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OF TURKU

# BEHAVIOR OF RESIN COMPOSITES AT THE INTERFACE BETWEEN ORTHODONTIC BRACKET AND TOOTH

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Dr. Durgesh Bangalore Huchaiah





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*Live as if you were to die tomorrow, learn as if you were to live forever*  
*M.K. Gandhi*

*To the memories of my Late Father,  
For being the driving force behind all my achievements  
Your presence would have made me much more enthusiastic and stronger  
I really miss you DAD.*

## **ABSTRACT**

Durgesh Bangalore Huchaiah

### **Behavior of resin composites at the interface between orthodontic bracket and tooth**

University of Turku, Faculty of Medicine, Department of Biomaterials Science, Finnish Doctoral Program in Oral Sciences- FINDOS, Institute of Dentistry, University of Turku. *Annales Universitatis Turkuensis*, Turku, Finland 2019

Adhesive interface between bracket and enamel is based on adhesion of resin-based material to enamel and to bracket, the latter being typically reinforced by mechanical retention of the bracket bonding surface. Bonding results are influenced by brackets, adhesive systems and by composite resin between bracket and enamel. The adhesion strength is also influenced by use of possible reinforcing materials at the interface. The main objective of this study was to study the behavior of resin composites at the bracket-tooth interface under different loading conditions with or without use of intermediate layers of reinforcing glass fibers. The orthodontic brackets were bonded using flowable composites with different visco-elastic properties and the values of debonding load and displacement were determined at the point of debonding. The degree of cure (DC %) of the glass fiber reinforced adhesive layer underneath the bracket and irradiance power of the light curing tip underneath the bracket was determined. Furthermore, the creep behavior of the interface adhesive materials was studied using orthodontic bracket-tooth and three-point bending test models. The adhesive interface was subjected to constant interfacial loading. To characterize the properties of the adhesive interface materials used, nanomechanical (nanohardness and elastic modulus) properties was evaluated. The outcome of the experimental study demonstrated that the incorporation of a glass-fiber reinforced composite (FRC) with a low elastic modulus at the adhesive interface between the orthodontic bracket and enamel increased the debonding force and strain compared to adhesive systems with higher elastic modulus. An enhanced degree of cure of the photopolymerizable adhesive reinforced with glass FRC was observed under the metal brackets. The creep test demonstrated that the incorporation of continuous glass fibers at the interface between orthodontic bracket and enamel increased the creeping and debonding time of the bracket and that the orientation of the fibers and the resin matrix type significantly affected the creep behavior of the adhesive materials. From the above outcome, it can be concluded that incorporation of glass FRC at the adhesive interface could be beneficial considering the long duration of orthodontic brackets remaining in the oral cavity.

**Keywords:** Adhesive Resins; Bonding; Creep; Cross-linking; Debonding; Degree of Conversion; Glass Fibers; Fiber reinforced composites; Irradiation; Interpenetrating Polymer Network; Orthodontic Brackets; Particulate Filler Composite; Shear; Strain

## TIIVISTELMÄ

Durgesh Bangalore Huchaiiah

### **Oikomishoidon braketin ja hampaan välissä olevan yhdistelmämuovin käyttäytyminen kuormituksessa**

Turun yliopisto, lääketieteellinen tiedekunta, hammaslääketieteen laitos, biomateriaalitieteen oppiaine, Kansallinen suun terveystieteiden tohtoriohjelma – FINDOS, Annales Universitatis Turkuensis, Turku, Suomi 2019

Hampaiden oikomishoidossa käytettävät kiinnikkeet, ns. braketit liimataan hampaan kiillepintaan. Liimasauman kestävyys riippuu hampaan pinnan käsittelystä ja liima-aineen koostumuksesta. Tämän väitöskirjatutkimuksen tarkoituksena oli selvittää braketin ja hampaan välisen liimasauman käyttäytymistä erilaisissa kuormitustilanteissa ja tilanteissa, joissa liiman koostumusta muutettiin muun muassa lisäämällä siihen lasikuitukomposiittia. Brakettien liimaamisessa käytettiin liimoja, joiden visko-elastiset ominaisuudet poikkesivat toisistaan, jonka takia niiden käyttäytyminen kuormitustilanteessa vaihteli, mikä olikin yksi tutkimuksen kohde. Liima-aineen kovettumista tutkittiin mittaamalla liima-aineen monomeerien reagoimista keskenään, eli niin sanottua kovettumisastetta (degree of monomer conversion, DC%) ja koska kovettumisreaktio käynnistetään valolla, selvitettiin lasikuitujen mahdollista vaikutusta valon kulkeutumiseen braketin ja hampaan väliseen tilaan. Kliinisesti liimasaumaan kohdistuvaa kuormitustilannetta jäljitettiin pitkäkestoisella staattisella kuormitustestillä, jossa liima-aineen polymeerirakenteen viruminen (creeping) määritettiin erilaisille liimakoostumuksille. Liima-aineet tutkittiin myös niiden nanomekaanisten ominaisuuksien suhteen määrittämällä pinnan nanokovuus ja kimmoisuusmoduuli. Tutkimuksen tulokset osoittivat, että itse liima-ainetta alhaisemman kimmoisuusmoduulin lasikuitukomposiitin käyttäminen braketin ja hampaan rajapinnassa lisäsivät kiinnitysvoimaa ja rajapinnan muodonmuutoksen määrää kuormituksessa. Lasikuitujen avulla pystyttiin lisäksi parantamaan liiman kovettumista kovetusvalon avulla. Mielenkiintoinen tutkimustulos liimasauman käyttäytymisestä pitkäaikaisessa kuormitustuloksessa liittyi myös lasikuituihin: lasikuitujen suunnalla suhteessa kuormittavan voimaan suuntaa oli vaikutusta liimasauman virumiseen ja braketin irtoamiseen hampaan pinnasta. Yhteenvetona tutkimustuloksista voidaan todeta, että lasikuitukomposiitin käyttämisellä oikomishoidon braketin ja hampaan välissä voidaan vaikuttaa liimasauman kuormituskestävyyteen ja sillä voi olla kliinisesti merkittävää hyötyä.

**Avainsanat:** Oikomishoito; braketti; kiinnike; liima-sauma; liima; yhdistelmämuovi; polymeroituminen; kovettumisreaktio; kuormitus; viruminen

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## ABBREVIATIONS

ANOVA	Analysis of Variance
ARI	Adhesive Remnant Index
ATR	Attenuated Total Reflectance
<i>Bis</i> GMA	<i>Bis</i> -phenol-A-glycidyl dimethacrylate
DC	Degree of Conversion
DMA	Dynamic Mechanical Analyzer
ESN	everStick NET
F	Force
FRC	Fiber Reinforced Composites
FT-IR	Fourier Transmission-Infrared Spectroscopy
GPa	Gigapascal
IPN	Interpenetrating Polymer Network
kV	Kilovolts
MARC	Managing Accurate Resin Curing
mN	Millinewton
mm	millimeter
Min	Minute
MPa	Megapascal, N/mm <sup>2</sup>
MPTS/MPS	3-methacryloxypropyltrimethoxysilane
n	Sample size
N	Newton
nm	nanometer
PFC	Particulate Filler Composite
PMMA	Poly(methylmethacrylate)
r	Pearson's Correlation Coefficient
R <sup>2</sup>	Simple Correlation Coefficient
RBC	Resin-Based Composite
s	Sonds
SBS	Shear Bond Strength
SEM	Scanning Electron Microscope
Semi-IPN	Semi-Interpenetrating Polymer Network,

## *Abbreviations*

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SPSS	Statistical Package for Social Sciences
SD	Standard Deviation
TEGDMA	Triethylene Glycol Dimethacrylate
UEDMA/UDMA	Urethane Dimethacrylate
UHMWPE	Ultrahigh-Molecular-Weight Polyethylene
UV-Vis	Ultraviolet Visible Spectrometry
Wt%	Weight Percentage
$\mu\text{m}$	Micro meter
$\mu\text{L}$	Micro liter
$\text{mW}/\text{cm}^2$	Irradiance Power

## **LIST OF ORIGINAL PUBLICATIONS**

This thesis is based on the following original publications, which are referred to in the text by Roman numerals I-IV. The original publications are reproduced with the permission of the copyright holders.

- I. Durgesh BH, Alkheraif AA, AlSharawy M, Varrela J, Vallittu PK. Damage of the interface between an orthodontic bracket and enamel – The effect of some elastic properties of the adhesive material. *Mech Compos Mater* 2016; 51(6):805-812.
- II. Durgesh BH, Alkheraif AA, Varrela J, Vallittu PK. Photo Initiated Curing of Bracket Adhesive by Light Transmission Through Glass Fibers. *J Biomater Tissue Eng* 2015; 5: 411–416.
- III. Durgesh BH, Alkheraif AA, Altwijry MA, Asiry MA, AlShahrani I, Varrela J, Vallittu PK. Creep behavior under shear stress of adhesive resin system at the interface between orthodontic bracket and enamel. *Mech Compos Mater* 2019; 55(2):275-284.
- IV. Durgesh BH, Alkheraif AA, Musaibah AS, Asiry MA, Varrela J, Vallittu PK. Creep behavior of resin composite interface between orthodontic bracket and enamel. *J Adhes Dent* 2018; 20(5): 417–424.

# 1 INTRODUCTION

The resin systems used in dentistry are typically dimethacrylate monomers and particulate fillers with light, chemical or dual curing initiator systems. As in other dental specialties, light cure adhesives are preferred over chemical cure adhesives for orthodontic bonding. The reason is that they allow sufficient working time during bracket placement and the irradiation of the adhesives can be postponed so that clinician gets sufficient time to fix any problems that may arise during bonding or treatment procedure. On polymerization, dimethacrylate monomers forms a highly cross linked polymer matrix which is defined by their brittleness and relatively high elastic modulus of the resin matrix (Vallittu, 2009).

Fiber reinforced composites (FRCs) have been clinically tested to be used in different fields of medicine and dentistry for more than 40 years ago. Not until 20 years ago their use became a clinical practice in dentistry and medical use is now starting. Among the different fibers available for reinforcement, glass fibers are preferred for dental applications considering the good adhesion with dimethacrylates monomers through silane coupling agents (Vallittu, 1993; Bouillaguet *et al.*, 2006). FRCs have been used in root canal posts and cores, fixed prosthetic appliances, periodontal splinting, restorative resin composites, orthodontic retainers, space maintainers and other active appliances (Vallittu and Özcan, 2017). They have also been studied as reinforcement between orthodontic bracket and enamel (Shinya *et al.*, 2009). Glass fibers have been used in different patterns to strengthen dental resin matrix, including continuous unidirectional roving, continuous bidirectional woven or mat, and discontinuous short-fiber reinforcements (Garoushi *et al.*, 2007). The unidirectional fibers exhibits anisotropic mechanical properties to the composite and are recommended for applications where the highest stress is known. The incorporation of bidirectional fibers, arranged perpendicular to each other (weave or mat) reinforces the composite in two directions (orthotropic property) and, are suitable in cases where the load direction remains unknown or when there is no space for incorporating unidirectional fibers. The mechanical properties of short fibers randomly oriented are equal in all directions (isotropic property) (Murphy, 1998).

The adhesion strength of orthodontic brackets bonded to enamel is affected by several factors. Among them, adhesive composition and characteristics and complex interactions of different materials at tooth-adhesive-bracket interface are the most prominent (Park *et al.*, 2009). Orthodontic adhesives are usually low viscous resins with increased amount of co-monomer in the formulations which facilitates improved flow of the resins into the micromechanical irregularities of the etched enamel (Eliades *et al.*, 2001). Based on the same concept, flowable resins have been used in orthodontic bonding and has met with success. Flowable resins have lower filler loading and has improved penetrability into the micro-

irregularities of the surface. Furthermore, there is no need for intermediate bonding resins when using flowable resin composites for bracket bonding which is an advantage over traditional orthodontic resins (D'Attilio *et al.*, 2005; Ryou *et al.*, 2008; Park *et al.*, 2009). Similar to bracket adhesion strength results, the debonding mechanisms are also affected by factors such as bond strength, viscosity and elasticity of adhesive resin and thickness of intermediate adhesive resin layer. Most of the adhesion strength studies in orthodontic literature have concentrated on adhesion strength of brackets under different conditions and compared different orthodontic adhesives. However, debonding mechanism of the brackets relative to the elastic properties of the polymeric matrix still remains subject of interest.

The curing depth of dental FRCs which is typically made up of dimethacrylate system is limited due to the fillers in the composite and clinical situations, such as curing the resin material under an orthodontic bracket. If the total energy required for polymerizing the resin by light irradiation is not attained, it could adversely affect technical and biological aspects of treatment process. The DC% is directly related to the material's physical properties: an increased DC% result in increased strength and stiffness of the material. The unreacted carbon double bonds in the final matrix may result in resin degradation and solubility, decreased mechanical properties and may trigger allergic reactions in some individuals. The DC% of light cure dimethacrylates can be improved by incorporation of reinforcing glass fibers. These fibers transmit the curing light to the resin matrix to initiate polymerization and the curing light scattered out from the glass fibers enhances the curing efficiency (Shinya *et al.*, 2009).

In fixed orthodontic therapy, an effective tooth movement which is three dimensional in nature is regulated by bonding interface between tooth and orthodontic bracket. The adhesive interface should transmit the forces from the bracket to the tooth and should be stable enough to resist the forces generated by the treatment mechanics, mastication, and routine activities. This said, the adhesive interface should also facilitate subsequent bracket debonding without damaging tooth tissues. The masticatory forces apply dynamic stress of low magnitude and the treatment mechanics (arch wires) predominantly apply static forces over a long period at the interface. Failure of the adhesive interface does not occur instantaneously and can be a consequence of slow deformation at the interface which may result in subsequent debonding of the orthodontic attachments (Zachrisson, 2007). The deformation can be elastic, plastic or creep in nature. The adhesive interface in orthodontic situation is exposed to forces for relatively long periods, and materials often respond by time and stress dependent creep deformation. The material enters into recovery phase as soon as the stress is removed (Bales, 1998).

## 2 REVIEW OF LITERATURE

### 2.1 Dental resin composites

Resin based composites (RBC) are described as a material containing *discontinuous dispersed (filler) phase mixed into a continuous (matrix) phase*. The material consists of three major components: resin matrix, fillers and coupling agents. The reinforcing filler phase is usually harder and tougher than the matrix, and thus helps in improving the overall properties. However, the resultant properties may not be completely related to those of single constituents (Ritter, 2018).

#### 2.1.1 Resin matrix

Initially, the organic resin matrix was based on mono methacrylate monomer. Polymers cured from these monomers presented with few drawbacks such as inadequate strength, polymerisation shrinkage and water solubility and hence were replaced by dimethacrylates. Dimethacrylate monomers have high molecular weight and form a highly cross linked polymer network thus overcoming the some of the disadvantages possessed by mono methacrylates. Various dimethacrylate monomers including Bisphenol-A-glycidyl dimethacrylate (BisGMA), ethoxylated BisGMA (BisEMA) and urethane dimethacrylate (UDMA) has been used in formulation of dental resin composites (Figure 1).

