructions are urethane dimethacrylate (UDMA) and urethane tetramethacrylate (UTMA) (Freilich *et al*. 1998a, 1998b). Chemical bonding of resin to the surface of glass fibers is achieved by polymerization reaction of monomers in contact with the silanated and sized glass fibers (DiBenedetto 2001, Matinlinna *et al.* 2018). Free radical polymerization of dimethacrylate monomers is made via a light initiation-activation system in a specific light curing device with or without vacuum. The light-initiated polymerization can be completed by post-curing at increased temperature.

For optimizing the handling and especially interfacial adhesion properties of the FRC in the dental construct of crown FDP, the polymer matrix which represents roughly one half of the volume and surface area of the FRC has been modified to contain both thermoplastic and thermoset components. Adhesion aspects are covered in detail in section 2.2 of this literature review. Combinations of linear (i.e. thermoplastic) and cross-linked (i.e. thermoset) polymer systems are called interpenetration polymer network (IPN) systems (Sperling 1994, Vallittu 2009, Vallittu and Matinlinna 2017). Dental IPNs are mainly semi-IPNs and used in denture base polymers, denture teeth, FRCs and restorative composite resins (Vallittu 1995, Garoushi *et al.* 2008). The crosslinked phase of the semi-IPN form consists typically of co-polymer of dimethacrylates or polymers of other multifunctional monomers or dendrimers (Viljanen *et al.* 2005, Vallittu 2009).
The IUPAC (International Union of Pure and Applied Chemistry) Commission on Macromolecular Nomenclature based name for the semi-IPN made of Bis-GMA, TEDGMA, and PMMA is net-poly(methyl methacrylate)-inter-net-copoly(bis-glysidyl-A-dimethacrylate)-triethyleneglycol dimethacrylate (Vallittu 2009, 2014).

2.1.3 Physical properties of FRC

Major concerns of dental resin composite are shrinkage during polymerization and easy crack propagation through the resin composite, and therefore attempts have been made to investigate and improve the mechanical properties of resin composites. The resin matrix and fillers play a significant role in lowering polymerization shrinkage and improving mechanical properties of resin composites (Phillips 1991, Ferracane 2011, Demarco *et al.* 2012, Rullman *et al.* 2017, Jung and Park 2017). Use of continuous unidirectional fibers provide anisotropic reinforcement for the FRC (Murphy 1998, Tezvergil *et al*. 2003a, Dyer *et al.* 2004), whereas continuous bidirectional (woven) fiber has orthotropic a reinforcing effect, and randomly oriented fibers have an isotropic effect (Vallittu 1999). *Figure 2* describes the reinforcing efficiency of Krenchel´s factor (Murphy 1998, Vallittu 2002b, Garoushi 2006).

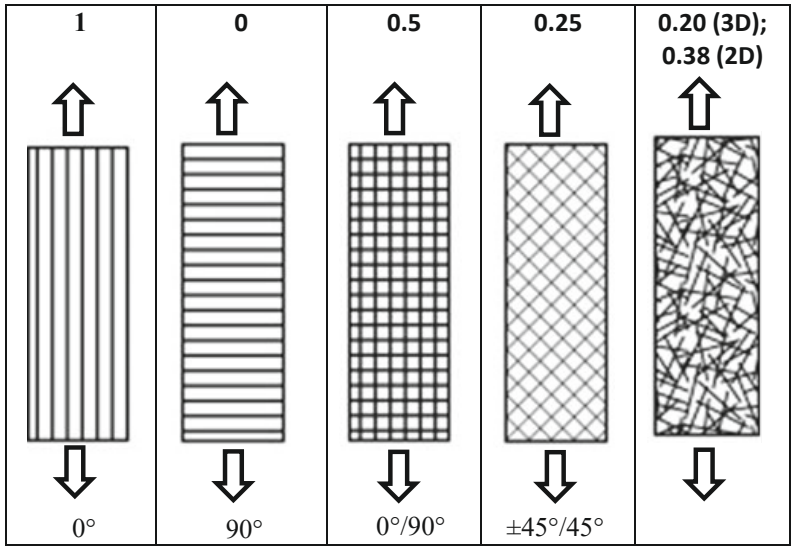


Figure 2. Reinforcing efficiency values of Krenchel`s factor. Arrows are showing direction of stress, unidirectional fibers 0°, unidirectional fibers 90°, bidirectional fibers 0°/90°, short random fibers, bidirectional fibers 45°/45° and short random fibers (l>lc).

One of the simplest and the most commonly used test methods to characterize properties of FRC is a flexural loading test (Baker *et al.* 2004). Static flexural loading test for ultimate flexural strength and modulus of elasticity (flexural modulus) describes the material´s basic mechanical properties which can be used in comparing effects of fiber loading, fiber geometry, and other factors which are related to the behaviour of FRC. However, it has been stated and shown that dynamic fatigue tests of FRC give different test outcomes than static tests because of possible gradual deterioration of the fiber-polymer matrix interface during loading and stress distribution in the test object (Vallittu *et al.* 1994a, 1994b, Ellakwa *et al.* 2002, Narva *et al.* 2005a, 2005b). Studies by Narva *et al*. (2005a, 2005b) highlighted the importance of location of the FRC rich area in the test specimen which may be composed of unfilled polymer too. This was also found in other studies which demonstrated the effects of compression and tensile stress distribution in the test specimen and location of FRC rich part in the test specimen to maximize the reinforcing effect (Nohrström *et al.* 2000, Dyer *et al.* 2005a, 2005b).

The flexural properties can be tested by three- and four-point bending test, the latter being used seldom, but which is the test set-up where stress distribution is more even (Baker *et al.* 2004). In dental materials research it is common that three-point bending test i.e. flexural loading test is used according to the ISO 10477:92

(span 20 mm and crosshead speed 1.0 mm/min) and ISO 1576 (span 65 mm and crosshead speed 5.0 mm/min) standards. Examples of different FRC flexural strength results from the literature are shown in *Figure 3*. *Figure 3* shows large variation in the measured of FRC values which relates to the fiber loading (quantity), location of fibers in the test specimen, and storing condition of specimens before and during testing. Storing the specimens in water considerably affects the mechanical properties, as can be seen in *Figure 3,* and which has also been shown in other studies (Miettinen *et al.* 1999, Vallittu 2000b, 2007, Lastumäki *et al*. 2001, Lassila *et al.* 2002). Water sorption lowers the strength and modulus of elasticity of the FRC and the magnitude of reduction is in relation to the water sorption of the polymer matrix: the higher the water sorption is, more reduction of the properties can be seen. For example, polyamide is known to absorb water up to 50% by weight and flexural properties after water saturation is significant weaker (Bastioli *et al.* 1990, Lastumäki *et al.* 2001).

Cross-linked Bis-GMA based polymer matrix and semi-IPN polymer matrix FRC have 15-20% reduction in flexural strength by water saturation (Lassila *et al.* 2002, Bouillaguet *et al.* 2006). If the interface between the glass fibers and the polymer matrix, and the glass fibers themselves are stable against water, the reduction of the strength is only due to plasticization effect and reduction is reversible, i.e. by dehydration; the properties reach the original level again. Reduction of the strength by plasticization of the polymer matrix has been shown to occur during the one-month water storage time and thereafter the properties remain on the same level at least for 10 years (Vallittu 2000b, 2007).

The bending properties of the composite resin are also influenced by the light polymerization process and possible post- polymerization by heat (Breeding *et al*. 1991, Unterbrink & Muessner 1995, Lassila & Vallittu 2004). The higher degree of monomer conversion (DC%) usually gives better mechanical properties. A higher DC% can be achieved by increasing either light intensity or polymerization temperature up to the level of glass transition temperature (Tg) of the polymer matrix. The effect of temperature and vacuum pressure conditions during the light polymerization process has also been investigated (Chee *et al.* 1988). Lassila & Vallittu (2004) presented that the flexural properties were higher with the test specimens polymerized with the light-polymerization oven where the temperature increased during polymerization. A higher polymerization temperature increases monomer movement during the initiation and propagation of polymerization and results in higher to DC%. This lowers the residual monomer content and decreases the quantity of leachable residual monomers too (Anusavice *et al.* 2013).

As a conclusion of the flexural strength results presented in *Figure 3* there can be seen that e.g. fiber orientation, fiber loading (volume fraction), fiber length and

storage condition influenced the strength. Flexural strength results of unidirectional FRC varied from 552 to 952 MPa in dry conditions (Lassila *et al*. 2002, Furtos *et al.* 2012, Brocks *et al.* 2013), and water-stored FRC varied from 293 to 499 MPa. The amount of fibers in the reviewed studies varied from 4 to 57 vol% (Vallittu 1999, Behr *et al.* 2000, Bae *et al.* 2001, Lassila *et al.* 2002). Flexural strength results in the reviewed studies of continuous bidirectional (woven) FRC with different fiber content (6-14 vol%) varies from 95 to185 MPa in dry conditions, and after 50 d water-stored flexural strength the result was 99 MPa (Vallittu 1999, Kanie *et al.* 2006, Furtos *et al*. 2012). Discontinuous randomly oriented short (3-5mm length) FRC flexural strength results varies from 166 to 265 MPa dry and 129 MPa in water stored specimens. Amount of fibers varied from 15 to 30 vol% (Petersen & Wenski 2002, Garoushi *et al.* 2006b, Suhas *et al.* 2018).

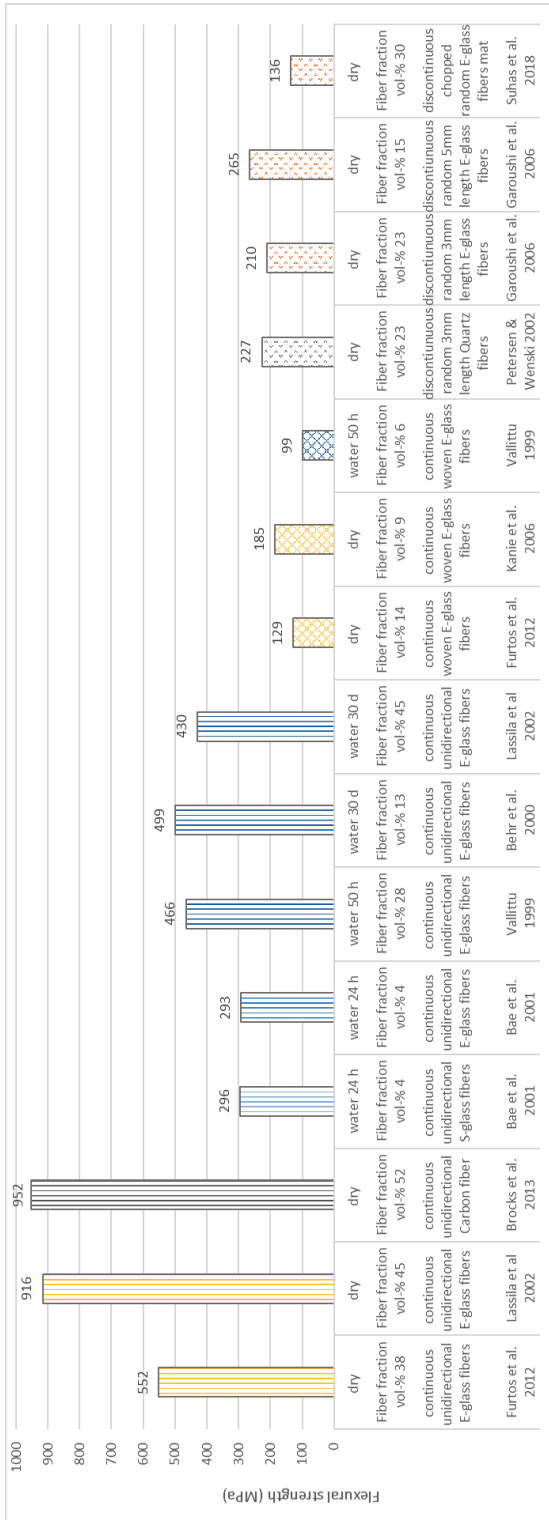


Figure 3. Examples of FRC flexural strength properties results from the reviewed literature.

2.2 Interfacial adhesion of resin systems to FRC

Polymer matrix of FRC materials used in dental technology contains linear or cross-linked polymers, or their combination (Vallittu 1999). This combination is called in dentistry semi-IPNs, which is covered in the end of section 2.1.2. of this literature review. It has been shown that the semi-IPN bonding is possible for FRCs containing both matrix types (Wolff *et al.* 2012). These are also known as multiphase polymer matrix (Vallittu and Sevelius 2000). Adhesion between multiphase polymer matrix type of FRC and PFC depends on fiber content and orientation, content of thermoplastic or thermoset matrix phase, age of the polymer matrix, and surface roughness. Indirect FRC FDP framework i.e. substructure fabricated with maximum pre-impregnated fiber content and polymerized in light curing oven, provide durable mechanical properties of the FRC substructure (Kallio *et al*. 2001, Lastumäki *et al.* 2002, 2003, Özcan *et al.* 2005).

Diffusion of monomers into well polymerized cross-linked Bis-GMA based polymer is difficult to obtain. This is the reason why crosslinked polymer based FRC and PFC materials do not allow the formation of IPN bonding (Vallittu 1995, Vallittu 1997a, 1997b, 1997d, Vallittu and Ruyter 1997, Buyukyilmaz and Ruyter 1997, Lastumäki *et al.* 2002). In order to improve the adhesion to the multiphase FRC substructure, an intermediate resin (IMR) or primers between this FRC and PFC has to be used (Lastumäki *et al.* 2002, 2003, Perea *et al.* 2014, 2015). The principle is based on the IMR's ability to diffuse and dissolve the linear phase of the multiphase FRC network, hence enabling the formation of secondary IPN upon polymerization of the newly applied PFC. A secondary IPN is formed when a second network is formed following the formation of the first network (Vallittu *et al.* 1994a, Vallittu 1995, 1999). For this purpose, however, the surface of FRC substructure should be treated with IMR from 4 to 15 minutes prior to adhering the new PFC layer. Consequently, the adhesion between IMR and multiphase FRC substructure is to be based on reactions between FRCs polymer matrices (Kallio *et al.* 2001, Lastumäki *et al.* 2002, 2003, Özcan *et al.* 2005). Lastumäki *et al.* (2002) showed that the content of IMR greatly influences the shear bond strength between the multiphase FRC matrix and new PFC. IMR containing BisGMA-HEMA or BisGMA-TEDGMA monomers improved the shear bond strength between multiphase FRC matrix and new PFC because those IMRs have good dissolving capacity and are able to dissolve the linear PMMA phase of the multiphase FRC matrix (Elliott *et al.* 2001, Lastumäki *et al.* 2002).

The composition of dental PFC involves a polymeric matrix, reinforcing fillers, stabilizers, initiators and activators that allow the light-polymerization of the organic matrix. Crosslinking is the general term for the process of forming covalent bonds (Ellakwa *et al.* 2001, Concalves *et al.* 2009, Anusavice *et al*. 2013).

Kallio *et al.* (2001, 2013, 2014) concluded that surface roughness did not considerably improve the bonding of new resin to the substrate of IPN based FRC, whereas the roughness contributed to bonding the new PFC to the PFC with a cross-linked polymer matrix. Garoushi *et al.* (2007) noticed that direct 3-unit FDP structure made with PFC containing short glass fibers and semi-IPN polymer matrix show better load bearing capacity than in those made with conventional PFC and perform similary to those reinforced with FRC substructure.

Another approach for adhering new PFC to polymer substrate is based on the use of an oxygen-inhibition layer. It allows the formation of covalent bonds by free radical polymerization between the old polymer and the new PFC. This generates crosslinked polymer matrix that can be chemically bonded to a composite (Vankerckhoven *et al.* 1982, Rueggeberg and Margeson 1990, Li 1997, AlJehan *et al.* 2016, Bijelic-Donova 2016). This kind of bonding can occur between FRC and PFC if the FRC framework is made without time delay, contamination or grinding of the oxygen inhibited layer on the FRC surface (Vallittu & Shinya 2017). It should be noted that if the FRC substructure surface has exposed glass fibers, a method to improve the adhesion of resin systems to OH-covered-FRC substrates with exposed fibers is based on the use of silane coupling agents (Matinlinna *et al.* 2007).

Adhesion of resin systems have different properties and the international test standards help to identify adhesive bond or joint mechanical properties that include strength, creep, fracture, and fatigue. The most commonly used bonding test used in dentistry is the shear bond strength test which is simple to perform (Curtis and Watson 2008). The failure modes should be divided into adhesive failure, cohesive failure, and mixed failure. The adhesive failure defines that failure occurred at the adhesive interface or the adhesive/resin interface. The cohesive failure defines that the failure occurred at the inside of the resin or substructure. The mixed failure includes both adhesive and cohesive failures (Chaia *et al.* 2015, Söderholm 2009).

2.3 Structure of dental FRC devices

Dental FRC devices consist of different kinds of one-phase or multiphase materials. In order to show good clinical performance, single crowns and FDPs need occlusal surfaces, which have a high wear resistance, as well as adequate strength against bending, torsion, and compression loads (Vallittu and Sevelius 2000). These aspects need to be considered for the structure composition of the FDP where resin composites of different kinds are used. The fabrication mechanism of indirectly made FDPs makes it possible to achieve a higher DC%, which is beneficial in terms of the strength of the material itself. On the other hand,

this higher DC% may have a negative effect on the interfacial adhesion of the FRC substructure, the veneering material, and the resin luting cement. This can result in lower structural integrity of the FDP under loading, meaning a lower capacity to withstand the occlusal forces. There are several adhesive interfaces in an FRC FDP (Goldberg and Freilich 1999a). These include the interface that is between the fibers ad polymer matrix, which has been discussed in part 2.1 of this review; the interface of the PFC to the FRC substructure (addressed in part 2.2); and the interface of resin luting cement to the FDP and to the surface of the abutment (enamel, dentine, core-built-up composite, metal alloy). The interfacial adhesion, called "bonding" is referred to as "technical bonding" when the substrates are not biological in origin. In the case of resin composite substrates, the quality of the interfacial adhesion depends on the processing methods of the structure and of primers / adhesives, (IMR) which are used to facilitate the adhesion at the interface (Kallio *et al.* 2001, Lastumäki *et al.* 2002, 2003, Tezvergil *et al.* 2003a, 2003b, 2004, 2005, Perea *et al.* 2014, 2015).

The aspects to be considered when designing an FRC FDP depend on the number of pontics and abutments, and the magnitude of masticatory forces. FRC FDP are exposed to static and cyclic loads, as well as to tensile stresses, which can cause fractures, and shear stresses that result in debonding. The design of an FRC substructure and a successful bond between FRC and PFC are crucial for its longevity (Freilich and Meiers 2004, Karbhari and Strassler 2007). The structure of FRC FPD contains typically the main FRC framework and surface bonding wings of continuous unidirectional fibers. The continuous unidirectional fibers provides anisotropic mechanical properties to an FRC and can reinforce the composite to the direction of the stress (Xu *et al.* 2003, Xie *et al.* 2007, van Heumen *et al.* 2009a, 2009b). The quantity of the fibers has a direct relationship on the load-bearing capacity of the framework. By the rule of thumb, an FRC FDP substructure needs to be reinforced with one roving of continuous unidirectional fibers in the anterior region, and two rovings for one replaced premolar. If it is needed to replace two premolars, the substructure needs to include two to three rovings of fibers. In a case where one molar needs to be replaced, three rovings of fibers should be included in the substructure of the FRC FDP, and for several replaced teeth, three or four rovings would be needed (Dyer *et al.* 2004). Obviously the quantity of fibers per roving has an impact on the load-bearing capacity and the above mentioned fiber quantities are only relevant with one FRC product. An FRC single crown structure should be reinforced with two layers of woven FRC having different fiber directions to increase the reinforcing effect (*Figure 4*). The two directions of fibers give an orthotropic reinforcing effect and increase the toughness of the structure (Vallittu 1999, 2002a, Dyer *et al.* 2005a, b). The woven substructure of crown and the main continuous unidirectional FRC substructure are attached to each other by light-polymerization (*Figure 4b*).