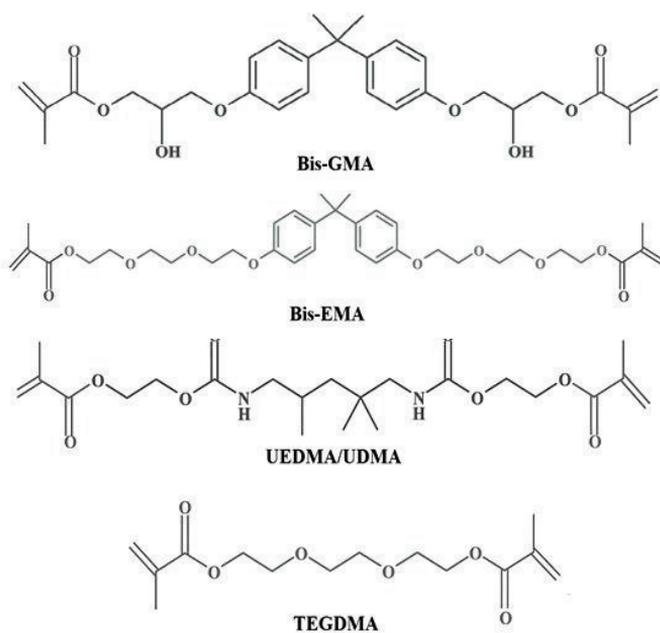


Figure 1: Chemical formula of the commonly used resin matrix monomers

The most commonly used organic phase (monomer) is BisGMA (Amirouche-Korichi *et al.*, 2009). BisGMA compared to other monomers offers less shrinkage, high strength and hardness, higher modulus and reduced toxicity. In contrast, BisGMA also presents with certain drawbacks such as high viscosity which limits the incorporation of inorganic fillers and thus leading to a low degree of conversion (DC%) (Amirouche-Korichi *et al.*, 2009). In solving such issue, co-monomers such as triethylene glycol dimethacrylate (TEGDMA), with low molecular weight and viscosity are incorporated as a diluent to lower the viscosity of resin monomer systems (Chen, 2011).

### 2.1.2 Inorganic fillers

The purpose of incorporating fillers within resin composites is to decrease the amount of matrix material and to increase the strength of the composite. The resultant composite would exhibit increased hardness, less wear and reduced polymerization shrinkage (Azzopardi *et al.*, 2009). The physical and mechanical properties of composite resin can be modified by filler composition and size, morphology, and distribution of filler particles. Resin based composites are classified as particulate filler composite (PFC) and fiber reinforced composites (FRC) according to the reinforcing filler (particles and fibers respectively) incorporated (Vallittu, 2001; McCabe and Walls, 2008). PFCs are generally isotropic which means they exhibit similar mechanical and physical properties in all directions (Vallittu, 2015; Vallittu and Özcan, 2017). In contrast to PFCs, FRC can be isotropic, orthotropic or anisotropic which means that material exhibits different mechanical and physical properties in different directions (Goldberg and Burstone, 1992; Vallittu, 2001; McCabe and Walls, 2008; Vallittu, 2015; Vallittu and Özcan, 2017). The commonly used fillers in PFC are quartz, colloidal silica, and silica glass containing strontium, barium and zirconium (Halvorson *et al.*, 2003). The quantity of fillers of PFC is generally 70%-80% by weight and the filler size ranges from 0.1 $\mu\text{m}$  to 100 $\mu\text{m}$  (Beun *et al.*, 2007). The fillers in FRC are long continuous or short discontinuous fibers made up of glass, carbon and polyethylene (Vallittu, 1998a; Garoushi *et al.*, 2007).

### 2.1.3 Coupling agents

Coupling agent is used to bond chemically and physico-mechanically the inorganic fillers and the organic matrix. The bonding is achieved by coating the fillers with a silane coupling agent that links the filler and matrix chemically through alkoxy silane and methacrylate functional groups. Silane coupling agent increases also the surface wettability which improves physico-mechanical attachment of resin to fillers. A typical organosilane coupling agent is 3-methacryloxy propyl trimethoxy silane (MPTS). Other coupling agent, acryloxy propyl trimethoxysilane (APM), and 10-methacryloxy decyltrimethoxy silane

(MDS) are also employed in dental resins (Matinlinna and Vallittu, 2007).

## 2.2 Classification of resin composites

Several authors have classified resin composites according to different parameters based on polymerization initiation systems, filler type, size and shape, and viscosity of resin composite (Lutz and Phillips, 1983; Willems *et al.*, 1992; Mitra *et al.*, 2003; Ilie and Hickel, 2011; Ilie *et al.*, 2013). Figure 2 presents the classification of resin composite based on different properties and compositions.

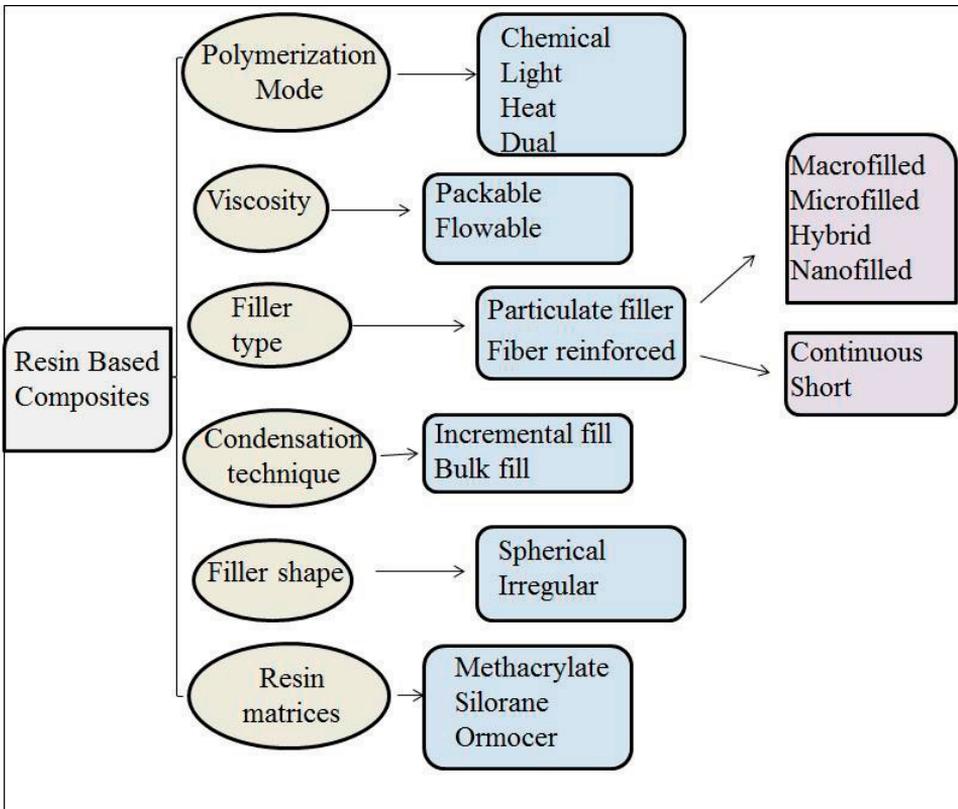


Figure 2: Classification of resin composites based on different properties and compositions

## 2.3 Particulate filler resin composite (PFC)

Particulate filler resin composite (PFC) contains particle fillers usually made up of quartz, colloidal silica, and silica glass containing strontium, barium and zirconium (Halvorson *et al.*, 2003). Based on filler size, the PFC are classified as macrofilled, microfilled, hybrid or nanofilled (Beun *et al.*, 2007). According to the volume fraction of fillers, PFCs are classified as compact-filled (> 60 vol % fillers) and midfilled composite (< 60 vol % fillers) (Willems *et al.*, 1992).

## **2.4 Fiber reinforced composite (FRC)**

Fiber-reinforced composites (FRCs) are a group of non-metallic biomaterials that are growing in popularity and are widely used in several dental applications. FRCs is a material combination of polymer matrix reinforced with fibers. The fibers act as reinforcing part when the load is directed towards the composite. It is of importance that load is transferred to fibers from polymer matrix to make the material strong and rigid. FRCs is materials that can be tailored according to the clinical situation and mimics mechanically, the properties of dentine or bone. The performance of FRCs depends on the interface properties as the resulting stresses from several sources are transferred to the fibers through this interface region (Ballo and Närhi, 2017). The fibers in FRC are long continuous or short discontinuous fibers usually made up of glass, carbon and polyethylene. The long continuous reinforcing fibers are unidirectional or bidirectional and can be oriented as rovings, weaves or mat. The short discontinuous fibers are normally oriented in random directions (Vallittu, 2018).

### **2.4.1 Clinical applications of FRC**

The FRCs are utilized in several fields of dentistry and medicine. They have been widely used for fabrication of fixed and removable dental prostheses, root canal posts and cores, in restorative resins, orthodontic retainers, space maintainers and active appliances, periodontal splints, facial prostheses and surgical applications of implantology. FRCs have also been tested for facial prostheses, surgical applications of implantology and cranial bone repair (Shinya *et al.*, 2009; Posti *et al.*, 2016; Piitulainen *et al.*, 2015; Vallittu, 2018).

### **2.4.2 Classification of FRCs**

FRCs are classified in several ways based on fiber type, fiber architecture, fiber orientation, and architecture (Vallittu, 1996; Butterworth *et al.*, 2003).

### **2.4.3 Properties of FRCs**

The main advantage of the FRCs is that it can be modified and adapted to a specific clinical situation. FRCs were developed to improve the properties of conventional PFCs such as polymerization shrinkage, inadequate mechanical properties, water sorption and brittleness (Vallittu, 1996). It has been reported that dental FRCs provide high strength, rigidity, flexural strength and load-bearing capacity of the construct as compared to PFCs (Vallittu, 2014 ). Furthermore, the polymerization shrinkage and thermal expansion is also reduced with the use of PFCs (Tezvergil *et al.*, 2003; Tezvergil *et al.*, 2006). There are several factors that contribute to the efficiency of fibers, and thereby to the physical properties of the FRC.

#### 2.4.4 Factors affecting FRCs

The properties of FRCs are influenced by factors such as the fiber type (e.g., glass, ultrahigh molecular weight polyethylene (UHMWPE), aramid (Kevlar<sup>R</sup>), and carbon/graphite) fiber length (continuous, discontinuous), orientation (unidirectional, bidirectional, and random), quantity of fibers in the matrix, fiber impregnation by resin, adhesion between fiber and resin matrix, and resin matrix used in FRCs (Vallittu, 2018).

##### 2.4.4.1 Reinforcing fiber type

###### a) Glass fibers

Glass fibers are the most commonly used reinforcing fibers in dental applications. They offer several advantages including high tensile and flexural strength, good compressive and impact strength, good chemical resistance and insulating properties besides being inexpensive (Lassila *et al.*, 2002; Al-Haddad, 2015). The glass fibers are available as A, C, E, R and S based on chemical composition. However, the E and S glass fibers are commonly used for dental applications (Zhang and Matinlinna, 2012).

###### i. E-glass

E stands for electric. E-glass is made of very low (<1%) alkali content alumino boro silicate with SiO<sub>2</sub> 54 wt%, Al<sub>2</sub>O<sub>3</sub> 14 wt%, CaO + MgO 22 wt%, B<sub>2</sub>O<sub>3</sub> 8.5 wt% and Na<sub>2</sub>O 0.5 wt%. These fibers have good strength and rigidity but relatively low fatigue resistance and tensile modulus (Vallittu, 1996; Zhang and Matinlinna, 2012).

###### ii. S-glass

S-glass fibers refer to high strength glass fibers made of alumino silicate without CaO but with high MgO content (SiO<sub>2</sub> 64 wt%, Al<sub>2</sub>O<sub>3</sub> 26 wt% and MgO 10 wt %). They have the highest tensile strength among all fiber types and hence the name S (strength) glass. They are rarely used because of their high production costs (Barbucci, 2002; Zhang and Matinlinna, 2012).

###### b) Ultrahigh molecular weight polyethylene (UHMWPE)

Polyethylene fibers have a ultrahigh modulus. They are cold gas plasma treated to enhance its adhesion to composite resins. They are white in color, chemically inert with low density and biocompatibility (Karaman *et al.*, 2002). Poor interfacial adhesion between the resin matrix and fibers is the main disadvantage of polyethylene fibers (Vallittu, 1997; Bahramian *et al.*, 2015).

###### c) Aramid

Aramid (aromatic polyamide, Kevlar<sup>TM</sup>) is a fiber with a rigid and anisotropic

molecular structure. Aramid fibers were developed in 1960s as an alternate for steel reinforcements in rubber tyres (Rosato and Rosato, 2005). They have high tensile strength, good impact resistance and low density but presents with poor compressive strength and they are recommended to be used with other fibers (Barbucci, 2002). They can be adhered to resin matrix of acrylates but the FRC can fail due to fibers anisotropy (Vallittu, 1993).

#### **d) Carbon/graphite fibers**

Carbon/graphite fiber is strong, biocompatible, corrosion resistant, and can be physic-mechanically adhered to the resin matrix. However, the potential dental use of carbon/graphite fibers is limited only to the reinforcement of first generation FRC root canal post material (Dean *et al.*, 1998). They also have certain disadvantages such as low impact strength, uneven surface topography and black color which limits its use in situations that require natural appearance of dentition (Bowman and Manley, 1984; De Boer *et al.*, 1984; Larson *et al.*, 1991).

#### **2.4.4.2 Fiber length**

For effective fiber reinforcement of polymers, it is always essential that the stress be transferred from polymers to fibers. This is achieved by incorporating fibers equal to or greater than critical fiber length ( $l_c$ ), which ranges from 0.5 to 1.6 mm for BisGMA based resin fibers and E-glass fibers (Cheng *et al.*, 1993; Vallittu, 2014). If the fiber length is shorter than critical length, deformation of matrix occurs around the fibers and there is no stress transfer to the fiber (Callister, 2007). Long continuous glass fibers, with or without surface treatment, have been used to reinforce dental acrylic resins and have demonstrated enhanced mechanical properties and fracture load (Stipho, 1998). Previous studies on short glass fiber reinforced composite resin have revealed improved flexural strength, fracture toughness and load bearing capacity (Garoushi *et al.*, 2013).

#### **2.4.4.3 Fiber orientation**

Reinforcing efficacy of fibers in FRCs is also dependent on fiber orientation. (Figure 3). Continuous unidirectional and bidirectional fibers are the two main structural types of FRC products presently available.