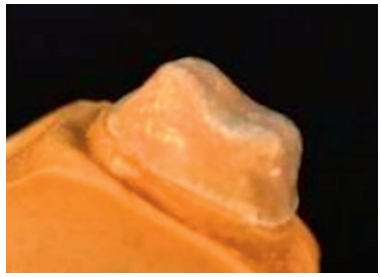
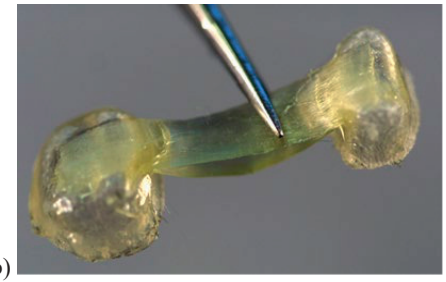
a)  b) 

Figure 4. Photographs of FRC framework of crown (a) of FDP (b). Note that FDP framework does not yet contain additional reinforcement for the pontics. (Stick Tech, GC)

Bonding between woven FRC and unidirectional FRC substructure is confirmed by an oxygen-inhibited layer (Vallittu and Sevelius 2000). If a continuous unidirectional FRC FDP substructure starts or ends with the surface bonding wings, the FRC wing should cover the maximum area of tooth enamel surface. If FRC FDP substructure starts or ends with a cavity, the main FRC framework runs along from the cavity wall. The second continuous unidirectional FRC roving is set reinforcing on the main FRC substructure. It is important to note the bridge structure that an increased risk for framework fractures is when the cross-sectional design of the connector is flat rather than round and thick in the palate–buccal direction in anterior FRC FPDs *(Figure 5)* (van Heumen *et al.* 2009a, 2009b).

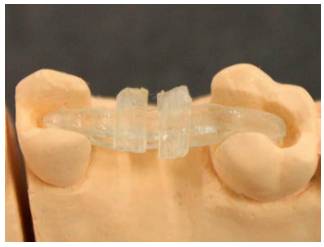
a)  b) 

Figure 5. Positioning of the fibers in inlay-retained FDP. Main framework of continuous unidirectional fibers runs from cavity to cavity and an additional fiber is placed perpendicular to the main FRC structure for reinforcing pontics. a) Occlusal view and b) buccal view.

One roving of fibers is placed near the gingival area and an additional one near the occlusal area *(Figure 5*). The main FRC substructure requires additional fibers to reinforce the pontics. One or more pieces of unidirectional FRC rovings are placed in the middle of the pontic perpendicular to the main FRC of the FDP. Additional fibers support the cusps of the pontic most effectively, and it increases the load

bearing capacity of the FRC FDP substructure (Behr *et al.* 2005, Xie *et al.* 2007). These lower the risk of delamination of the pontic from the FRC FDP structure (van Heumen 2008, Vallittu and Shinya 2017). An example of an FRC FDP substructure layering with PFC veneering material can be seen in *Figure 6.*

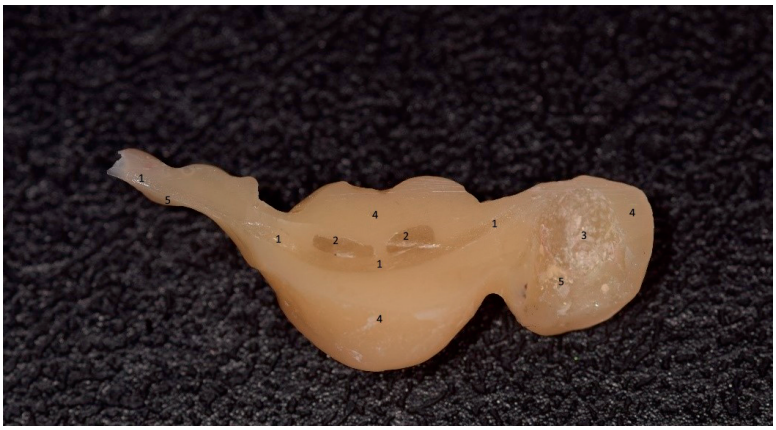


Figure 6. Longitudinal section of an FRC FDP showing the multiphase structure and location of the adhesive interphases. 1. Main continuous unidirectional FRC framework between abutments. 2. Continuous unidirectional FRC for pontic reinforcement. 3. Continuous multidirectional FRC for crown unit reinforcement. 4. PFC veneering composite. 5. Bonding site for resin cement.

2.4 Lacing of polymer matrix with releasing antimicrobial substances

Some additives are incorporated into resin composites such as plasticizers, antistatic agents, rheology modifiers, etc. (Matisons 2009). Additionally, pigments or optical modifiers are added to match the PFC color with the tooth structure, as well as ultraviolet absorbers and other additives to improve the color stability. The pigments used to shade the resin composites are usually metal oxide particles, which are used for creating a natural look of the restoration. Opacifiers are also added to modify the translucency of the restoration, in a way that it can mimic the enamel and dentin (Anusavice *et al.* 2003). Other additives are compounds that confounds microbial adhesion to polymer surfaces or have antimicrobial properties (McCourtie *et al.* 1985, Brännström 1996, Waltimo *et al.* 2004). This is important as there may be more than 700 bacterial species in the oral cavity, so drug additives can confuse microbial adhesion to oral cavity and polymeric surfaces (Aas *et al.* 2005).

Bacterial adhesion is a complex phenomenon that is influenced by the surface material properties, the bacterial and protein pellicle properties, and the environment where the biofilm formation occurs (An and Friedman 1998). Different theories have been developed to model the physicochemical interactions that determine bacterial adhesion (Hermansson 1999), but these models are limited because they are based on physicochemical interactions between surfaces and neglect the biological aspects of adhesion, such as the role of specific bacterial structures called adhesins, which are involved in adhesion to another cell or to an abiotic surface (Klemm and Schembri 2000). Recent reports have identified new classes of polymers with reduced bacterial adhesion (Hook *et al.* 2012), and research to eliminate or reduce infections by developing anti-infective and anti-adhesive devices has been done. These devices may be produced by either mechanical design alternatives, physicochemical modification of the biomaterial surface, anti-infective agents bound to the surface of the material, or release of medicine into the adjacent surroundings (e.g. chlorhexidine, antibiotics) (Hetrick & Schoenfisch 2006, Bryers 2008). Solute diffusion, material degradation, and polymeric matrix swelling are suggested to be the main driving forces for solute transport from drug containing polymeric matrices (Jones *et al.* 1996, Artifin *et al.* 2006, Wang & von Recum 2011).

Polymer matrices of dental resin composites can be filled with fluoride, chlorhexidine or other antiseptic agents which are released from the matrix (Mirth *et al.* 1989, Friedman and Steinberg 1990, Yue *et al.* 2004, Wiegand *et al*. 2007). The antimicrobial agent, CHX, is a disinfectant and antiseptic agent that is used for skin disinfection before surgery and for sterilizinge surgical instruments (WHO Model formulary 2008). It has also been used for the treatment of periodontitis, preventing dental plaque and for treating oral yeast infections (Gjermo *et al.* 1974, Bonesvoll 1977). Indeed, some in vivo and in vitro investigations have shown that CHX release might be a suitable alternative when used as an antimicrobial agent for oral conditions (Riggs *et al.* 2000, Irwin *et al.* 2003, Hiraishi *et al.* 2010). CHX is a potent oral antimicrobial agent that can suppress mutans streptococci levels, and potentially also reduce caries incidence (Emilson 1994).

CHX has been incorporated e.g. into glass-ionomer cements or resin-modified glass-ionomer cements to improve their antimicrobial properties (Ribeiro and Ericson 1991, Sanders *et al.* 2002, Palmer *et al.* 2004). Palmer *et al.* 2004 noticed that only a small portion of CHX salt (3 - 5%) was released from an experimental glass ionomer over a period of 240 days. It was demonstrated that, when CHX was added to the glass ionomer cements alone, without other compounds like fluoride, setting specimens showed significant antibacterial effects on the mutans streptococcus levels (Elgamily *et al.* 2018). Previous studies have also shown that with incorporated CHX diacetatea, to self-curing system based on PEMA and

tetrahydrofurfuryl methacrylate can be achieved with a CHX release at a higher percentage (6 - 12 %) over 14 days (Patel *et al*. 2001). From a resin composite laced with CHX, fifty percent of incorporated CHX diacetate was found to be released in 1 week (Leung *et al.* 2005). Anusavice *et al.* 2006 stated that the release of CHX from a UDMA and TEGDMA resin system can be effectively controlled by the CHX diacetate content and pH. Their results showed that the rates of release were significantly higher in a pH 4 buffer solution. This was attributed to the increase of CHX diacetate solubility at a lower pH. The higher level of filler loading reduced the DC%, leading to a greater loss of organic components and higher chlorhexidine release rates.

Stanislawczuk *et al.* (2014) found that incorporation of different concentrations of CHX diacetate did not decrease the ultimate tensile strength and DC% of the adhesive resin, as well as, the water sorption and solubility values. However, several studies have shown that the addition of CHX affects the mechanical properties of polymers (Wilson and Wilson 1993, Riggs *et al.* 2000, Anusavice *et al.* 2006) and bonding resins (Hiraishi *et al.* 2008). This seems to be dependent on the CHX concentration (Pallan *et al.* 2012).

3 AIMS OF THE STUDY

The general objective of this series of studies was to investigate FRC structures and adhesive interfaces of FDPs. An investigation in to the incorporation of CHX to the FRC and its release was also made. The working hypothesis of the studies was that polymer matrix composition and orientation of fibers contribute to the bonding and physical properties of FRC, and that by incorporating CHX to the polymer matrix of FRC, release of CHX into water could be found.