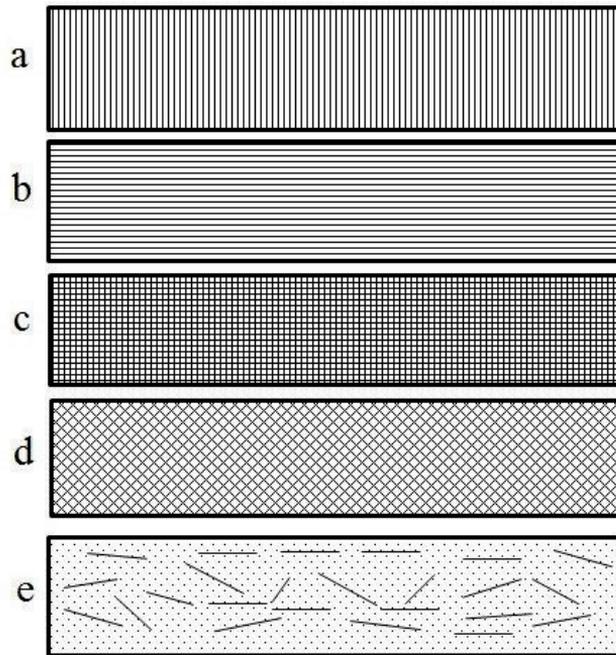


Figure 3: Long continuous fibers oriented as rovings (a, b), weaves (c, d) and mat (randomly oriented fibers) (e)

The unidirectional fibers exhibit anisotropic mechanical properties to the composite and are recommended for applications where the direction of the highest stress is known. The reinforcing efficiency, also known as Krenchel's factor ( $K_{\theta}$ ) (Murphy, 1998) of continuous unidirectional fibers is theoretically 100% ( $K_{\theta} = 1$ ), which means that reinforcing properties obtained are in one direction. The incorporation of bidirectional fibers, arranged perpendicular to each other (weave) reinforces the composite in two directions (orthotropic property). The theoretical reinforcing efficiency of such fibers is reduced by 50% ( $K_{\theta} = 0.5$ ) and furthermore, the Krenchel factor drops to 25% in case of bidirectional mat fibers. Bidirectional fibers are suitable in cases where the load direction remains unknown or when there is no space for incorporating unidirectional fibers. The mechanical properties of randomly oriented short fibers are equal in all directions (isotropic property). They have  $K_{\theta} = 0.38$  when considered in flat surfaces, but the efficiency of reinforcement decreases ( $K_{\theta} = 0.20$ ) in three dimensional structures (Vallittu, 1996; Vallittu, 2001; McCabe and Walls, 2008; Garoushi *et al.*, 2009). The reinforcing efficiency of fibers is high when they are oriented to their long axis and perpendicular to an applied load (Galan and Lynch, 1989).

#### 2.4.4.4 Quantity of fibers in the matrix

The overall mechanical performance of FRCs is determined by relative proportions of FRC constituents which are expressed as weight or volume fractions. Previous studies have reported an increased flexural strength with increased fiber content (Nohrstrom *et al.*, 2000; Agarwal and Broutman, 1990; Barbero, 2010). Any change in fiber or matrix content is found to alter the FRC behavior considerably. This theory, known as ‘law of mixture’ is presented in the form of equation (1) (Al-Haddad, 2015).

$$E_c = E_f V_f + E_m V_m \quad (1)$$

$E_c$  = Overall property of the composite

$E_f$  = Fiber property

$V_f$  = Total volume fraction of the fibers

$E_m$  = Property of the matrix and

$V_m$  = Total volume fraction of the matrix

According to the above law of mixture equation, an increase in a particular constituent on which the performance of the FRC relies upon, increases the overall properties of the composite. Correspondingly, fibrous mechanical properties of FRC are determined by an increased fraction of reinforced fibers (Vallittu, 1999; Garoushi *et al.*, 2006).

#### 2.4.4.5 Fiber impregnation by resin

The resin penetration to the spaces between the fibers is termed resin impregnation (Vallittu and Özcan, 2017). It is of importance that the fibers are impregnated (total embedding of the fibers) with resin matrix for reinforcing effect. An adequate impregnation will provide basis of interfacial adhesion and thus enabling effective transfer of stresses from matrix to the fibers (Vallittu, 2001) (Figure 4). The fibers are usually available in dry or resin pre-impregnated forms. Dry fibers require wetting with a resin matrix before their application whereas the pre-impregnated forms are specially manufactured by various techniques (Goldberg and Burstone, 1992).

Commonly, the resin pre-impregnated forms are available as FRC ‘pre-pregs’, a FRC strip containing both fibers and unpolymerized resin matrix. The use of pre-pregs instead of dry fibers ensures high degree of resin impregnation, prevents void formation and reduces technique sensitivity when fibers are used (Goldberg and Burstone, 1992; Vallittu, 1998b).

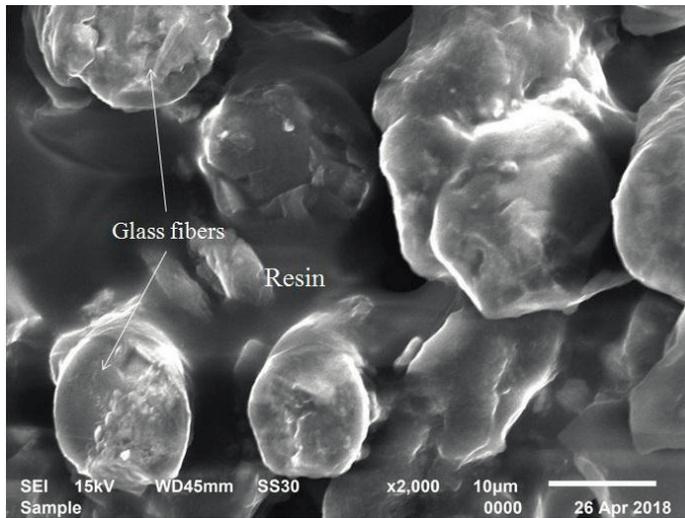


Figure 4: Scanning electron microscopy image of the fracture surface of FRC showing well impregnated fibers in polymer matrix

#### 2.4.4.6 Interfacial adhesion between fiber and resin matrix

For effective transfer of load in FRC from polymer matrix to reinforced fibers, adequate adhesion of fibers to the polymer matrix is required (Vallittu, 1995; Murphy, 1998). A strong interfacial adhesion is essential in achieving optimal mechanical properties for the FRC and it allows effective stress transfer from matrix to reinforcing fibers. On contrary, poor adhesion negatively affects mechanical properties, and increases water sorption leading to adhesion failure and subsequent fracture of resin matrix (Miettinen *et al.*, 1997). The durability of the interfacial adhesion is also affected by environmental factors such as temperature, loading stress and moisture (Vallittu, 2001).

The adhesion between fibers and resin matrix occurs by mechanical or chemical mechanisms. The mechanical method of adhesion depends on surface topography of fibers and is facilitated by physical interlocking of fiber and matrix. Chemical adhesion occurs by covalent bonding between fiber and resin matrix. The adhesion strength of chemical method is determined by type and number of covalent bonds formed, matrix type, microstructure of the fibers and surface treatment of fibers (DiBenedetto, 2001; Debnath *et al.*, 2003).

Various surface treatments have been studied for improving the interfacial adhesion between fibers and resin matrix (Kim and Mai, 1998). Commercially available glass fibers are usually pretreated with silane coupling agents to promote adhesion (physico-chemical method). Silanes are reactive with both C=C bonds in a resin matrix and inorganic glass surfaces. The silanes act by surface wetting of the fibers and enabling chemical adhesion of fibers to the resin matrix (Matinlinna *et al.*, 2004; Matinlinna and Vallittu, 2007).

#### 2.4.4.7 Resin matrix used in FRCs

The FRC polymers based on their polymer structure can be either linear (thermo-plastic) or cross-linked (thermoset). A linear polymer forms when the monomer unit has only a single reactive functional vinyl group, which in dental resins usually is a methyl methacrylate (MMA) group. The linear polymer chains are bonded by relatively weaker cohesive forces of van der Waals (London forces). Cross-linked polymers form when two or more reactive groups usually dimethacrylate groups, that are bonded by covalent bonds. Polymerisation of cross-linked polymers initiated by blue light ends up in degree of monomer conversion DC% ranging from 55%-65%. A small portion of unreacted monomers, also known as residual monomers, remain in the polymer structure (Ruyter and Oysaed, 1982; Cogswell, 1992).

The resins in dental FRCs are based on Bisphenol-A-glycidyl dimethacrylate (BisGMA), triethyleneglycol dimethacrylate (TEGDMA) and urethane dimethacrylate (UDMA) producing cross-linked polymer matrices. A certain amount of linear polymer structure, poly methyl methacrylate (PMMA) is added to cross-linked polymers to adjust properties of the prepreg such as the adhesive properties and clinical handling. This combination or mixture of cross-linked and linear polymer resin matrix results in formation of semi interpenetrating polymer network (semi-IPN) (Vallittu, 2009). The IPNs are routinely used in denture teeth, denture base polymers, FRCs and restorative resin composites. The dental IPNs are mainly semi-IPN containing one or more cross-linked polymers and one or more linear or branched polymers. In a typical semi-IPN system, the cross-linked part is usually formed by dimethacrylate or multifunctional monomers and dendrimers and linear part is formed by PMMA. According to International Union of Pure and Applied Chemistry (IUPAC), the nomenclature for semi-IPN polymer structure made of BisGMA, TEGDMA and PMMA is termed as *net-poly* (methyl methacrylate)-*internet*- copoly (Bis-glycidyl-A-dimethacrylate)-triethyleneglycol dimethacrylate (Vallittu, 2009; Vallittu and Özcan, 2017).

## 2.5 Orthodontic bonding and adhesives

The evolution of direct bonding was one of the major steps in the field of orthodontics. The success of a fixed orthodontic appliance depends on the attachments (orthodontic brackets and molar bands) which are surely bonded to the tooth surface to prevent any detachment during orthodontic therapy (Millett *et al.*, 2016). Failure of the attachment could result in treatment delay, pose a potential risk to the airway, be costly in terms of materials, and cause time loss for the patient (Zachrisson *et al.*, 1996). The bond between the bracket and enamel is based on mechanical locking of an adhesive to the surface treated enamel and to the me-

chanical locks formed in the base of the orthodontic bracket (Proffit and Fields, 2012). Orthodontic brackets are subjected to stresses resulting from several sources, such as mastication, archwires, and routine activities. Stresses are distributed at the adhesive interface between orthodontic bracket and enamel (Wang *et al.*, 2004) (Figure 5). The predominant static stress, when present over a long period of time may, lead to failure of the interface and subsequent removal of the bracket (Goertzen and Kessler, 2006). Failure of the adhesive interface does not occur instantaneously and the slow deformation at the interface may cause bracket loosening thereby affecting their performance (Zachrisson, 2007).

The adhesive should provide good adhesion strength but also facilitate debonding of the bracket at the end of treatment without enamel damage or loss. The quality of the adhesive layer at the interface between orthodontic bracket and enamel surface is an important factor determining the success of the adhesion. Many parameters such as interface adhesive thickness (Evans and Powers, 1985), filler content of the adhesives (Faltermeier *et al.*, 2007), the DC% of the adhesive layer (Shinya *et al.*, 2009), and the integrity of interface complex (Uysal *et al.*, 2009) have been studied.

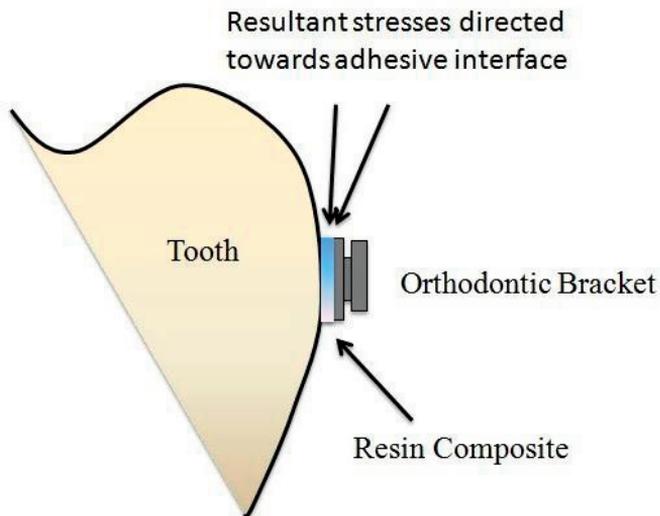


Figure 5: Schematic diagram presenting the adhesive interface

Orthodontic adhesives used for orthodontic bonding are slight modifications of restorative resin composites (Sakaguchi and Powers, 2012). The orthodontic adhesives differ from restorative resins in the increased amount of co-monomer in the formulation, which reduces viscosity of the orthodontic adhesive. Lower viscosity of orthodontic adhesives allows exceptional diffusion into the surface treated enamel and results in enhanced interfacial bond between enamel and the

orthodontic bracket (Eliades *et al.*, 2001). Previous studies have indicated that bond failure in enamel-bonded orthodontic brackets with a mechanical interlock can occur at the resin-bracket base interface, within the resin itself, or between the resin and enamel. However, the relatively greater bond failure occurs at the adhesive interface because of stress concentrations and defects in the resin film (Wang and Lu., 1991, Wang *et al.*, 1994, Sunna and Rock, 1998). Thus, it becomes necessary to improve or reinforce the adhesive interface for obtaining optimal and effective bond strength. Over the years several methods have been followed to improve the bond strength by using flowable composites, incorporating glass fibers at the interface, different surface treatments of the tooth and the bracket system (Eliades *et al.*, 2001, Ryou *et al.*, 2008, Shinya *et al.*, 2009, Guarita *et al.*, 2015 ).

## **2.6 Interfacial adhesion**

Adhesion refers to the molecular attraction exerted between the surfaces of bodies in contact (Fraunhofer, 2012). Adhesion between the constituents is the major factor affecting the properties of resins composites. Adhesion depends on adhesive joint formation, mechanical properties of components, size and shape of specimens, mechanical loading design and other factors. Accordingly, the adhesion principles are complex involving physical, chemical and mechanical aspects (Petrie, 2007). Dental adhesion has two aspects: adhesion to the tooth and adhesion to the restorative material, the adhesion quality depending on properties of the tooth and the material (Özcan *et al.*, 2012).

### **a) Adhesion to enamel**

Acid etching combined with BisGMA based resins have revolutionized the field of adhesive dentistry. Consequently, the focus has shifted from macro-mechanical to micro-mechanical and surface treatment approaches enabling new treatment modalities in orthodontics and minimally invasive dentistry. Enamel constitutes 96% inorganic matrix (hydroxyl apatite crystals) by weight, and the remaining 4% is made of water and collagen proteins. The enamel structure is formed by a higher order structure containing repetitively organized enamel rods (Habelitz *et al.*, 2001). Micro-mechanical adhesion requires demineralization of the enamel surface layer with acid etchants. The most commonly used acid etchant is phosphoric acid (35-37 wt%) because of its efficacy in etching enamel to frosty white appearance (Özcan *et al.*, 2012). Selective acid etching of enamel surface by phosphoric acid dissolves enamel rods and provides surface micro-roughness with increased surface energy that is necessary for micro-mechanical adhesion. The change in surface topography of the enamel facilitates penetration of the monomer from primers and bonding agents into the porous substructure to form resin tags at the enamel adhesive interface (Van Meerbeek *et al.*, 2010).

**b) Adhesion to orthodontic brackets**

Orthodontic brackets bonded to teeth acts as a medium to transfer force from the activated archwire to the teeth to facilitate tooth movement. The brackets must be able to deliver orthodontic forces, resist masticatory loads, be esthetically stable and easily removed following conclusion of the treatment. Hence, it is always desirable to have a bracket with good retentive bonding between the resin and bracket base but not too excessive so as to prevent any damage to the tooth or restoration during the debonding procedure (Guarita *et al.*, 2015). Orthodontic brackets can be metallic (stainless steel, titanium, or gold) or tooth (esthetic) colored (plastic or ceramic) (Subramani *et al.*, 2013).

There are several factors that influence the bond strength of brackets including the size and design of the bracket base (Wang *et al.*, 2004). Orthodontic brackets have a mechanical undercut which facilitates the flow of the orthodontic adhesive to extend into these undercuts before polymerization (Knox *et al.*, 2000). The retention of metal brackets is enhanced with a fine brazed mesh, milled undercut, primer application, sandblasting, chemical etching, sintering with porous metal powder, laser-structured bases, metal plasma-coating of bracket bases, and fusing metallic or ceramic particles to the bases (Wang *et al.*, 1994, Bishara *et al.*, 2004). The retention of ceramic brackets can be enhanced by surface treatment of bracket bases by grinding with diamond burs, hydrofluoric acid application, silane application, aluminum oxide sandblasting, and silica coating + silane (silicatization) (Guarita *et al.*, 2015).

**2.7 Degree of conversion (DC%)**

Degree of conversion from monomer to polymer determines the extent of polymerisation within the resin composites (McCabe and Walls, 2008). It is imperative to have a high degree of monomer conversion for achieving best results from the resin composite. Ideally, resin composites should have all of its monomer converted to polymer during polymerization. However this is not possible to achieve in practice. For dimethacrylate based monomers, DC% ranging from 55 to 75% under conventional light irradiation has been reported (Galvão *et al.*, 2010). Thus, there is a significant amount of unreacted carbon double bonds (C=C) in the final matrix. The unreacted monomers affect negatively the resin composites in the form of resin degradation and solubility, and decreased mechanical properties, and they may cause allergic reactions in some individuals (Lovell *et al.*, 1999). The DC% depends on many factors such as type of curing light, distance of curing tip from composite surface, type of monomer used, thickness of the composite and filler size and shape (Shadman *et al.*, 2012).

The optical properties of FRCs are related to the refraction index of fibers and the surrounding matrix. The polymerization reactions of light cured dimethacrylates could be enhanced by the presence of reinforcing glass fibers that

transmits the light to the resin matrix to initiate polymerization. This could be explained by the scattering effect of glass fibers which improves the curing efficiency (Shinya *et al.*, 2009). During polymerization, optical properties of the resin system change (Lehtinen *et al.*, 2008).

## 2.8 Nanomechanical properties

Nanoindentation method has been widely used in the evaluation of the mechanical properties of dental hard tissues and biomaterials. This method determines the mechanical properties of a material from its load displacement response which involves applying a small load (nanoscale) to indent a specimen and thereafter continuously recording the load and displacement (Fujisawa and Swain, 2007). The obtained data obtained indicates the required load to indent a specimen and the elastic recovery of the specimen on unloading (Figure 6). Furthermore, nanoindentation method facilitates accurate measurement of indentation load and indentation depth.

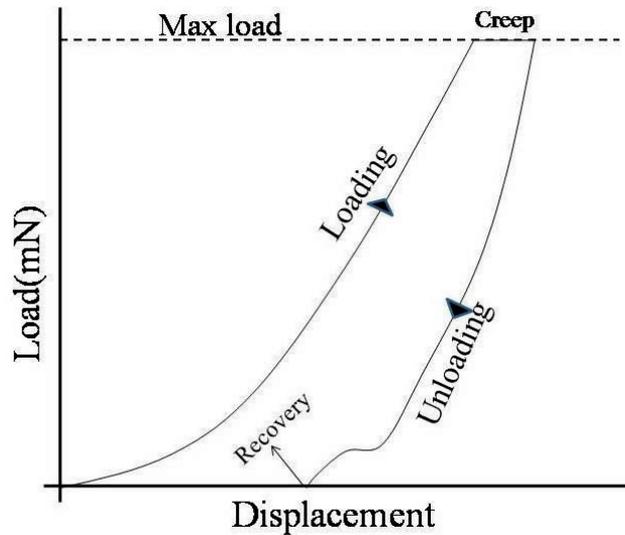


Figure 6: Schematic presentation of a typical load displacement curve

Surface hardness (H) and elastic modulus (E) are the mechanical properties most commonly measured using load and displacement indentation techniques. Measurements of mechanical properties by nanoindentation offer several advantages. It is relatively non-destructive, it requires less time for specimen preparation and, it allows simultaneous comparison of properties of different materials (Peskersoy and Culha, 2017). Hardness is the resistance of a material to indentation or penetration. Nanohardness measurements obtained by nanoindentation technique reflect the plastic depth of the material rather than the final depth, similarly to microhardness measurements. It is important to characterize the hardness of a material because of its relationship with other physical properties such as strength and DC%. Elastic modulus defines the relative stiffness of a material. It is preferable to have materials with high elastic modulus to withstand deformation and to prevent any catastrophic failures (El-Safty *et al.*, 2012).

## 2.9 Creep

The viscoelastic behavior of the resin composite depends entirely on the stress experienced by the polymer matrix. This behaviour significantly influences the performance of the material. In fixed orthodontics, the stress concentrated at the adhesive interface may cause elastic, plastic or creep deformation. In elastic deformation, the material returns to its original form following stress removal. To the contrary, plastic and creep deformation are permanent in nature and lasts even after stress removal. Plastic deformation occurs instantaneously once the applied stress exceeds the elastic limit of the material. Creep deformation occurs when a constant stress is applied over a period of time and the stress is below the elastic limit of the material (Bales, 1998). The material enters into recovery phase as soon as the stress is removed.

The deformation response of polymeric materials can be studied by measuring the strain produced during a particular period of constant stress application (creep), followed by stress removal and subsequently measuring the relaxation response of the material (recovery) over a selected duration (Garoushi *et al.*, 2012). The advantages of the method are in providing information about the material's ability to resist the stresses without catastrophic failure, and in describing how the stresses are accommodated under constant stress and how the material relaxes towards its original form on removal of the stress (Vaidyanathan and Vaidyanathan, 2001).

### **3 AIMS OF THE STUDY**

The present study was designed to investigate the behavior of resin composites at the interface between orthodontic bracket and tooth under different conditions with or without use of intermediate layers of glass fibers. The specific aims were:

1. To investigate the magnitude of debonding stress of an orthodontic bracket bonded to the enamel with resin systems having different visco-elastic properties. The working hypothesis was that there was no significant difference in the debonding stress of an orthodontic bracket bonded with resin systems of different visco-elasticity. Furthermore, correlation between the elastic modulus of the interfacial resin systems to the debonding force and the percentage of strain was investigated. (I)
2. To investigate the effect of orientation of continuous E-glass reinforcing fibers under metal orthodontic brackets in relation to the direction of irradiation of the curing light to the DC% and to the total irradiance under the bracket. The working hypothesis was that the glass fiber orientation did not significantly affect the DC% and the total irradiance under the bracket. (II)
3. To determine the creep behavior of dimethacrylate resin composites with particulate fillers and glass fiber fillers used for orthodontic bonding. The working hypothesis was that there was no significant difference in the shear stress creep behavior between particulate filler resin composite and glass fiber reinforced resin composite. (III)
4. To determine the creep behavior of resin composite interfaces between orthodontic bracket and tooth under constant interface loading. The experimental interfaces, reinforced with fiber reinforced composite (FRC) with either unidirectional or bidirectional continuous fibers and used with two different resin matrices, were compared with regular particulate filler composite (PFC). The working hypothesis was that there was no significant difference in the shear stress creep behavior between FRC and PFC interfaces, and that the orientation of the fibers did not influence creeping. (IV)

## 4 MATERIALS AND METHODS

### 4.1 Materials

The complete list of materials used in these studies are presented in Table 1

**Table 1:** Materials used in studies I-IV

Materials	Composition	Manufacturer	Study
Transbond XT <sup>®</sup> (TB)	BisGMA*, n-dimethyl benzocaine, hexa-fluoride-phosphate	3M Unitek, Monrovia, California	II, III, IV
Transbond XT <sup>®</sup> Primer	BisGMA*, TEGDMA**	3M Unitek, Monrovia, California	II, III, IV
G-Fix <sup>®</sup> (GF)	Dimethacrylate monomer, phosphoric ester monomer, silica nanoparticle, particulate filler resin composite	GC Corporation, Tokyo, Japan	I, III
G-Aenial Universal Flo <sup>®</sup> (GU)	UDMA****, BisGMA-TEGDMA particulate filler resin composite	GC Corporation, Tokyo, Japan	I, III
everStick NET <sup>®</sup> (ESN)	Fiber impregnated with BisGMA, PMMA***  (Diameter and thickness of a single glass fiber of the weave was 6 µm and 60 µm respectively)	Stick Tech Ltd, Turku Finland	I, II, IV
E-glass fibers	SiO <sub>2</sub> 57%; Al <sub>2</sub> O <sub>3</sub> 10%; CaO 20%; MgO 6%; B <sub>2</sub> O <sub>3</sub> 7%; (4000 in number and 15 µm in diameter)	Ahlstrom, Karhula, Finland	II, III, IV
Stick Resin <sup>®</sup>	BisGMA, TEGDMA**	Stick Tech Ltd, Turku Finland	I, II, III, IV
Orthodontic brackets (Premolars)	Stainless steel	Lancer Orthodontics; Milano, Italy	I, II, III, IV

\*Bisphenol-A-glycidyl dimethacrylate

\*\*triethyleneglycoldimethacrylate

\*\*\* polymethylmethacrylate

\*\*\*\*urethanedimethacrylate

#### 4.1.1 Procurement of teeth specimens and preparation (Study I, III and IV):

A total of two hundred and ten premolar teeth (Study I-60) (Study III-90) (Study IV-60) extracted for orthodontic therapy from 16 to 40 year-old individuals were used in this series of studies. Tissue samples taken for therapeutic or diagnostic purposes, or to establish the cause of death, may be surrendered and used for medical research, method development, quality management and teaching purposes with permission from the health care unit or other unit for whose activities the sample was taken, as long as no personal data are used in the surrender or use situation (Ministry of Social Affairs and Health, Finland 2012). Teeth were collected at different time intervals according to the study needs. Teeth with any enamel defects such as dental caries, hypoplastic enamel, or enamel fractures were discarded and replaced appropriately. The teeth were cleaned of any tissue remnants and blood stains and later stored in 0.5% fresh chloramine-T solution at 4° C till the start of the experiment. The teeth were individually embedded in self cured acrylic resin so as to have the buccal bond surface parallel to the applied force during the test procedure. The enamel surface were cleaned and polished with slurry of water and non-fluoridated pumice for 10 s, rinsed under water stream for 10 s, and then air dried. Following drying, the enamel surfaces were etched with 37% phosphoric acid for 15 s washed using air-water spray, and dried with oil free air jet. The prepared teeth specimens were kept ready for orthodontic bracket bonding.

#### 4.1.2 Orthodontic bonding (Study I, III and IV)

##### 4.1.2.1 Orthodontic bracket bonding to the enamel with flowable resin composites of different visco-elastic properties (Study I).

A total of 60 premolar teeth were allocated into 4 groups. The group's allocation is presented in Figure 7.

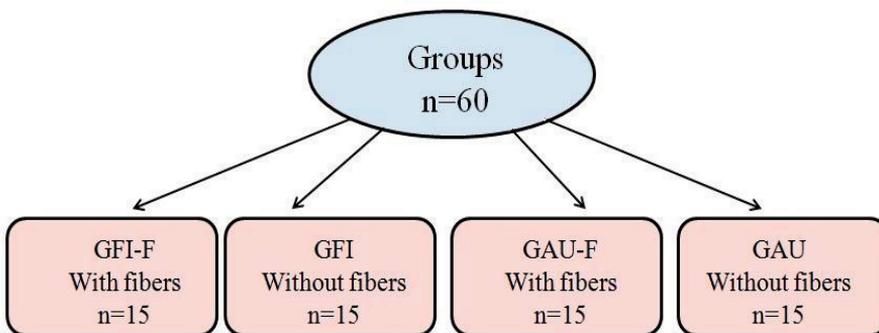


Figure 7: Flow chart of group allocation (1)

**Group 1 (GFI-F):** Orthodontic brackets were bonded at the center of the buccal surface of the tooth by incorporating a continuous bidirectional glass fiber weave between the tooth and bracket. The glass fiber prepreg weave was cut to the size of the bracket and wetted from the surface with the Stick resin. A thin layer of a

flowable resin (G-FIX) was applied to the tooth enamel, and the fibers were bonded at the center of the facial surface of the tooth, with a pressure sufficient to expel the excess adhesive, and light cured for 5 s using a hand light-curing unit (Elipar free light, 3M ESPE, Germany). A thin layer of adhesive was used to cover the fiber net. A single coat of Transbond XT primer was applied onto the bracket mesh surface and was placed on the resin applied on the tooth surface and pressed hard to expel any excess adhesive. The specimen was light cured for 20 s on both medial and distal surfaces. The wavelength of the light curing unit was between 420-540 nm and irradiance power was 1505 mW/cm<sup>2</sup>. The light curing unit was monitored by NIST-referenced USB 4000 Spectrometer (Managing Accurate Resin Curing, MARC) System (Bluelight Analytics Inc., Halifax, Canada).

**Group 2 (GFI):** Brackets were bonded using G-FIX flowable resin without fibers.

**Group 3 (GAU-F):** Brackets were bonded using a G Aenial Universal Flow (GAU) flowable resin composite incorporating a fiber layer. The procedure of bonding was similar to group 1.

**Group 4 (GAU):** Brackets were bonded using GAU without fibers.

#### **4.1.2.2 Degree of conversion (DC%) and irradiance power measurement (Study II)**

In this study, adhesive resins and FRC prepreps were covered with an orthodontic metal bracket, light cured, and the DC% and light irradiance power were measured from the surface of the sensor under the materials. The group's allocation is presented in Figure 8.