Specific aims were:

1. To determine bonding properties of veneering PFC to continuous unidirectional FRC with semi-IPN polymer matrix.

2. To investigate bonding characteristics of PFC to FRC with discontinuous random oriented fibers.

3. To study CHX release and flexural properties of FRC reinforced provisional FDP polymer.

4. To characterize some physical properties of BisGMA and UTMA based FRC materials.

4 MATERIALS AND METHODS

The materials used in the studies are listed in *Tables 1-4*. Flexural strength specimens were fabricated according to the International Standards of Dentistry protocols ISO1567 (specimen size: 3.3×10.0×65.0 mm) and ISO 10477:92 (specimen size: 2x2x25 mm). Shear bond strength with ISO 11405 and water sorption was measured following the procedure specified in ISO 10477:92.

Table 1. Basic compositions and additional compounds of FRC materials used in the studies. (Data predominantly from manufacturer`s information)

Material name	Manufacturer	Composition	Study
Stick	Stick Tech Ltd., Turku, Finland	E-glass (continuous unidirectional) PMMA(1	I-IV
EverStick C&B	Stick Tech Ltd., Turku, Finland	E-glass (continuous unidirectional) PMMA, Bis-GMA(2	IV
Experimental FRC Veil	Stick Tech Ltd., Turku, Finland	E-glass (Random continuous fiber veil/mat) PMMA, Bis-GMA	II
Dentalon Plus	Heraeus Kulzer GmbH, Wehrheim, Germany	Power liquid system of PEMA(3, PBMA(4	III
Experimental BR-100	Kuraray Medical Inc., Tokyo, Japan	E-glass UTMA(5-based resin with ultra fine silica fillers	IV
Chlorhexidine Digluconat sol 20%	University Pharmacy, Helsinki, Finland	Chlorhexidine digluconat (6	III

1)Polymethyl methacrylate, 2) 2.2-bis[4-(2-hydroxy-3 methacryloxypropoxy)phenyl]propane 3) Poly(ethyl methacrylate), 4) Poly(butyl methacrylate), 5) Urethane tetramethacrylate 6) 1,1´-Hexamethylenebis[5-(4-chlorophenyl)biguanide]

Table 2. PFC materials used in this study. (Data predominantly from manufacturer`s information)

Brand	Manufacturer	Composition	Study
Gradia®	GC Dental Products Corp., Tokyo, Japan	Silica particulate fillers, UDMA(1, CQ(2	I-II
Panavia F	Kuraray Medical Inc., Tokyo, Japan	Silica, MDP(3, hydrophobic and hydrophilic dimethacrylates, BPO(4	IV

1) Urethane dimethacrylate, 2) Camphorquinone 3) 10-Methacryloyloxydecyl dihydrogen phosphate, 4) Benzoyl peroxide

Table 3. Adhesive resins (intermediate resin, IMR) and primers materials used in this study. (Data predominantly from manufacturer`s information)

Brand	Manufacturer	Composition	Study
Composite primer	GC Dental Products Corp., Tokyo, Japan	Methacrylates dissolved in a 2-hydroxyethyl methacrylate solvent	I
Stick Resin	Stick Tech Ltd., Turku, Finland	BisGMA-TEGDMA [1] CQ -amine initiator system[2]	I, II
Clearfil SE Bond Primer	Kuraray Medical Inc., Tokyo, Japan	HEMA[3], hydrophilic dimethacrylate, MDP[4], dl-CQ, NDT[5], water	IV
Clearfil SE Bond bond	Kuraray Medical Inc., Tokyo, Japan	Silica, BisGMA, HEMA, Hydrophobic dimethacrylate, MDP, NDT	IV
Clearfil Porcelain Bond activator	Kuraray Medical Inc., Tokyo, Japan	Hydrophobic dimethacrylate, MPTS[6], Bis-PMA[7]	IV
K-etchant, etching agent gel	Kuraray Medical Inc., Tokyo, Japan	Phosphoric acid	IV

1)2,2-bis[4-(2-hydroxy-3-methacroyloxypropoxy)phenyl]-propane-triethyleneglycoldimethacrylate, 2) Camphorquinone, 3) 2-hydroxyethyl methacrylate, 4)10-Methacryloyloxydecyl dihydrogen phosphate, 5) N,N`-Diethanol-p-toluidine,6) 3-methacryloxypropyl trimethoxy silane, 7) Bismetakryloksipropoksifenyylipropaani

4.1 Bond strength of polymerized PFC to glass FRC

All FRC types (*Table 1*) whose adhesive properties were tested in *Studies I-IV* were placed into cylinders (Ø18 mm) filled autopolymerized cavity in acrylic resin and then polymerized for 10-40 s with hand light-polymerization unit (Optilux 501, sds Kerr, Danbury, USA). Additionally some of the test specimens followed by light-polymerization in an oven (LicuLite, Dentsply, Dreieich, Germany) for 30 min. Then the FRC substrate surfaces were wet ground with 1200 gritt (FEPA, Struers A/S, Rodovre, Denmark) silicon carbide grinding paper or optionally the substrate surface will be left untreated (containing oxygen inhibited resin layer) (*Study II)* before attaching to the PFC or cement (*Table 2*). The PFC and the cement was applied on the FRC substrate surface by using a translucent tubular polyethylene mold with an inner diameter of 3.6 mm. These composites packed against the FRC substrate with a composite-filling instrument. In *Study I* the dimethacrylate IMR (*Table 3*) applied on the surface (treatment time 5 s / direct technique and manufacturer`s guide or 5 min / indirect technique) before the light-polymerization the PFC. Shear bond strength of PFC to FRC´s was measured for dry and thermocycled specimens (n=6 in *Studies I-II* and n=15 in *Study IV*). Specimens were mounted in a jig (Bencor Multi-T shear assembly, Danville Engineering Inc., San Ramon, CA, USA) of the universal testing machine (Loyd

LRX, Loyd Instruments LTD, Fareham, UK) and shear-bond force applied until fracture occurred. The specimens were loaded at a crosshead speed of 1.0 mm/min and the force-displacement curve was analyzed with Nexygen 4.0 software (Loyd Instruments Ltd, Fareham). Differences of the bond fracture in *Study II* were visually analyzed by two operators and divided into two groups: cohesive and adhesive fracture. All shear bond test groups are listed in *Table 4*.

Table 4. Codes for the shear bond test groups (Tc= thermocycled in water 5°C-55°C).

Group	FRC material	FRC substrate curing	Surface treatment	IMR influence time	IMR curing time	VCR curing time	Stored
Study 1							
1	unidirectional	10 s + 30 min	Wet ground 1200 grit	5 s	20 s	40 s + 30 min	Dry
1tc	unidirectional	10 s + 30 min	Wet ground 1200 grit	5 s	20 s	40 s + 30 min	Tc 12 000
2	unidirectional	10 s + 30 min	Wet ground 1200 grit	5 min	20 s	40 s + 30 min	Dry
2tc	unidirectional	10 s + 30 min	Wet ground 1200 grit	5 min	20 s	40 s + 30 min	Tc 12 000
3	unidirectional	10 s	Wet ground 1200 grit	5 s	20 s	40 s + 30 min	Dry
3tc	unidirectional	10 s	Wet ground 1200 grit	5 s	20 s	40 s + 30 min	Tc 12 000
4	unidirectional	10 s	Wet ground 1200 grit	5 min	20 s	40 s + 30 min	Dry
4tc	unidirectional	10 s	Wet ground 1200 grit	5 min	20 s	40 s + 30 min	Tc 12 000
5	unidirectional	10 s	Wet ground 1200 grit	-	-	40 s + 30 min	Dry
5tc	unidirectional	10 s	Wet ground 1200 grit	-	-	40 s + 30 min	Tc 12 000
Study 2							
1	random veil	40 s	Wet ground 1200 grit	-	-	40 s + 30 min	Dry
2	random veil	40 s	Wet ground 1200 grit	-	-	40 s + 30 min	Tc 6 000
3	random veil	40 s	Untreated	-	-	40 s + 30 min	Dry
4	random veil	40 s	Untreated	-	-	40 s + 30 min	Tc 6 000
5	unidirectional	40 s	Wet ground 1200 grit	-	-	40 s + 30 min	Dry
6	unidirectional	40 s	Wet ground 1200 grit	-	-	40 s + 30 min	Tc 6 000
7	unidirectional	40 s	Untreated	-	-	40 s + 30 min	Dry
8	unidirectional	40 s	Untreated	-	-	40 s + 30 min	Tc 6 000
Study 4							
1	unidirectional a	40 s + 20 min + 7 days in room temperature	Wet ground 1200 grit	5 min	20 s	40 s	Room temperature 24h + Tc 5 000
2	unidirectional a	40 s+ 7 days in room temperature	Wet ground 1200 grit	5 min	20 s	40 s	Room temperature 24h + Tc 5 000
3	unidirectional b	40 s + 20 min + 7 days in room temperature	Wet ground 1200 grit	5 min	20 s	40 s	Room temperature 24h + Tc 5 000
4	unidirectional b	40 s+ 7 days in room temperature	Wet ground 1200 grit	5 min	20 s	40 s	Room temperature 24h + Tc 5 000

4.2 Flexural properties of FRC reinforced provisional FDP polymer

Porous PMMA preimpregnated continuous unidirectional glass fiber reinforcement was laced with CHX in a water solution for a minute (Waltimo *et al.* 2004) and then fiber reinforcements were dehydrated in a desiccator for one week before using them in the FRC test specimen's fabrication. Test specimens without CHX in glass fiber reinforcement were made for comparison and the control specimens did not contain glass fibers in the test specimens.

Bar shaped test specimens 3.3×10.0×65.0 mm were fabricated from provisional FDP polymer (mixture of PEMA powder and n-poly(butyl methacrylate) monomer liquid, PBMA) with E-glass fiber reinforcements. The reinforcements were further impregnated with slurry viscosity mixture of PEMA powder and PBMA monomer liquid for 10 min. After further-impregnation, two 65 mm length fiber reinforcements were placed into the mould and the mixture of PEMA/PBMA poured on the reinforcements. The powder-to-liquid ratio of the resin mixture was 2 g to 1.2 ml. The resin polymerized in water at (55 ± 1) ºC for 15 min under air pressure of 300 kPa (Ivomat Type IP2, Ivoclar A.G. Schaan-Liechtenstein). The polymerized test specimens were finished to predetermined dimensions by wet grinding with silicon carbide grinding paper (No. 1200 FEPA, Struers A/S, Rodovre, Denmark).

Flexural strength and modulus of test specimens (n=6) tested with three-point bending test after storing the specimens dry or in water at 37 ºC for two weeks (*Study III).* The test was made with Lloyd LRX (Lloyd LRX, Lloyd Instruments Ltd., Fareham, UK) universal testing machine, and the specimens were loaded at a crosshead speed of 5.0 mm/ min. The force-displacement curve registered with Nexygen 4.0 software (Lloyd Instruments Ltd, Fareham, UK).

In *Study IV* the bar-shaped specimen dimension was 2x2x25 mm and the specimens (n=6) were polymerized either with a hand light-polymerization unit (Optilux 501, sds Kerr, Danbury, USA) for 40 s, or, additionally, in a light-curing oven (LicuLite, Dentsply, Dreieich, Germany) for 20 min**.** The water storing time was for 30 days followed by measure of flexural strength and modulus. All flexural test groups listed in Table 5.

Table 5. The test groups of specimens of flexural test and water sorption.

Group	Specimens type	Type of the test
Study 3		
1	PEMA[1]/PBMA[2] polymer	Flexural test for dry specimens
2	PEMA/PBMA polymer + glass fibre reinforcement	Flexural test for dry specimens
3	PEMA/PBMA polymer + glass fibre reinforcement laced with CHX[3]	Flexural test for dry specimens
4	PEMA/PBMA polymer + glass fibre reinforcement laced with CHX	Flexural test for specimens stored 2 weeks in water
5	PEMA/PBMA polymer + glass fibre reinforcement (3 vol%) laced with CHX	Release of chlorhexidine digluconate
Study 4		
1	Bis-GMA[4] resin impregnated glass-fibres	Flexural test and water sorption for specimens stored 30 days in water
2	Bis-GMA resin impregnated glass-fibres	Flexural test and water sorption for specimens stored 30 days in water
3	UTMA[4]-based resin with ultra-fine silica filler impregnated glass-fibres	Flexural test and water sorption for specimens stored 30 days in water
4	UTMA-based resin with ultra-fine silica filler impregnated glass-fibres	Flexural test and water sorption for specimens stored 30 days in water

1) Poly(ethyl methacrylate) 2) Poly(butyl methacrylate 3) 1,1´-Hexamethylenebis[5-(4-chlorophenyl)biguanide] 4) 2.2-bis[4-(2-hydroxy-3 methacryloxypropoxy)phenyl]propane 4) Urethane tetramethacrylate

4.3 Water sorption and CHX release

Specimen preparation is described in paragraph 4.2. In *Study III* release of CHX from the FRC test specimen into water was determined during 180 days of water storage. Test specimens were stored in contact with 40 ml of deionized Milli-Q water at 37 ºC (inclosed Falcon flasks) for the following time points: 0, 1, 3, 7, 10, 14, 21, and 180 days. The released CHX was measured using high performance liquid chromatography (HPLC). More precisely, all the aliquots of each specimen were separately collected, and the supernatants analyzed. Shimadzu's (LC-2010) modular HPLC system (Shimadzu Corporation, Kyoto, Japan) was used by using the following components (connected to the computer): a system controller (SCL-10Avp), a liquid chromatograph pump (LC-10Advp), a UV-VIS detector (SPD-10Avp), an on-line degasser (DGU-14A), and an auto injector (SIL-10Advp). The incorporated columns used in the system were Phenomenex's C18 precolumn (Phenomenex, Torrance, CA, USA) and Phenomenex's C18 analysis column (type: RP18, length: 150 mm, internal Ø: 2 mm, and particle size: 5 mm). Finally, the collected data were processed using Shimadzu's CLASS VP software. The used flow rate was 0.6 ml/min, the run time was 25 min, and the used wavelength (λ) of UV light was 254 nm. A filtered mobile phase was used, and it contained acetonitrile (HPLC grade, Rathburn Chemicals Ltd., Walkerburn, Scotland, UK)

and 7 mmol sodium laurylsulphate (SDS, SERVA Electrophoresis GmbH, Heidelberg, Germany) in Milli-Q water containing glacial acetic acid (0.4 vol %, Merck KGaA, Darmstadt, Germany). The analysis was carried out using a gradient run, where the concentration of acetonitrile was changed from 10 to 90 vol %, while, at the same time, the concentration of SDS solution was changed from 90 to 10 vol % within the run time.

The CHX standards were prepared in the following manner: The CHX-water solution was first evaporated dry using a rotary evaporator (Heidolph, Laborota 4000, Heidolph Instruments GmbH & Co.KG, Schwabach, Germany), then, 250 mg of CHX was weighted and diluted in de-ionized Milli-Q water to give standards with CHX concentrations of 10, 50, and 100 ppm in de-ionized Milli-Q water. Filtered (0.45 μm) standards and samples of each supernatant (100 μl) were injected into the chromatograph and six parallel determinations were done per time point. The quantities of released CHX calculated from the areas under the curve at peaks produced by CHX, in which the retention time was 17 min. From the sample supernatant, the concentration of released CHX (CHX (μg/ml)) was determined using linear regression equations obtained from calibration graph ($R2 > 0.99$). The quantities of released CHX was calculated in ppm.

In *Study IV,* the bar-shaped specimens were stored in 120 ml water (grade III) for 30 days at 37 ºC. The dry weight (W_d) of the specimens were measured with a balance (Mettler A30; Mettler Instrument Co., Highstone, N.J., USA) to an accuracy of 0.1 mg. During storage in water, the specimens weighed at 1, 3, 7, 14, 21, and 30 days, and the weight of specimens that had absorbed water (W_w) were measured following the procedure specified:

Water sorption = $(W_{wx}-W_d) /W_d$, where x is days of water immersion.

4.4 SEM/EDS analysis

The FRC materials using in *Studies II* and *IV* were examined with a scanning electron microscope (SEM) (JSM-5500; Jeol Ltd., Tokyo, Japan) to determine surface fractured morphology (*Study II* cohesional and adhesional), impregnation of the fiber by the resin, diameter of the single fibers, area percentage of the fibers, and the cross-sectional fiber distribution of the FRC test specimen (*Study IV*). Evaluation was made at the cross section of specimens which were wet-ground with 4000-grit (FEPA) and carbon sputtered (SCD 050; Bal-Tec, Balzers, Liechtenstein).

In addition, in *Study IV*, the surface was analyzed using the EDS (energy dispersive X-ray spectroscopy) system (Spirit; Princeton-Gamma Tech, Princeton, N.J., USA) to measure the elemental composition of the inorganic phase (glass fibers and possible particulate fillers in the polymer matrix) of the FRCs.

4.5 Degree of monomer conversion (DC%)

The DC% of the polymer matrix of the FRC substrate after hand light polymerization (10 s) and light-curing in a light curing oven (30 min) was determined with Fourier Transform Infrared Spectroscopy (FTIR) (Spectrum One, Perkin Elmer, USA) using Attenuated Total Reflectance (ATR) sampling accessory. The spectra recorded with 16 scans using resolution of 4 cm^{-1}. The degree of conversion (DC% = (1-C/Ux100 %)) (C = conversion of aliphatic and aromatic peaks from light polymerized FRC and U = conversion of aliphatic and aromatic peaks from unpolymerized FRC) was calculated from the aliphatic C=C peak at 1636 cm^{-1} normalized against the aromatic C=C peak at 1608 cm^{-1}. The spectral range was (4000 cm^{-1} – 650 cm^{-1}) and FTIR analysis was made 15 min after polymerization of FRC material (Yoshida & Greener 1993).

4.6 Fiber content analysis

Fiber content as a percentage by volume (vol %), in the test specimens with fiber reinforcement, was calculated based on the weight of the fibers, density of E-glass (2.54 g/cm^3) and the volume of the specimens. The quantity of fibers was determined by combustion of a piece of FRC in a furnace (Radiance MSL, Jelrus) at (700 + 20) ºC for one hour. The weight of the glass FRC material pieces was measured with a balance (Mettler Toledo GmbH, Switzerland) before and after combustion. The fiber content as a percentage by volume was calculated with the formula: Vf = (Wf / ef) / (Wf / ef + Wp / ep) Where *Wf* is the weight proportion of E-glass; *ef* is the density of E-glass (2.54 g/cm^3); *Wp* is the weight proportion of polymer matrix; and *rp* is the density of Bis-GMA (1.226 g/cm^3): *rp* (1.238 g/ cm^3) is mean of density of TEGDMA and Bis-GMA (Lastumäki *et al.* 2001).

4.7 Statistical analysis

Data from *Studies I-IV* were analyzed using SPSS (Statistical Package for Social Science, SPSS Inc., Chicago, IL, USA).

In *Study I* the adhesion behavior of veneering composite to the initially light

polymerized FRC substrate was compared with well-polymerized FRC substrate. The treatment time of FRC substrate by the IMR for 5 s and 5 min was also compared. Differences was compared with the shear bond strengths between 5 s and 5 min intermediate resin treatment times with the analysis of variance (ANOVA).

In *Study II* mean values of shear bond strength of PFC were computed from the load value of the highest point of load-displacement curve and compared by ANOVA. Independent variables for the shear bond strength values were the FRC surface treatment (ground or untreated), the storage condition (dry or thermocycled), and fiber orientation (unidirectional or random continuous glass fiber).

In *Study III* the tested factors were the type of test specimens (unreinforced polymer, glass FRC, glass FRC with CHX) and the storing conditions (dry or two weeks in water). The dependent variables were the flexural strength and modulus of the different groups. ANOVA was used, followed by Scheffe's and Dennett's T3 post hoc analysis.

In *Study IV* data were analyzed using as independent factors of polymerization method and the brand of the material. To determine statistically significant results, the Tukey post hoc test used. Weibull analysis was carried out from shear bond results using Weibull++6.0 software (Relia Soft Corporation, Tucson, Ariz., USA).