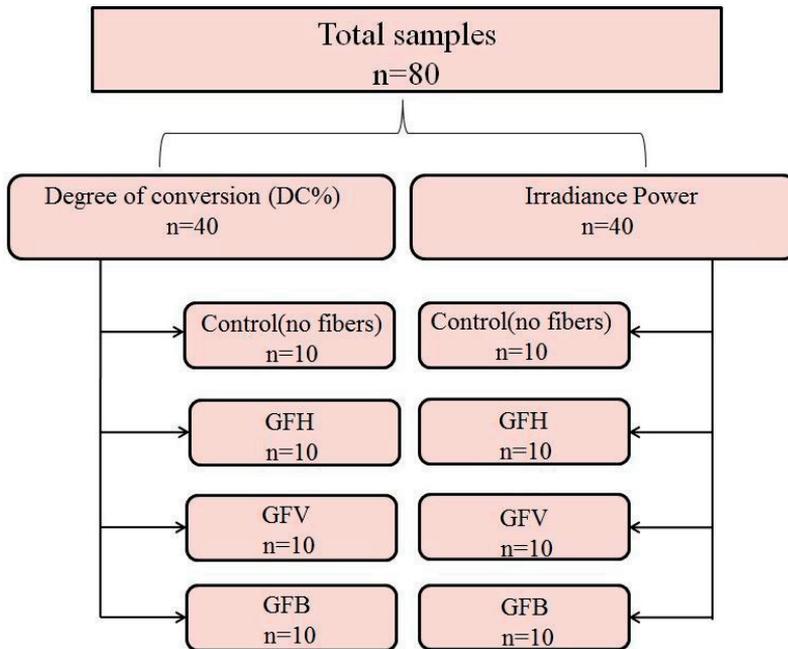


Figure 8: Flow chart of group allocation (II)

The DC% and irradiance power were measured separately under different experimental setups. Both the parameters tested had 4 groups with identical material combination of adhesive materials and fiber prepreps as described below:

**Control / No fiber group:** In this group, the plain adhesive material (Transbond XT) was used.

**GFH:** In this group, continuous unidirectional silanized E-glass fiber roving was used. The glass fiber roving was cut to the mesio-distal dimension of the bracket and impregnated with photo polymerizable dimethacrylate stick resin. The resin impregnated glass fiber roving was placed in a horizontal direction (representing the mesio-distal direction on the dental arch) under the bracket and adhesive resin Transbond XT.

**GFV:** In this group, the glass fiber roving was cut to the occluso-gingival direction dimension of the bracket and was impregnated with photo polymerizable dimethacrylate stick resin. The resin impregnated GF roving was placed in a horizontal direction (representing the occluso-gingival direction on the dental arch).

**GFB:** In this group, a layer of bidirectional glass fiber fabric impregnated with dimethacrylate monomer system and poly(methylmethacrylate) (semi interpenetrating polymer network (IPN)) was added under the bracket and adhesive resin Transbond XT.

#### 4.1.2.3 Creep behavior of dimethacrylate resin composites with particulate fillers and glass fiber fillers used for orthodontic bracket bonding (Study III)

A total of 90 premolar teeth were allocated into 6 groups. Three groups were bonded without fibers (n=15) and three with fibers (n=15). The group's allocation is presented in Figure 9.

A single coat of Transbond XT primer was applied onto the enamel surface of all the teeth and the bonding was followed as described below:

**Group 1 (TB):** A thin layer of resin composite (Transbond XT) was applied to the bracket mesh surface and placed on the buccal surface of the tooth. The bracket was pressed and kept intact for 30 s by hand pressure and the excess resin expelled from the surfaces was removed using a scaler. The specimen was light-cured for 20 s on both mesial and distal surfaces.

**Group 2 (GF):** The orthodontic brackets were bonded using G-Fix flowable resin composite and the procedure was identical to that of group 1 specimen.

**Group 3 (GU):** The orthodontic bracket was bonded using G-Aenial Universal Flo flowable resin composite and the procedure was identical to that of group 1 and 2 specimens.

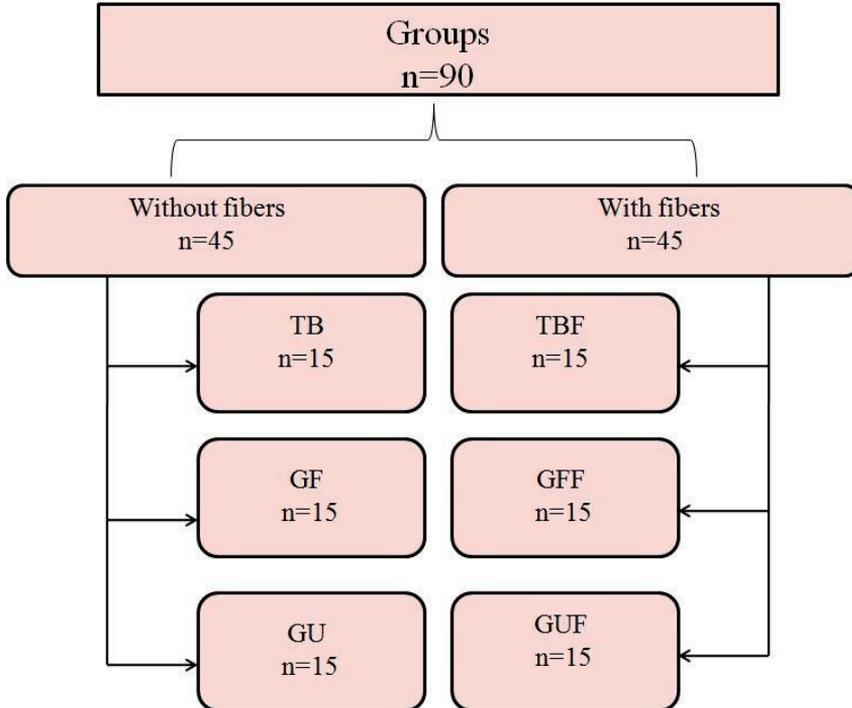


Figure 9: Flow chart of group allocation (III)

**Group 4 (TBF):** The metal brackets were bonded by incorporating unidirectional silanized E-glass fiber roving between the tooth and bracket. The glass fiber roving was cut to the size of bracket width, impregnated with stick resin and was oriented in an occluso-gingival direction. A thin layer of Transbond XT resin composite was applied to surface of the bracket and pressed against the tooth and fibers for 30 s by hand pressure. The excess resin was removed using a scaler and light cured for 20 s on both mesial and distal surfaces

**Group 5 (GFF):** The procedure was similar to that of group 4 except that the brackets were bonded using G-FIX resin composite.

**Group 6 (GUF):** The procedure was similar to that of group 3 and 4 specimens except that the bracket was bonded using G-Aenial Universal Flo resin composite.

#### 4.1.2.4 Creep behavior of resin composite interfaces reinforced with FRC of unidirectional or bidirectional continuous fiber and conventional particle filler composite (PFC) (Study IV).

A total of 60 premolar teeth were allocated into 4 groups (n=15). The group's allocation is presented in Figure 10.

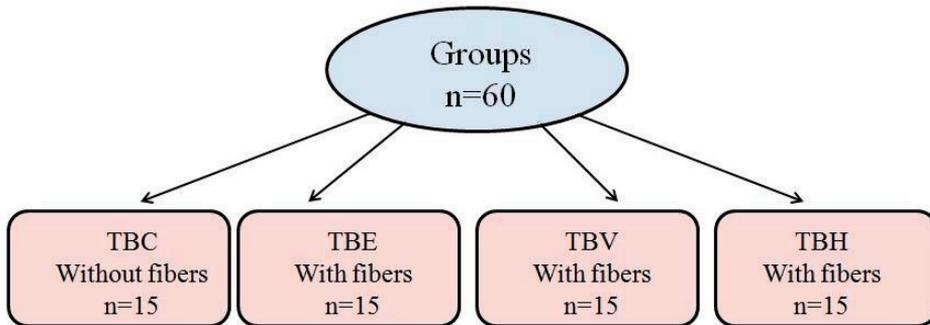


Figure 10: Flow chart of group allocation (IV)

**Group 1 (TBC)/Control:** A thin layer of Transbond XT resin composite was applied onto the bracket mesh and pressed against the buccal surface of the tooth surface for 30 s by hand. The excess resin around the bracket was removed using a scaler. The specimen was light-cured for 20 s on both mesial and distal surfaces

**Group 2 (TBE):** In this group, a layer of continuous bidirectional glass fiber weave (everStick NET) was added between the bracket and tooth. The glass fiber weave was cut to the size of the bracket. A thin layer of Transbond XT resin composite was applied onto the bracket mesh; the glass fiber weave was placed on the composite and pressed firmly against the tooth surface for 30 s by hand. The excess resin around the bracket was removed using a scaler and the specimen was light-cured for 20 s on both mesial and distal surfaces.

**Group 3 (TBH):** In this group, continuous unidirectional silanized E-glass fibers were used between bracket and resin composite. The E-glass fiber weave was cut to the size of the bracket width and was wetted with stick resin. A thin layer of thin layer of Transbond XT resin composite was applied onto the bracket mesh, the E-glass fiber weave was placed in a horizontal direction (mesio-distal width of the bracket) on the resin composite and pressed firmly against the tooth surface for 30 s by hand. The excess resin around the bracket was removed using a scaler and the specimen was light cured for 20 s on both mesial and distal surfaces.

**Group 4 (TBV):** The bonding of orthodontic bracket in this group was similar to that of the specimens of group 3 except for the orientation of the E-glass fiber weave which was placed in a vertical direction representing occluso-gingival width of the bracket.

#### **4.1.3 Specimen preparation for nanoindentation test (Study I and IV)**

Three disc-shaped specimens measuring 12 mm in diameter and 2 mm in thickness per each resin material tested (GFI and GAU) were prepared using a metallic mold. The mold was placed on the microscope glass slide and resin composite material was packed into the mold. The top portion of the mold was covered by another glass slide and compressed to remove excess materials and to ensure uniform distribution of composite material in the mold (Figure 11). The specimens were light cured according to manufacturer's instructions from both the top and bottom surfaces. For specimens (ESN) incorporating everStick NET, fiber weave, wetted with stick resin, was stacked in layers to obtain a specimen of 2 mm in thickness. The specimens were irradiated in multiple areas to ensure optimum polymerization. All the specimens were kept dry at room temperature for 24 h before nanoindentation testing (Study I).

For determining the differences in the nano-mechanical (nanohardness and elastic modulus) properties of Transbond PFC, woven FRC, and unidirectional FRC resin matrix, the conventional composite resin (without fibers) was carefully removed from the interface of bracket edges after bracket debonding. The resin was embedded in auto-polymerizing resin and polished using Flexi snap kit abrasive disks in decreasing grit size of the abrasive material (Study IV).



Figure 11: The mold used for preparing round specimen for nanoindentation test (Study I and IV)

#### 4.1.4 Specimen preparation for flexural strength (creep and recovery) test (Study III and IV)

Five rectangular specimens ( $10.0 \times 4.0 \times 2.0$ ) mm<sup>3</sup> were prepared for each resin composite material tested with and without incorporation of glass fibers. A 10 mm of unidirectional silanized E-glass fiber roving impregnated with stick resin, was embedded within the resin composite materials (Transbond XT/G-Fix/G-Aenial universal flo) and molded into rectangular shape (Figure 12) using a metal mold. The rectangular specimens were irradiated using a light curing unit for 20 s on both sides of the specimen. The cured specimens were polished and stored in de-ionized water for 24 hours before the start of the test procedure (Study III).

For specimens in study IV, the rectangular specimens were prepared incorporating bidirectional glass fiber weave and unidirectional E-glass fibers oriented as shown in Figure 13.

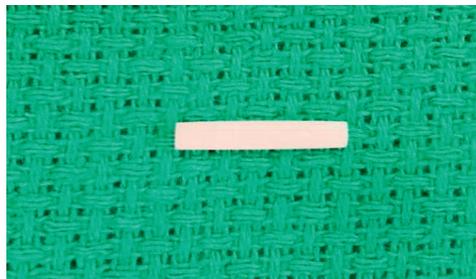


Figure 12: Rectangular specimen for flexural strength (creep and recovery) test (Study III and IV)

**Specimens incorporating bidirectional glass-fiber weave (TBE):** A suitable length of everStick NET fiber weave was laminated with stick resin and incorporated between Transbond XT composite resin layers (Figure 14a). The fiber orientation was 0/90 degrees to the long axis of the specimens. The top surface of the specimens was covered with a plastic matrix to obtain a smooth surface. To standardize the thickness of the specimens, 50 g of weight was placed on the

specimens for 30 s. The excess resin was carefully removed, and specimens were irradiated using a light curing unit for 20 s on both sides of the specimens.

**Specimens incorporating unidirectional glass fibers along the long axis of the specimen (TBV):** A 10 mm of unidirectional silanized E-glass fiber roving impregnated with stick resin was embedded within Transbond XT resin composite (Figure14b). The E-glass fibers were oriented vertically (along the long axis of the specimens) and the excess resin was carefully removed, and specimens were irradiated using a light curing unit for 20 s on both sides of the specimens.

**Specimens incorporating unidirectional glass fibers perpendicular to the long axis of the specimen (TBH):** A 4 mm of unidirectional silanized E-glass fiber roving impregnated with stick resin was embedded within Transbond XT resin composite (Figure14c). The excess resin was carefully removed, and specimens were irradiated using a light curing unit for 20 s on both sides of the specimens.

**Specimens without fibers (TBC) (control):** The specimens were prepared without intermediate fiber layer (Study IV).

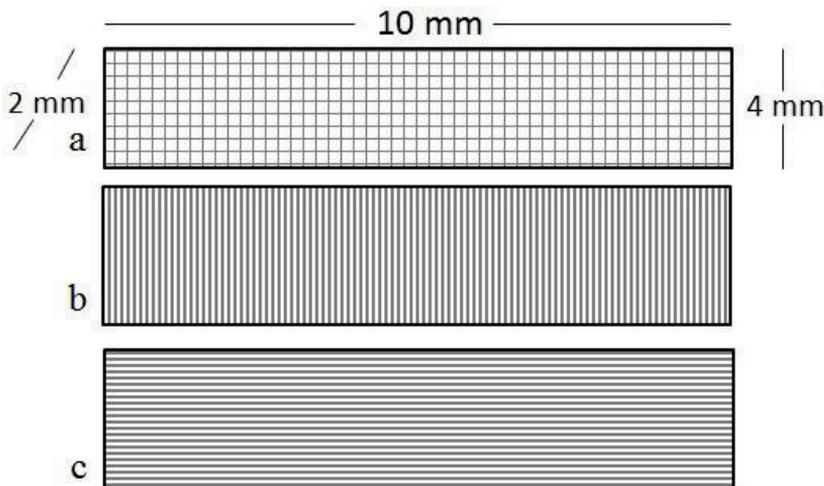


Figure 13: Fiber arrangement for preparing rectangular specimens for three point bending test. a) Bidirectional continuous fibers (everStick NET); b) E-glass fibers oriented vertically (along the long axis of the specimen) and c) E-glass fibers oriented horizontally (perpendicular to long axis of the specimen)

## 4.2 Methodology

### 4.2.1 Determining the magnitude of debonding stress of orthodontic brackets bonded with resin systems having different visco-elastic properties (Study I).