5 RESULTS

5.1 Results of shear bond strength

The main bond strength result was that the random continuous glass fiber veil FRC-material with or without oxygen inhibited resin layer (ground or untreated) on the substrate surface offered a good adhesion site for the PFC. The highest shear bond strength between the FRC and the PFC was achieved with the untreated substrate of random oriented glass veil FRC stored dry (29.8 ± 3.4 MPa), and thermocycling did not influence the result (29.4 ± 3.6 MPa). With the control (unidirectional FRC) material, the highest shear bond strength was obtained with untreated substrate and thermocycled specimens (15.2 ± 3.6 MPa).

Comparison of groups (the brand of FRC, polymerization method, storage time and direct or indirect laboratory technique made bonding with PFC to unidirectional FRC) did not reveal any difference in values of shear bond strength, with the characteristic shear bond strength varying between 20.1 and 23.7 MPa. The weakest shear bond strength values 10.8 ± 4.0 MPa were obtained with thermocycled specimens of group which the unidirectional FRC substrate has IMR only 5 s, and the FRC was polymerized by hand light-polymerization unit. All the shear bond test results are listed in *Figure 7* and a typical load displacement curve is shown in *Figure 8.*

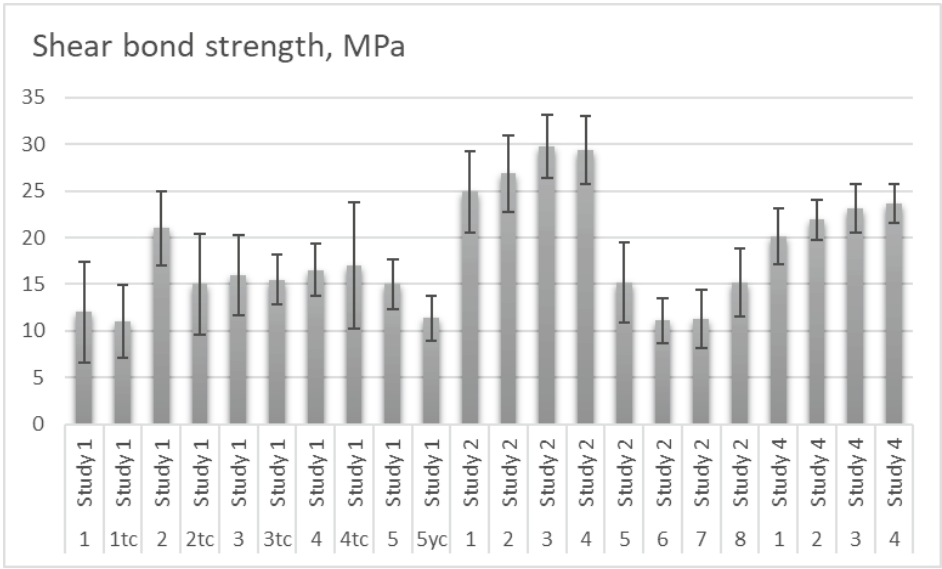


Figure 7. Mean shear bond strength of the specimens of different groups (n=6). Codes of the shear bond test groups are listed in Table 5.

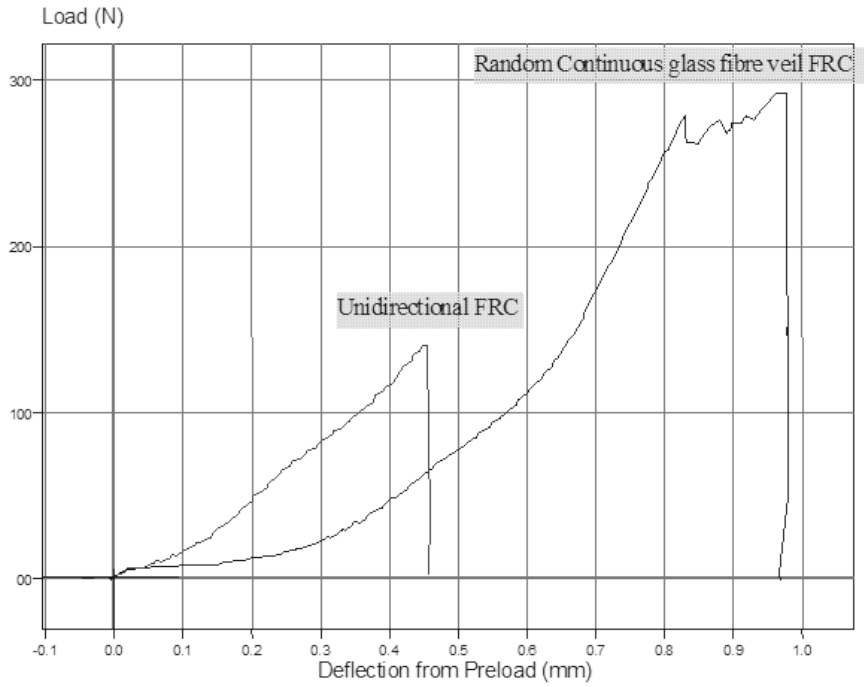


Figure 8. A typical load displacement curve for determining the shear bond strength of veneering composite to the FRC substrates. Adapted from original publication II.

5.2 Results of flexural strength

The flexural strength of test specimens is shown in *Figure 9*. The unidirectional glass FRC considerably increased the flexural strength and modulus. The highest flexural strength was in oven polymerized and water stored unidirectional Bis-GMA resin impregnated FRC 796.0 ± 105.0 MPa and modulus of elasticity of 26.7 GPa. The same FRC after being cured by hand-light curing device and being water stored has a strength of 559.0 ± 81.0 MPa and modulus of elasticity of 26.1 GPa.

In the FRC impregnated with UTMA, the flexural strength was with oven polymerized and water stored groups 689.0 ± 19.0 MPa and modulus of elasticity of 25.5 ± 1.0 GPa. The groups with hand-unit polymerized and water stored have 547.0 ± 72.0 MPa strength and modulus 24.2 ± 1.1 MPa.

In the CHX laced FRC reinforced provisional FPD polymer groups, stored for 2 weeks in water, the strength was 115.0 ± 19.0 MPa and modulus of elasticity of 3.9 ± 0.6 GPa. The lowest result was the unreinforced provisional FPD polymer-group with 43 ± 3 MPa strength and modulus of elasticity of 1.7 ± 0.2 GPa.

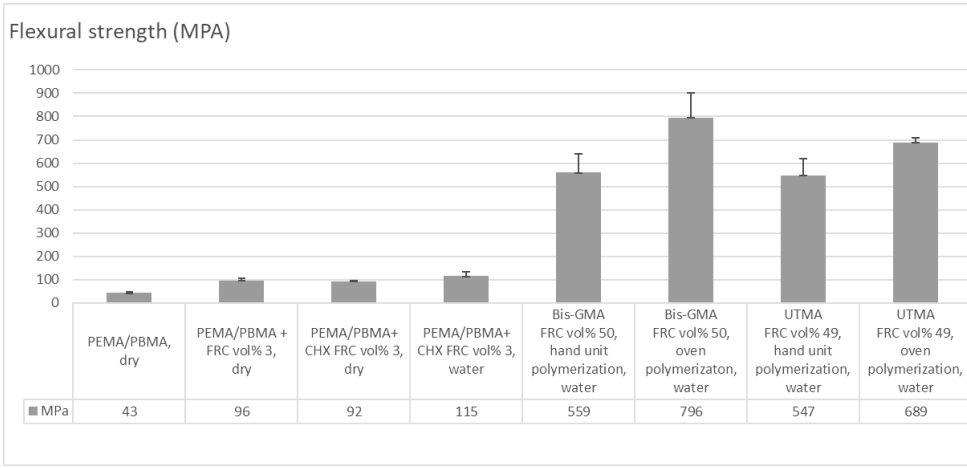


Figure 9. The flexural strength results (vol% is fiber content in the specimen).

5.3 Results of water sorption and CHX release

CHX was leached from the CHX FRC test specimens during the first three weeks (from 13 ppm to 36 ppm). Incubation time in water was 180 days and after 21 days of incubation, the extracted CHX concentration was 90 % of the total CHX content in FRC *(Study III)*.

In *Study 4* water sorption of Bis-GMA resin impregnated FRC was higher in both the hand-unit polymerized and oven polymerized groups compared UTMA-based resin impregnated FRC.

5.4 Results of DC%

FTIR analysis of the unidirectional FRC in *Study 1* showed that DC% was 77.4 % after oven polymerization and 66.9 % after polymerization with hand light unit. FTIR spectra of polymer matrix of dimethacrylate FRC is shown in *Figure 10*.

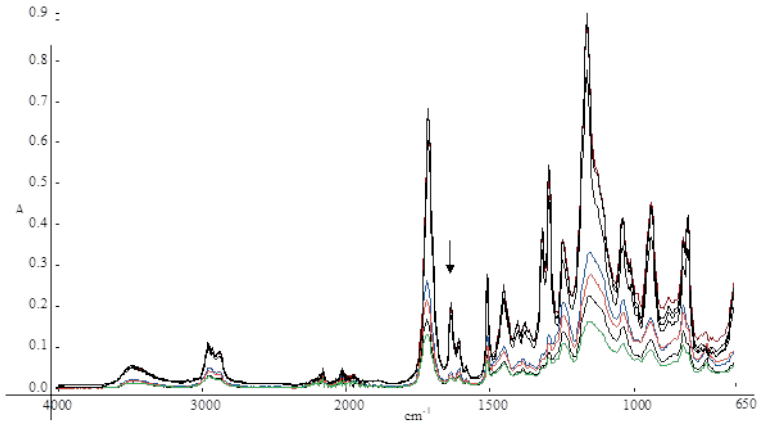


Figure 10. FTIR spectra of polymer matrix of dimethacrylate FRC showing C=C double-bond peaks (arrow) at 1636 cm -1 for unpolymerized resin matrix and for that being polymerized in light curing oven for 30 min. Adapted from original publication I.