All the specimens were stored in de-ionized water at room temperature for 24 hours prior to mechanical testing.

#### **4.2.1.1 Debonding Test**

The teeth specimens were mounted in a universal testing machine (Instron Corporation, Canton, Massachusetts, USA), so as to have the enamel surface parallel to the shearing rod. The shearing rod was stretched in an occluso-gingival direction at a crosshead speed of 1 mm/min and the maximum load necessary to debond the bracket from the tooth was recorded. In addition, the displacement was also recorded, and the strain was calculated.

#### **4.2.1.2 Evaluation of fracture sites**

Following debonding, all the bracket bases and enamel surfaces were evaluated using a light stereomicroscope (Nikon SM2-10, Tokyo, Japan) at a 20× magnification to determine the failure mode and also to evaluate the character of debonded surface. The failure sites were classified using the 4-point scale (Type 0, 1, 2, or 3) according to the Adhesive Remnant Index (ARI) as listed below.

0 = No adhesive remaining on the enamel surface

1 = Less than 50% of the adhesive remaining on the enamel surface

2 = More than 50% of the adhesive remaining on the enamel surface

3 = All adhesive remaining on the enamel surface with a distinct impression of bracket mesh (Artun and Bergland, 1984).

#### **4.2.1.3 Scanning electron microscopy (SEM) analysis**

A representative specimen (tooth and bracket) from each group was further analyzed using SEM after debonding. The SEM micrographs were obtained using a scanning electron microscope (Jeol JSM-5900 LV SEM, Tokyo, Japan) at an operating voltage of 10 kV and a 300× magnification.

#### **4.2.1.4 Nanoindentation test (I and IV)**

The hardness and elastic modulus of the round specimens were determined using a nano-indentation device (Bruker, Tucson, AZ, USA). The device was equipped with a Berkovich diamond indenter tip and the testing was performed at a controlled temperature of 23° C in low noise conditions with loading and unloading rates of 0.01 and 0.02 mN/s respectively. The resting period of 5s was maintained between loading and unloading and indentation load ranged from 0 and 10 mN.

### **4.2.2 Measurement of degree of conversion (DC%) and irradiance power (Study II)**

#### **4.2.2.1 Measurement of DC%**

The measurement of DC% was performed using Fourier transform infrared spectroscopy (FT-IR) (Spectrum 100, Perkin Elmer Precisely, UK) device with an attenuated total reflectance (ATR) sampling accessory. The bracket base was

covered with Transbond XT adhesive (with or without intermediate fiber layers) and pressed firmly with a 1 mm thick glass slide against the 3.2 mm diameter Zn-Se ATR crystal to ensure proper contact of the specimen (Figure 14). The excess resin was carefully removed from the bracket surface before polymerization. The mesial and distal sides of the bracket edges were irradiated for 20 s each using a hand held light curing unit.

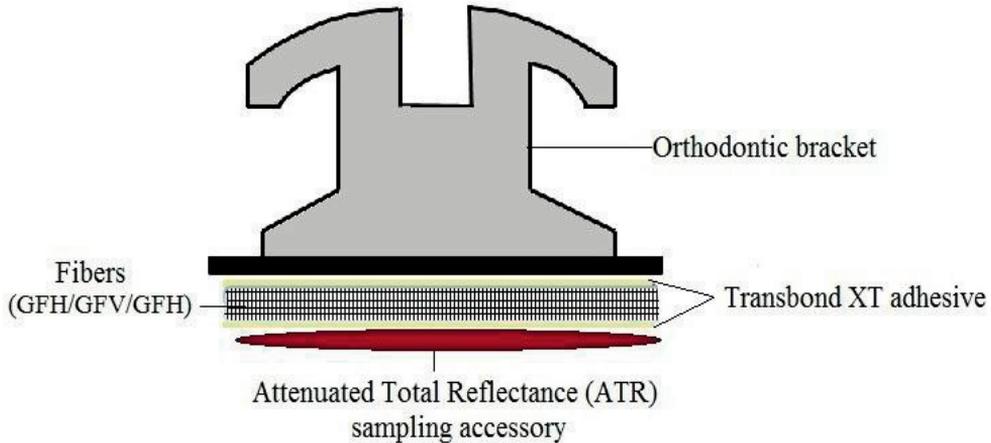


Figure 14: Schematic presentation of the adhesive layers incorporating intermediate glass fibers underneath the metal bracket for DC% measurement

The FT-IR spectra of the adhesive resin material (with or without intermediate fiber layers) before and after light exposure were recorded. The FT-IR spectra were recorded at 2, 4, 6, 8 and 12 min and each spectrum was recorded with 20 scans of  $8\text{ cm}^{-1}$  resolution. The intensities of the absorbance aliphatic C=C peak at  $1638\text{ cm}^{-1}$  and aromatic C=C reference peak at  $1608\text{ cm}^{-1}$  were measured by applying standard baseline technique. The ratio of the absorbance intensities of aliphatic C=C and aromatic C=C was compared before and after polymerization to determine the amount of the unreacted aliphatic C=C bond by using the following equation (2) (Viljanen *et al.*, 2004; Viljanen *et al.*, 2005; Shinya *et al.*, 2009).

$$DC = \left\{ 1 - \frac{C_{aliphatic}/C_{aromatic}}{U_{aliphatic}/U_{aromatic}} \right\} \times 100 \quad (2)$$

#### 4.2.2.2 Measurement of irradiance power

The irradiance power of Elipar Free Light 2 curing unit tip underneath of bracket and adhesive resin (with or without intermediate fiber layers) was measured using spectro-radiometrically calibrated NIST-referenced USB 4000 Spectrometer (MARC (Managing Accurate Resin Curing)). The MARC device is a fiber optic spectrometer equipped with a 3648-element linear CCD array detector

(TCD1304AP, Toshiba, Japan) (Figure 15). The sensor in the detector is a CC3-UV Cosine Corrector designed to collect radiation over 180°. Irradiance at wavelengths of 420–540 nm was used during the 20 s curing.

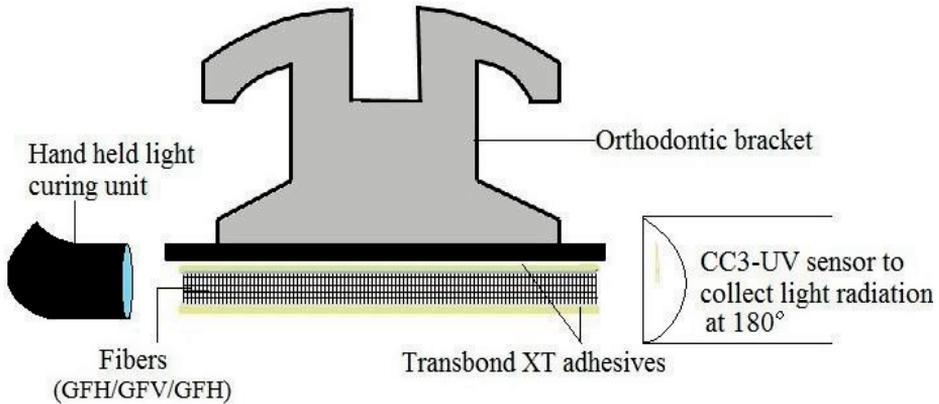


Figure 15: Schematic presentation of the adhesive layers incorporating intermediate glass fibers underneath the metal bracket for irradiance power measurement

#### 4.2.3 Determination of creep behavior of resin composite interfaces of dimethacrylate resin composites with particulate fillers and glass fiber fillers (Study III)

Shear stress creep behavior was tested using two testing set-up: tooth-bracket interface experimental model and three-point bending model.

**a) Tooth-bracket interface experimental model:** The static creep behavior was tested using a universal testing machine (Instron Corporation, Canton, Massachusetts, USA). An orthodontic bracket, bonded on a tooth specimen, was placed on the sample holder. A constant load of 20 N (equivalent to the minimal debonding force of an orthodontic bracket) was directed towards the adhesive interface using a knife edged guillotine rod stressing at the interface (Figure 16). The duration of the sample loading period varied for the groups and the load applied was constantly monitored during the entire experimental procedure. The strain-% and time required to debond the bracket base from the adhesive interface was recorded by the software connected to the universal testing machine.

#### **b) Creep and recovery test in a three-point bending model**

The creep and recovery behavior of adhesive materials with or without fibers incorporation were measured using the Dynamic Mechanical Analyzer in three-point bending mode. The testing conditions of DMA device was a preload of

0.0005 N and a maximum load of 35 N, a controlled temperature of 23° C, and a force resolution of 0.00001 N. The three-point bending is considered to present a “pure” mode of deformation because the tested specimen is freely supported by fulcrums, without any clamping effects (Figure 17). In this model, a constant stress is applied to the specimen surface as the upper arm contacts the specimen, and the resultant strain is measured over time. Once the stress is removed, the recovery strain of the specimen is also measured.

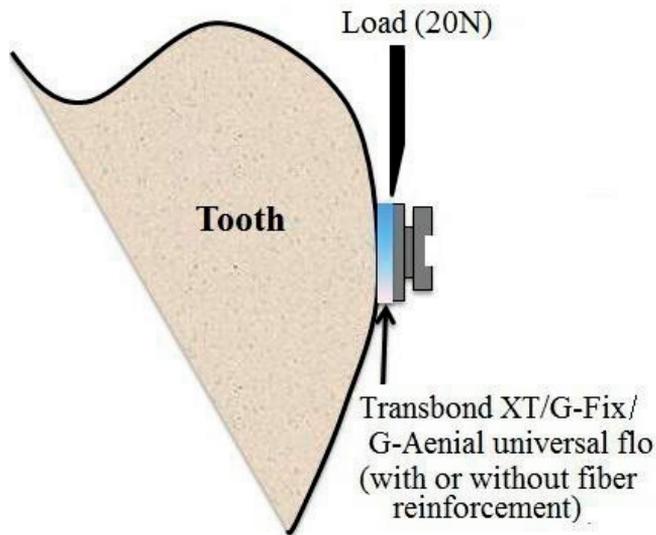


Figure 16: Schematic presentation of the interface loading in a universal testing machine



Figure 17: Specimen for creep and recovery test in a three-point bending model

#### 4.2.4 Determination of creep behavior of resin composite interfaces reinforced with FRC of unidirectional or bidirectional continuous fiber and conventional particle-filled composite (PFC) (IV).

The creep behavior of the interface materials was tested using two test models: tooth-bracket interface experimental model and three-point bending model.

**a) Tooth-bracket interface experimental model:** The loading of the adhesive resin-orthodontic bracket interface was performed with a dynamic mechanical analyzer (RSA-G2, TA instruments; New Castle, DE, USA). The constant load application was at two different sites. First, the loading cell of the DMA device (maximum load: 35 N) was directed onto the resin interface between enamel and bracket. Secondly, the interface was loaded with weights equaling 250 g freely suspending from the archwire slot using orthodontic ligature wire (Figure 18). The applied load and the shear stress were monitored constantly during the entire test procedure to determine strain at the interface. Following bracket deflection, the loading ceased automatically, and the data were recorded with the help of the software connected to the DMA device.

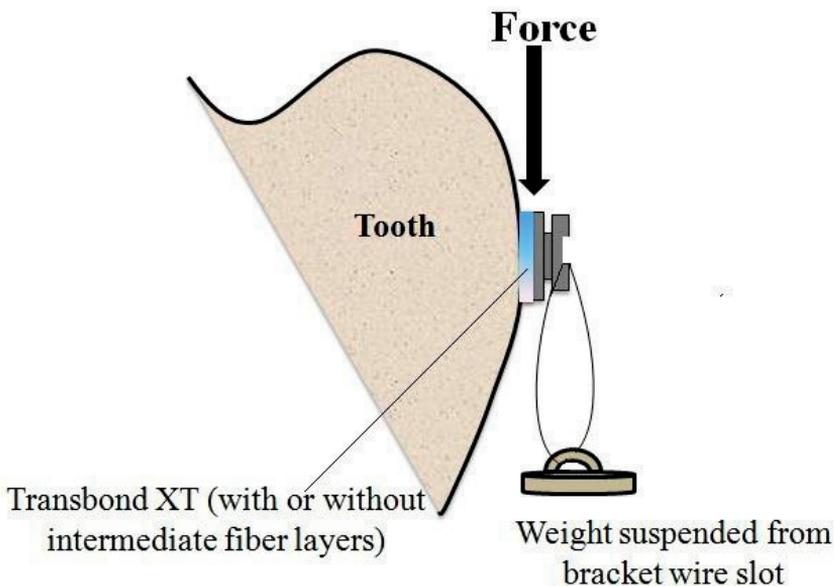


Figure 18: Schematic presentation of the interface loading for determining creep behavior

#### **b) Creep and recovery test in a three-point bending model**

The creep and recovery behavior of adhesive materials with or without fibers incorporation were measured using the Dynamic Mechanical Analyzer in three-point bending mode similar to the one described above.

#### **4.2.5. Statistical analysis**

All the data obtained were analyzed using Statistical Package for Social Sciences (SPSS) (SPSS Inc., Chicago, IL, USA) v. 18. One way analysis of variance (ANOVA) and suitable post *hoc* analyses test were applied to the data. A 'P' value  $\leq .05$  was considered as statistically significant. Linear or non-linear regression analysis was performed for studies 1 and 3.

## 5 RESULTS

### 5.1 Effect of elastic properties of the adhesive material at the interface between orthodontic bracket and enamel (Study I)

The mean values of the load required to debond the brackets and the strain% are presented in Table 2. The load required to debond a bracket was found to be highest for the groups incorporating reinforcing fibers. Among the fiber groups, Group GFI-F required increased load to debond the bracket followed by Group GAU-F. Among the non-reinforced groups, Group GFI required increased load followed by Group GAU. Significant differences were observed between the groups for the load (N) and strain-% ( $P < .05$ ).

Table 2: Mean values of the load (N) and strain-% of the samples in the test groups (I)

Groups (n=15)	Load (N)	Strain-%
GFI-F	$77 \pm 1.96^A$	$13.50 \pm 1.77^A$
GFI	$50.21 \pm 0.89^B$	$8.80 \pm 0.91^B$
GAU-F	$60.26 \pm 1.19^C$	$10.56 \pm 0.73^C$
GAU	$36.82 \pm 0.84^D$	$6.56 \pm 0.46^D$

Different capital letters in a column mean statistical significant differences between the groups ( $P < .05$ )

Adhesive Remnant Index (ARI) scores revealed more remnants on the bracket surfaces when the adhesive's polymer matrix had a low elastic modulus (GFI-F and GAU-F). In the groups with reinforcing glass fibers, the fracture occurred near the bracket surface. No instances of enamel fracture were observed during the debonding process in any of the groups (Table 3).