5.5 SEM/EDS Results

SEM micrographs of the fracture surfaces showed that the random continuous glass fiber veil substrate differed from continuous unidirectional FRC surface (*Figure 11*) in *Study 2,* and in *Study 4* the impregnation degree with different resin (Bis-GMA and UTMA-based) was good. The Bis-GMA resin impregnated FRC showed also a more even fiber distribution between fiber and matrix than UTMA-based FRC. Single glass fiber diameter of Bis-GMA resin impregnated FRC was 20.2 µm (SD 1.9), and in UTMA-based FRC it was 9.8 µm (SD 1.1).

Elemental SEM/EDS analysis of the inorganic phase of FRCs showed similar main compounds: SiO_2, CaO, and Al_2O_3. SEM did not detect the inorganic alkali in the polymer matrix, but EDS analysis showed signs of carbon and oxygen in Bis-GMA resin impregnated FRC and SiO_2 signals at UTMA-based FRC in *Study 4.*

a) b)

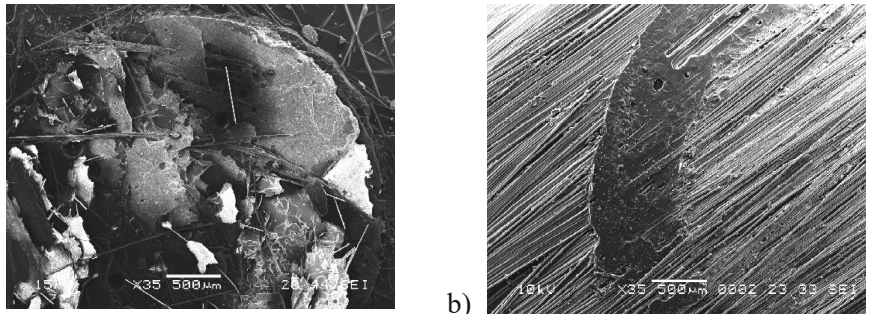


Figure 11. SEM photomicrographs of the substrate surface after the loading test. a) random oriented continuous unidirectional FRC, b) continuous unidirectional FRC. (Original magnification 35x)

5.6 Fiber content

The combustion analysis showed that the weight fraction of the inorganic phase (consisting only of fibers) in unidirectional PMMA preimpregnated FRC was 42 vol % (56 wt %) in *Study II*, PEMA/PBMA preimpregnated CHX FRC was 3 vol % (4 wt %) in *Study III,* and Bis-GMA resin impregnated FRC it was 50 vol % (66.0 wt %) while for UTMA-based FRC the weight fraction was 49 vol % (65 wt %) in *Study IV*. The quantity of glass fibers in random continuous glass FRC was 8 vol % (15 wt %) in *Study II*.

5.7 Statistical results

There was a significant difference on the shear bond strength between the groups when the IMR was allowed to influence for 5 s or 5 min ($P = 0.042$) shown with the univariate ANOVA (*Study I*) and the type of substrate ($P < 0.001$) with 3-way ANOVA (*Study II*). *Study IV* showed a similar result by polymerization; the polymerization device did not affect the bond strength values and the modulus of the groups was similar. The shear bond strength data were analyzed using Weibull analysis, which the Weibull modulus of the tested specimens showed a similar result. Instead, the two-way ANOVA revealed that the polymerization method had a statistically significant effect ($P < 0.001$) on the flexural strength values, whereas impregnated with UTMA or Bis-GMA resin of the fiber matrix showed no significant effect ($P = 0.221$) (*Study 4*). In the flexural strength and flexural modulus, with Tukey and Scheffé multiple comparisons, ANOVA showed a significant differences regarding reinforced and unreinforced test specimens ($P < 0.001$) (*Study III*).

6 DISCUSSION

This thesis is based on in vitro studies designed to determine the manufacturing process of indirect FRC structures to be used in dental technology. From a dental technological perspective, it is necessary to emphasize the importance of optimizing the bond strength of veneering PFC to FRC frameworks. The most commonly reported failure types with indirect FRC are delamination of the PFC, fracture of the FDP or debonding (van Heumen *et al.* 2009a, 2009b). These series of studies consider the bonding and flexural strengths and an insight incorporation of chlorhexidine digluconate into FRC and its release.

6.1 Bonding properties of laboratory used PFC to continuous unidirectional FRC with semi-IPN polymer matrix

Indirect FRC substructure is polymerized in a light curing oven, and if the oven has a vacuum, the oxygen inhibition layer on the surface will be lost. Different laboratory polymerization devices affect also the DC % differently. Early investigations have shown that the FRC substructure containing cross-linked polymer matrix only with high DC % does not offer adequate adhesion for veneering composites (Rosentritt *et al*., 1998, Özcan *et al.* 2005). In this thesis, in *Study I,* the DC % was 77.4 % after oven polymerization, and the main finding was that the final polymerized FRC can be refreshed again using the intermediate resin for 5 min. During the treatment time, monomers of the resin penetrated to the polymer matrix of the FRC, and FRC matrix offered a relatively good adhesion site for PFC. The composition and structure of the polymer matrix of the FRC material contained both linear and crosslinked polymer between the glass fibers from which the linear polymeric phases were dissolved in the monomers of the IMR. This resulted in the formation of secondary-IPN bonding of PFC to the FRC substrate, as has been suggested previously (Kallio *et al.*, 2001, Lastumäki *et al.* 2002, Lastumäki *et al.* 2003).

The results of “fresh” FRC substrate (like obtained in the direct technique) were the FRC substrate was polymerized only by the hand light polymerization unit resulting in a conversion rate of 66.9 %, but still gave equal or even lower shear bond strengths to PFC. It has been assumed that the polymerization after hand light curing will continue for about 24 h after exposure of the composites to light and will achieve a good DC% (Saunders 1990; Boyer *et al.* 1984; Leung *et al.*1983; Boyer *et al.*1978). According to the results, the use of IMR proved unnecessary to “fresh” FRC substrate. The FTIR analysis in *Study 1* was carried out 15 min after polymerization, suggesting that especially in the lower DC % group, there should have been enough radical activity left for chemical bonding of the PFC to the FRC substrate. Earlier it was found that the IMR is not necessarily needed with flow

viscosity PFC (Kallio *et al.* 2001). The PFC used in *Study I* and *II* was a highly viscous paste like composite, which benefits using IMR to adhere the composite to the FRC surface.

In *Study IV*, it was hypothesized that the bonding properties of Bis-GMA resin impregnated FRC should be better than those to UTMA resin impregnated FRC. However, this could not be confirmed within the limitations of this study. The hypothesis was based on the semi-IPN polymer resin matrix composition of Bis-GMA resin FRC, which have a pronounced benefit for the bonding of the materials by the ability of the adhesive monomers to diffuse into non-cross-linked phases of FRC structure when applied to the surface for a sufficient time, (5 min) like in *Study I.* It was hypothesized that in the UTMA resin impregnated FRC with high crosslink in structure, containing dimethacrylate-polymer matrix is not theoretically possible to obtain interdiffusion bonding. However, UTMA resin impregnated FRC did show comparable or somehow higher bond strength values. That is probably due to the IMR of cement used in the study did not have the capability to form interdiffusion bonding to Bis-GMA resin impregnated FRC because the dissolving parameter of the resin system differs from that of the PMMA phase of the polymer matrix of Bis-GMA resin FRC. The SEM-EDS analysis showed a high area percentage of glass in both FRC materials on the bonding surface. It has been shown that primers including HEMA and acidic phosphate monomers give better bond strength to FRC substrate than that obtained with containing HEMA primers only (Tezvergil *et al.* 2004). Thus, the results of the present study suggest that the amount of glass on the bonding surface as substrates that were ground also has a significant role in the bonding of new composites to FRCs.

The shear bond strength data were analyzed using Weibull analysis, in which the failure probability could be predicted at any stress level. A high Weibull modulus indicates more predictable failure behavior and a homogenous interface between the substrate and the adhered material. The Weibull modulus of the tested specimens showed a similar result. It could have been expected that the FRC substrate, which is only hand-polymerized and has a lower degree of conversion and cross-linking density, would provide a better bonding facility for the free radical bonding of the possible unreacted groups (Lastumäki *et al.* 2001).

6.2 Bonding characteristics of laboratory used PFC to glass FRC with continuous random fiber orientation

Fibers´ bonding mechanisms are based on silanization and mechanical attachment (Kallio *et al.* 2001, Lastumäki *et al.* 2003, Vallittu 2009). *Study I* showed adhesion

after the fiber surface was silanized by IMR while in *Study II* the fiber surface was not silanized at all by IMR. The main finding of *Study II* was that the random continuous glass fiber veil FRC-material with or without oxygen inhibited resin layer (ground or untreated) on the substrate surface offered very good adhesion site for the PFC. This could be due to lower fiber content whereby the monomers of the PFC can penetrate FRC surface irregularities because there was more semi-IPN polymer matrix. The continuous unidirectional FRC surface did not provide such micromechanical attachment for the PFC because the fiber content was higher, and the surface area of the polymer matrix was lower for interdiffusion bonding. Some studies have shown that an oxygen inhibited surface layer was need for good bonding, although controversial results have also been reported (Kupiec and Barkmeier 1996, Brosh *et al.*1997, Li 1997, Lucena-Martin *et al.* 2001, Al Musa and Al Nahedh 2015, Bijelic-Donova *et al.* 2015).

The random glass fiber veil FRC had likely a rougher surface than continuous unidirectional FRC because the fibers were shorter. The rougher surface might have provided microretention to PFC and that could also be one explanation why the veil material had higher shear bond strength (Rosentritt *et al.* 1998, Kallio *et al.* 2001). SEM-micrographs of the present study revealed cohesional type of failure within random glass fiber veil FRC substrate for ground and untreated veil FRC substrates. With veil FRC substrate, the loading produces crack branching and formed several independent cracks which propagated three-dimensionally at the interphase region. This type of fracture surface is typical for a tough type of interfacial fracture.