The results of the nanoindentation test to determine the elastic modulus of the test specimens are presented in Figure 19. Group GAU demonstrated an increased load penetration depth indicating a high elastic modulus. This was followed by Groups GFI and ESN, respectively.

Table 3: Fracture modes according to the Adhesive Remnant Index (ARI) (I)

Groups (n=15)	Adhesive remnant index (ARI) scores			
	0	1	2	3
GFI	3	4	3	5
GFI-F	1	2	4	8
GAU	3	6	6	2
GAU-F	2	3	3	7

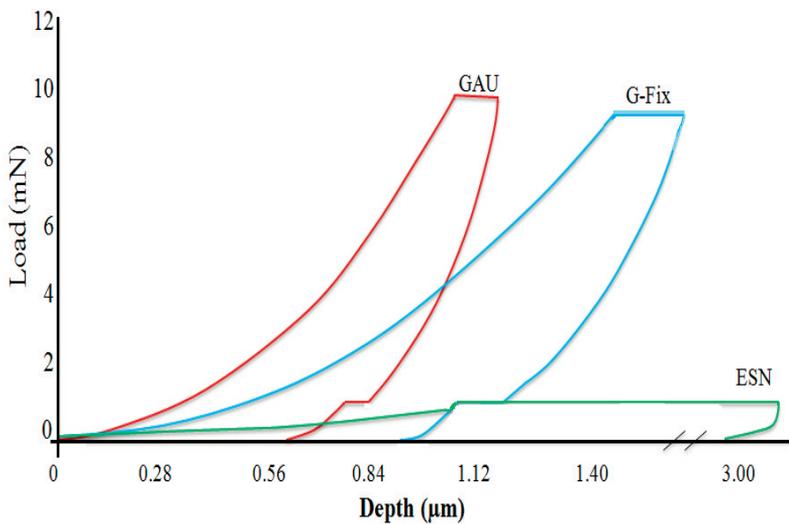


Figure 19: Load penetration depth graphs for determining the nanomechanical properties of the test specimens (I).

The representative SEM micrographs demonstrated that the groups with glass fibers (GFI-F and GAU-F) had more of adhesive retained on bracket surface, and an impression of the fiber texture could be detected on the enamel surface. In non-reinforced groups, the adhesive was found on the surface of bracket in GFI group, but in the group GAU adhesive remnants were found on both enamel and bracket surfaces (Figure 20).

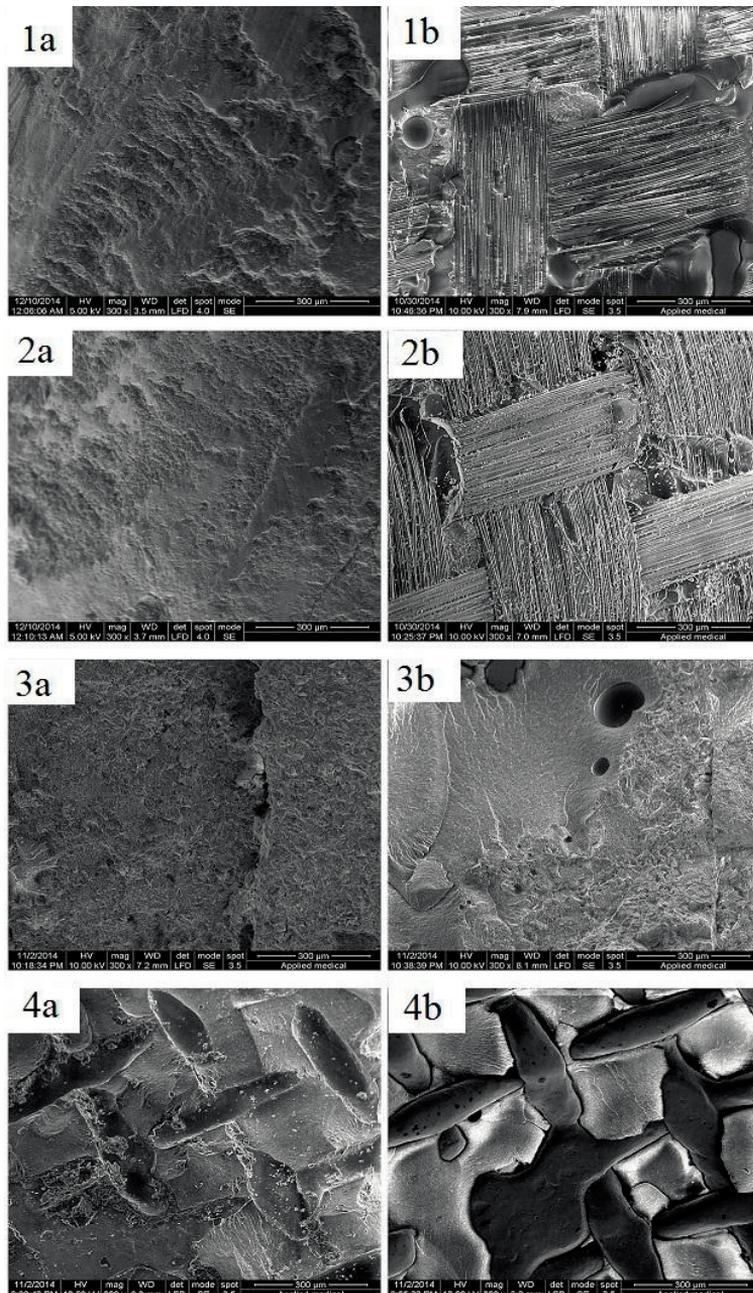


Figure 20: Representative SEM micrographs of the enamel surface and bracket after debonding (1a, 2a, 3a, 4a (enamel surface) and 1b, 2b, 3b, 4b (bracket)) of groups GFI-F, GAU-F, GFI, and GAU respectively (I)

## 5.2 Effect of continuous E-glass fiber orientation on degree of conversion (DC%) and irradiance power (Study II)

**Degree of conversion results:** The Fourier transform infrared spectroscopy (FT-IR) measurements showed an increased DC% over time in all the groups tested (Figure 21). The final DC% values after 12 minutes of light irradiation are presented in Table 4. Following 12 minutes of light polymerization, the groups with continuous unidirectional fiber groups (GFH and GFV) demonstrated an increased DC% compared to groups with bidirectional glass fibers (GFB) and control. The DC% was 55.4% and 54.7% for the unidirectional FRC groups, GFH and GFV respectively, and 45.8% for group GFB and 38% for the control group. A significant difference in the DC% was observed between the groups except between groups GFH and GFV ( $P < .05$ ).

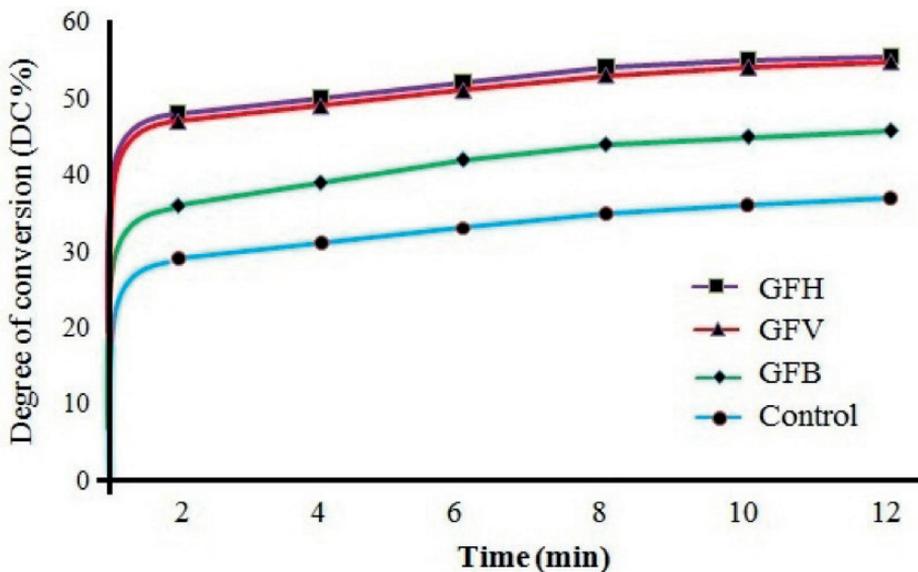


Figure 21: Degree of conversion of the groups plotted against irradiation time (II)

**Irradiance power results:** The mean irradiance power ( $\text{mW}/\text{cm}^2$ ) values of the fiber orientation systems tested are presented in Table 4. The mean irradiance power was found to be high in the groups incorporating unidirectional glass fibers (GFV and GFH) compared to group with bidirectional fibers (GFB) and control. The irradiance power was 95 and 94.2 for groups GFV and GFH respectively followed by group GFB with 83.8 and control group with 74.4 (Figure 22). A significant difference in the irradiance power was observed between the groups except between groups GFH and GFV ( $P < .05$ ).

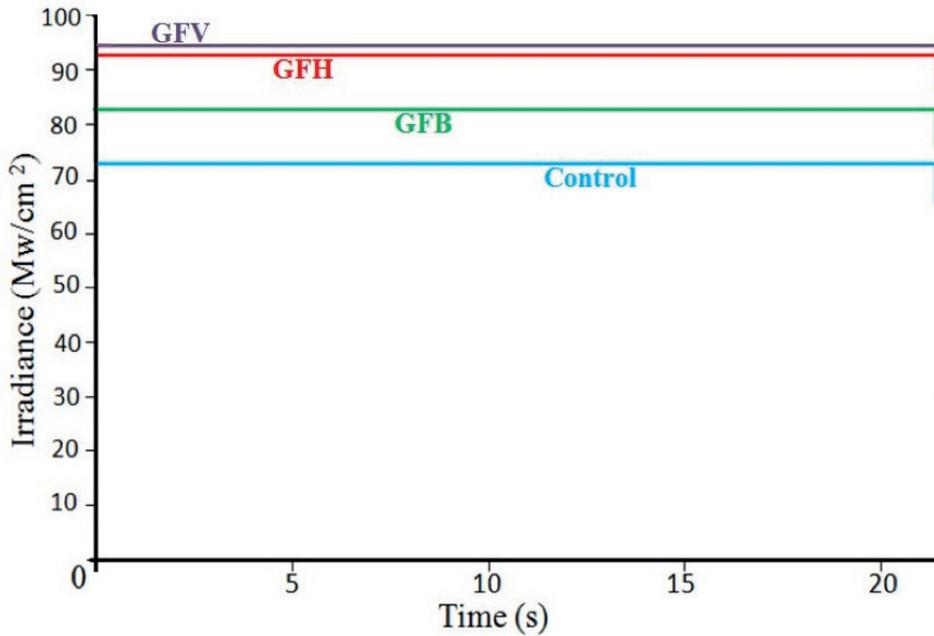


Figure 22: The irradiance power of the light curing device under the bracket for a period of 21.5 s (II)

Table 4: Mean DC% and irradiance power of the groups (II)

Groups (n=10)	DC% Mean ± SD	Irradiance power Mean ± SD
Control	38.0 ± 1.94 <sup>a</sup>	74.4 ± 4.29 <sup>a</sup>
GFH	55.4 ± 1.31 <sup>b</sup>	94.2 ± 3.85 <sup>b</sup>
GFV	54.7 ± 1.49 <sup>b</sup>	95.0 ± 4.26 <sup>b</sup>
GFB	45.8 ± 0.81 <sup>c</sup>	83.8 ± 4.31 <sup>c</sup>

\* Different lower case letters in a column indicates mean with statistical difference ( $P < .05$ )

The regression analysis plotting DC% against irradiance power showed a positive correlation between them (Figure 23)

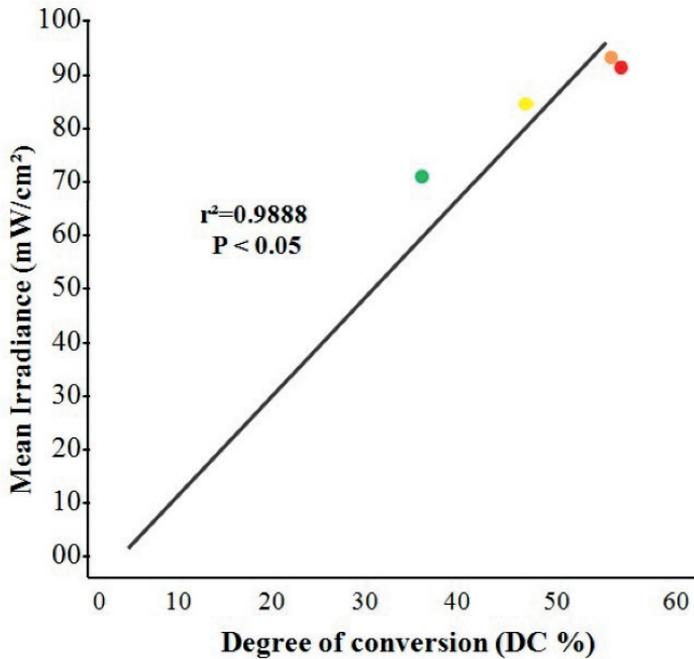


Figure 23: Regression line of irradiance power (mW/cm<sup>2</sup>) plotted against degree of conversion (DC%) (II)

### 5.3 Creep behavior of resin composite interfaces of dimethacrylate resin composites with particulate fillers and glass fiber fillers (III)

Table 5 present the mean strain and time required for debonding of the groups tested. The glass fibers reinforced groups (TBF, GFF, and GUF) demonstrated increased strain values compared to non-reinforced groups (TB, GF, and GU). Group GFF presented with highest strain values among both non-reinforced and reinforced groups. This was followed by Groups TBF<GF<TB<GUF<GU. Significant differences were observed between the groups except for groups TB and GF (non-reinforced groups) and TBF and GFF (reinforced groups) ( $P < .05$ ). The assessment of debonded surfaces presented with more of adhesive failures in all the groups.

Table 5: Mean values of strain-% and debonding time (III)

	Groups	Strain-%	Time (min)
<b>Groups without fiber reinforcement</b>	Group 1 (TB)	8.23 (0.49) <sup>a</sup>	237 (2.42) <sup>a</sup>
	Group 2 (GF)	9.19 (1.05) <sup>a</sup>	285.4 (1.89) <sup>a</sup>
	Group 3 (GU)	6.53 (0.68) <sup>b</sup>	157.2 (1.55) <sup>b</sup>
<b>Groups with fiber reinforcement</b>	Group 4 (TBF)	10.9 (0.34) <sup>c</sup>	312.6 (2.13) <sup>c</sup>
	Group 5 (GFF)	11.4 (0.50) <sup>c</sup>	377.4 (2.02) <sup>c</sup>
	Group 6 (GUF)	8.10 (0.72) <sup>a</sup>	227.1 (1.89) <sup>a</sup>

Same lower case alphabets within a column indicate that data are not statistically different ( $P > .05$ )

Dynamic mechanical analysis of the rectangular specimens demonstrated increased compliance of the Group GF followed by GU and TB groups in non-reinforced groups. In groups with reinforcing fibers, increased creep compliance was observed for Group GFF, intermediate for Group TBF group and least compliance was seen in Group GUF. The incorporation of glass fibers at the adhesive interface increased the compliance of Group TB compared to Group GF (Figure 24).