At the random continuous veil FRC interface, many fibers were pulled out, which suggest that the fibers have acted as a crack stopper like in earlier techniques by using woven glass fibers (Vallittu 2002). The cracks did not continue along the interface if there were fibers perpendicular to the direction of crack propagation. Fracture surface of the unidirectional FRC was smooth and the fracture was considered an adhesional failure (Samadzadeh *et al.* 1997, Petersen and Wenski 2002, Coker *et al.* 2003). It can be concluded also that by using the random glass veil FRC, it seemed to be possible to improve attachment of pontics to the framework of FPD, and veneering composite to the cores of the crowns. This is similar to a new short fiber composite intended for clinical use in posterior large restorations (Garoushi *et al.* 2011, 2013, Bijelic-Donova *et al.* 2016, Lassila *et al.* 2016).

The highly viscous PFC and high fiber content were assumed to be the reason for the relatively low bond strength values of PFC to the control continuous unidirectional FRC having the semi-IPN polymer matrix of the same kind. The material has shown in *Study I* good adhesion to the PFC with the use of the IMR.

This, however, requires the solubility parameter of the IMR to be close to that of the solubility parameter of the polymer matrix of the substrate. By increasing filler loading, the bond strength was decreased, especially if the aspect ratio of the fillers was high (Lastumäki *et al.* 2002, AlJehani *et al.* 2016).

Some earlier studies showed that the bond strength slightly increased after thermocycling with polymer composite materials (Kallio *et al.* 2001, Lastumäki *et al.* 2002). Generally, there was a trend that random glass fiber veil FRC was less influenced by thermocycling. This could be due to isotropic thermomechanical properties of the FRC substrate compared to anisotropic properties of continuous unidirectional FRC (Vallittu 1999, Tezvergil *et al.* 2003). In *Study I* and *II* there were no statistically significant effect differences between the thermocycled test specimens and dry stored. It has been shown previously that random orientation of fibers results in lower flexural strength and modulus of the FRC than that obtained by continuous unidirectional fibers. This has been illustrated by the reinforcing efficiency of the fibers (Krenchell´s factor) (Murphy 1998, Chen *et al.*1999, Behr *et al.* 2001). Based on this, it would be advisable to use continuous unidirectional FRC to reinforce bending performance and random-oriented fiber veil to improve bonding properties.

6.3 Release of CHX and flexural properties of glass fiber reinforced provisional FDP polymer

Study III demonstrated the effect of E-glass fiber-reinforcement on the fracture resistance and release of CHX from provisional FDP polymer. The fracture strength of the FDP polymer increased considerably by adding glass fiber reinforcement with continuous unidirectional fibers (*Figure 9)*. It is known that good impregnation of glass fibers with high viscous resin systems are an essential requirement for the potential of clinical use (Vallittu 1999).

It is desired that the polymer in the reinforcement prior the use is in highly porous form. The porosities have been shown to allow monomer liquid systems to penetrate the reinforcement and form multiphase polymer matrix for the FRC once the resin has been polymerized (Vallittu 1999). In *Study III,* the new approach was to reinforce the provisional FDP polymer with CHX-laced E-glass FRC. The porosities of the preimpregnated FRC were reservoirs for the CHX. The experiment proved to be promising because the results showed no reduction in the flexural properties compared to those of conventional fiber reinforcements, and the majority of CHX was released within three weeks of water immersion. It was hypothesized, that leaching of CHX from the FRC test specimens could weaken the material. This hypothesis was rejected and the CHX-laced fiber reinforcements

can possibly also be used in removable denture base polymers such as those suggested by Narva *et al.* (2001) and Liu *et al.* (2001). The reason for the unchanged or even slightly increased flexural properties (flexural strength hand modulus) suggests that leaching of CHX from the test specimens was subsequently compensated by water sorption, and the net effect on the flexural strength was therefore minor. Similar results have also been obtained regarding adhesion to dentin; chlorhexidine pretreatment of dentine surface can preserve the bond strength of the fiber post to resin composite to root dentin for 12 months (Cecchin *et al*. 2011, Lindblad *et al.* 2012). However, the mechanism of action of CHX in dentin bonding was explained by reduced activity of dentin degrading enzymes.

Study III demonstrated the expected release of CHX from the FRC test specimens. The release rate shows similar diffusion kinetics as found for instance with residual methyl methacrylate monomers of denture base polymers (Vallittu *et al.* 1995). The diffusion-based release suggests that the therapeutic use of CHX-laced FRC may need to be limited to temporary use only, such as a temporary bridge. On the other hand, as was shown, the CHX did not result in any weakening of the material even in longer term and therefore the fiber-reinforced device could technically be used even for a longer period. The antimicrobial agent modified FRC materials may also have other clinical applications in dentistry than provisional FPDs. For example, the material could be used in temporary periodontal splinting during the healing phase of periodontal surgical operations, or as a reservoir for antimicrobial agents in endodontic therapy. However, further investigations are necessary to determine more exactly the antimicrobial activity of CHX and possible development of microbial resistance during long term use. If that were the case, CHX FRC matrix will improve the patient's gums.

6.4 Characterization of physical properties of BisGMA and UTMA based FRC materials.

Water sorption is an important property determining the long-term strength and stability of the restoration. Previous studies have shown that the number of fibers in the composite matrix influences the water sorption (Lassila *et al.* 2002, Polat *et al*. 2003*).* In optimally impregnated systems, increased inorganic fiber and filler volume fraction decreases water sorption. It has been shown that there are no significant reductions of flexural properties in long-term water storage after 10 years (Vallittu & Matinlinna 2017).

It should be noted that in *Study IV* a method of measuring water uptake (or weight gain) was used instead of the precisely determined water sorption. As the flexural strength of the test specimens after the water storage period was also of major

interest, the test specimens were not dehydrated during measurement of water sorption at each time-point. In the highly cross-linked matrix systems, the solubility of the material into water is quite low (50.1 %), which was expected to be the case in the present study, so the water sorption and water uptake values can be considered practically equal. Water saturation by diffusion into the bar-shaped test specimen occurred during the first week in both materials. A somewhat higher diffusion speed was observed for Bis-GMA resin impregnated FRC compared with UTMA resin impregnated FRC. *Study IV* showed significant differences between the tested materials, possibly due to differences in the matrix compositions of the materials. Bis-GMA resin impregnated FRC is based to a large extent on BisGMA monomer, which consists of two -OH groups in the monomer molecule. Lassila *et al.* (2002) showed that water sorption of UDMA-based FRC was 1.2 wt %, which is close to the water sorption of UTMA resin impregnated FRC found in *Study IV*.

In *Study IV* the flexural strength values obtained after 30 days water immersion were higher (547 - 796 MPa) than in previous studies (*Figure 2*) carried out by Behr *et al.* (2000), who reported that after 30 days of water immersion the flexural strength value was 499 - 545 MPa with different FRC materials, i.e. lower than the values obtained in this study for dimethacrylate resin and UTMA resin impregnated FRC. Several in vitro investigations have been implemented to measure the fracture strength of FRC FDPs under mechanical loading conditions (Dyer *et al.* 2004, 2005, Özcan *et al.* 2005). When making a comparison, it is worth remembering e.g. the size of the test specimen, the content / position / type of fiber, the form of storage, and the storing time (Kangasniemi *et al.* 2003). A combustion test of dimethacrylate resin FRC and UTMA resin impregnated FRCs gave approximately equals amount of fibers in the polymer matrix. The slightly higher flexural strength values obtained for dimethacrylate resin FRC compared to UTMA resin impregnated FRC in the present study may have been caused by the semi-IPN polymer matrix of the dimethacrylate resin FRC. The partially non-cross-linked polymer matrix is not as brittle as the crosslinked UTMA resin impregnated FRC polymer matrix, which may result in higher flexural strength values. SEM/EDS analysis showed that the polymer matrix of UTMA resin impregnated FRC also consisted of inorganic fillers meaning that the actual fiber fraction was higher in dimethacrylate resin FRC than UTMA resin impregnated FRC. This was also confirmed by the image analysis. *Study IV* demonstrates the strength properties after water saturation, so results of the dry specimens are not available; we can only assume, under previous studies (*Figure 3*), that the dry values would be even higher.

In *Study IV* half of the FRC test specimens were polymerized in a light-curing oven, indicating an indirect procedure, and the DC% was higher in those “direct” groups compared to the groups polymerized with a hand light-polymerization unit

only. Post-polymerization in the oven has been shown to provide more conversion of the polymer matrix of FRC compared to the hand light-polymerization method, which explains the differences in the strength of FRCs obtained in the present study according to the polymerization method.

6.5 Future investigations

This series of in vitro studies was carried out during a time when FRCs were developing rapidly and gaining popularity in many different dental applications (2004).

Further studies should be carried out with respect to fracture propagation paths and toughness properties of interfaces in indirectly made FRC FDPs. This is due to the fact that fracture toughness has proved to be a more significant parameter than static flexural testing in predicting clinical success of FRC devices.

In terms of leaching substrates from FRC, antimicrobial aspects from dental perspective should be studied in more detail. Recent advances of FRC in medical implants suggest also the importance of studies of drug releasing implant systems (Piitulainen 2015).

7 CONCLUSIONS

This series of studies aimed to evaluate the interfacial adhesion aspects between fiber reinforced composite and particulate filled composite systems as well as release of chlorhexidine digluconate form a modified fiber reinforced composite. The following conclusions can be made:

1. Applying the intermediate resin increased the shear bond strength values of veneering composite to fiber reinforced composite with a high degree of conversion multiphase polymer matrix.

2. The random continuous glass fiber veil fiber reinforced composite material with or without oxygen inhibited resin layer on the substrate surface and offered good adhesion site for the particulate filled composite. The adhesion is considerably better than the continuous unidirectional fiber-reinforced composite substrate.

3. Chlorhexidine digluconate-laced glass fiber-reinforcement can be used with provisional fixed dental prostheses polymer and the release of the chlorhexidine digluconate occurs within three weeks of water immersion.

4. There were minor differences between UTMA-based resin and Bis-GMA resin impregnated glass-fibers.

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