The regression analysis of strain-% plotted against debonding time showed a positive but non-significant correlation between the variables when the glass fiber reinforced groups ( $P=.193$ ) and non-reinforced groups ( $P=.0120$ ) were analysed separately (Figure 25). Nevertheless, the pooling of all subgroups of both the reinforced and non-reinforced groups demonstrated a statistically significant correlation ( $P=.008$ ).

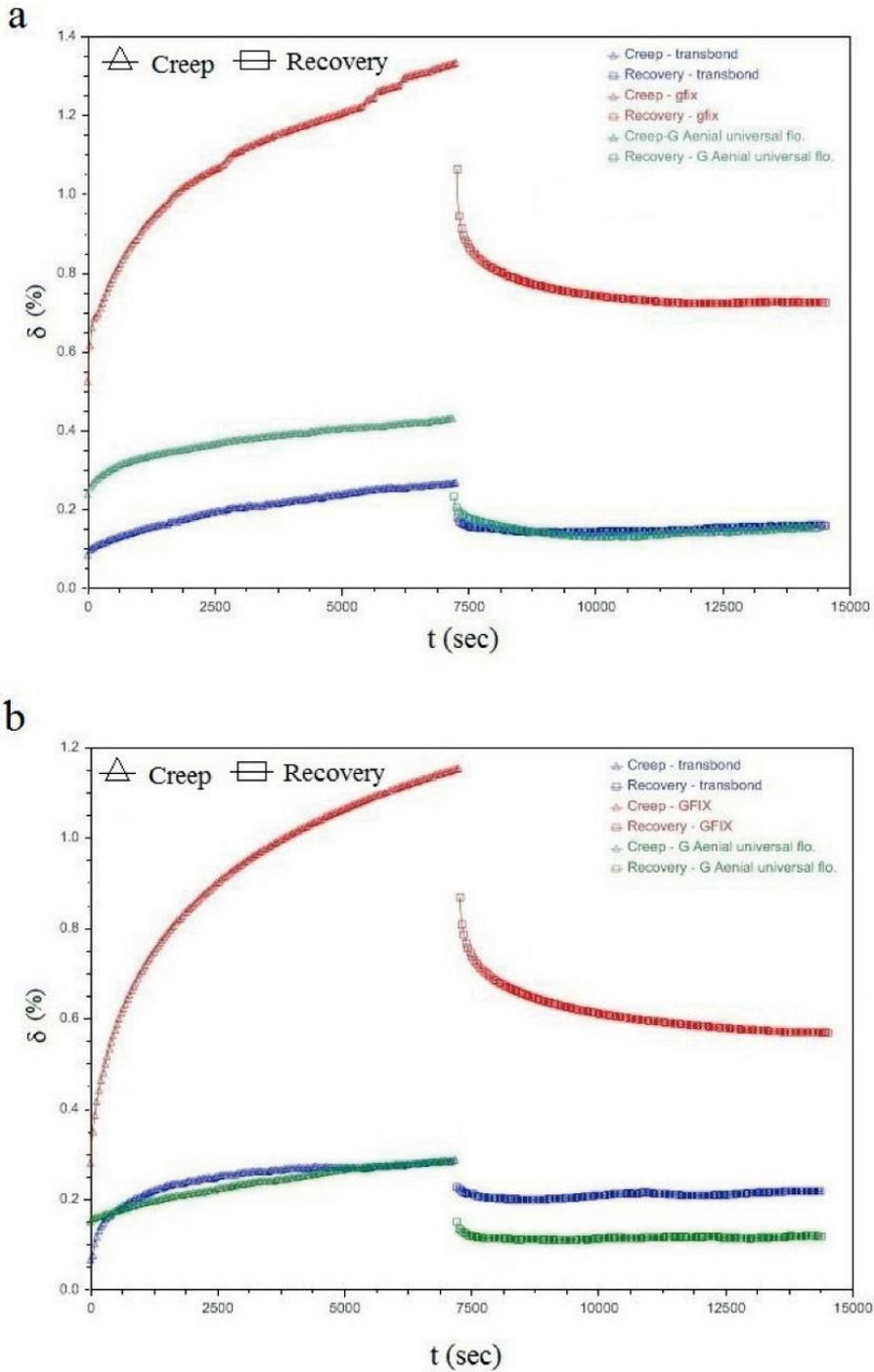


Figure 24: Dynamic mechanical analysis of the rectangular specimens

a) Without fibers      b) With fibers

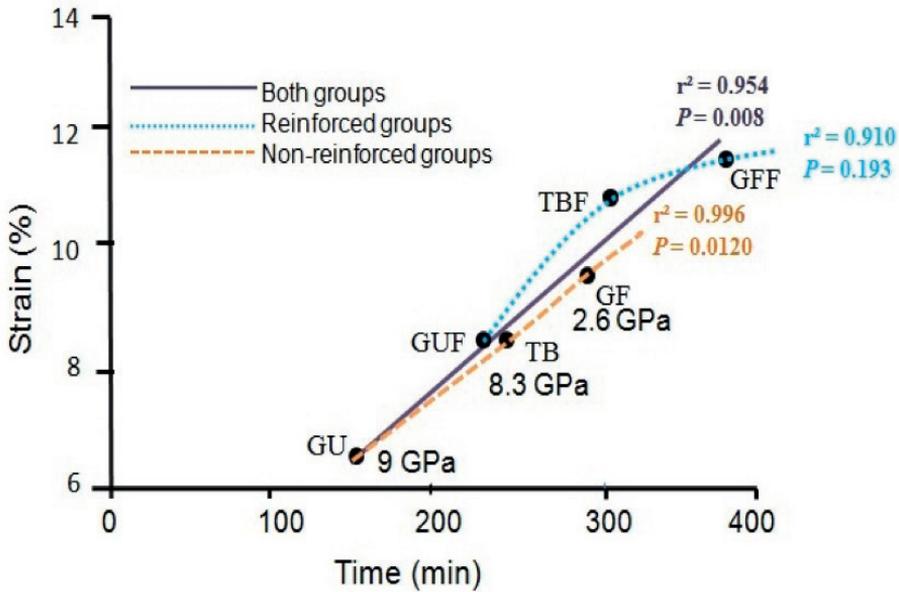


Figure 25: The regression line relating strain against debonding time (GPa values refer to the elastic modulus of the tested material) (III)

#### 5.4 Creep behavior of resin composite interfaces reinforced with FRC of unidirectional or bidirectional continuous fiber and conventional particle-filled composite (PFC) (IV)

Table 6 present the mean strain-% and time required for causing bracket deflection of the tested groups. The time required for interfacial strain to deform the adhesive interface was less in the control Group TBC with PFC, followed by groups TBE, TBV, and TBH with FRCs. The adhesive interface loading of cross-linked polymer matrix (groups TBV and TBH) differed statistically significantly from the IPN matrix interface (Group TBE) and control Group (TBC) ( $P < .05$ ). No significant difference was observed in strain-% or time between the groups TBC and TBE; TBV and TBH ( $P > .05$ ).

Table 6: Mean values of strain-% and time required for bracket debonding (IV)

Group	Strain-%	Time (min)
Group 1 (TBC)	7.10 (1.08) <sup>a</sup>	112 (1.12) <sup>a</sup>
Group 2 (TBE)	8.53 (0.89) <sup>a</sup>	125 (0.87) <sup>a</sup>
Group 3 (TBV)	10.73 (0.77) <sup>b</sup>	137.5 (2.05) <sup>b</sup>
Group 4 (TBH)	11.67 (0.44) <sup>b</sup>	147.5 (1.88) <sup>b</sup>

Different alphabets within a column indicate statistically significant values between the groups ( $P < .05$ )

The creep deformation occurring at each time point (creep compliance) in the three point bending mode demonstrated an increased compliance with Group TBH incorporating glass fibers oriented perpendicularly to the long axis of the specimen. The least creep compliance was seen with Group TBC (PFC), followed by groups TBV (glass fibers oriented parallel to the long axis of the specimen) and TBE (bi-directional fibers) (Figure 26).

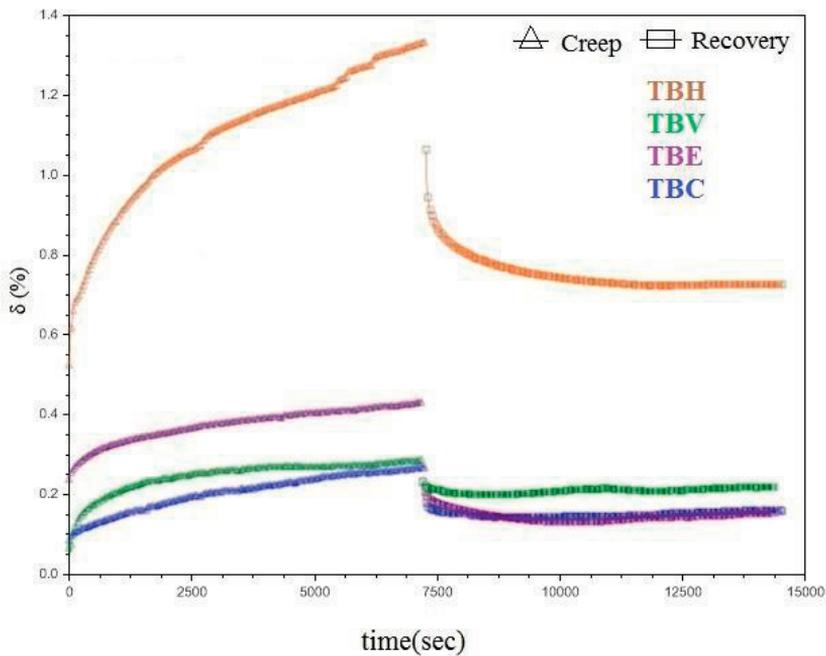


Figure 26: Creep compliance (strain) of the materials of different groups

Table 7 presents the nano-mechanical properties of the resin composite polymer matrix collected from the interface between bracket and tooth. Group TBC with PFC interface showed the highest nanohardness and elastic modulus, while the smallest values were seen in group TBE (semi-IPN matrix interface). Significant differences were observed between the groups ( $P < .05$ ) except for groups with cross-linked interface matrices (TBV and TBH) ( $P > .05$ ).

Table 7: Mean nanohardness and elastic modulus (GPa) of the study groups (IV)

Groups	Nanohardness	Young's Modulus
Group 1/TBC	0.22 ± 0.02 <sup>a</sup>	14.32 ± 1.09 <sup>a</sup>
Group 2/TBE	0.01 ± 0.03 <sup>b</sup>	1.10 ± 0.89 <sup>b</sup>
Group 3/TBV	0.15 ± 0.04 <sup>c</sup>	3.75 ± 1.14 <sup>c</sup>
Group 4/TBH	0.14 ± 0.06 <sup>c</sup>	5.19 ± 1.29 <sup>c</sup>

\* Different lower case alphabets within a column indicate statistically significant values between the groups ( $P < .05$ )

The load penetration depth of the indenter tip was more for Group TBC, followed by Groups TBH and TBV. Group TBE with semi-IPN interface required the least load, and a small increase in the penetration depth of TBH and TBV during unloading was observed (Figure 27). The load penetration depth corroborated well with the nano-mechanical properties (nanohardness and elastic modulus) values of the tested groups. An increased load penetration depth was directly related with increased nano-mechanical properties of the groups.

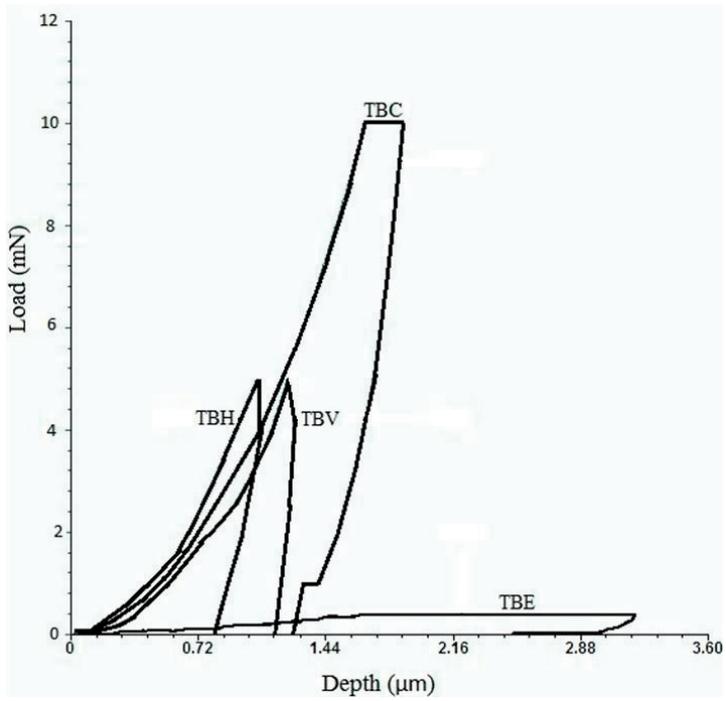


Figure 27: Load penetration depth graphs for determining the nanomechanical properties of the test specimens (IV)

## 6 DISCUSSION

This series of studies aimed at studying the behavior of resin composites at the bracket-tooth interface under different conditions with or without use of intermediate layers of glass fibers. Adhesive interface between bracket and enamel is based on adhesion of resin based material to enamel and to bracket. The adhesion of the bracket is typically reinforced by mechanical retention on the bracket bonding surface. Debonding of the bracket can occur either from the interface to enamel or to bracket, or within the interface material. The mechanism of debonding is related to the adhesion strength, elasticity and viscosity of the adhesive resin and thickness of the adhesive resin layer. Bonding strength is influenced by brackets, adhesive systems and composite resin. Bonding strength can also be enhanced by use of glass fibers. To better understand the influence of glass fibers in orthodontic bonding it is necessary to study the effect of fiber orientation on curing efficacy of adhesives and also the effect of fiber orientation on the debonding force. The curing efficacy of the adhesives used in bonding was determined using FTIR and MARC device. The effect of fiber orientation on the debonding force was assessed by bonding the bracket to tooth using layers of unidirectional glass fibers in horizontal and vertical directions and subjecting to debonding by static and creep forces with different directions of stress.

### 6.1 Effect of elastic properties of the adhesive material at the interface between orthodontic bracket and enamel (Study I)

This study investigated the elastic modulus of the interface material between orthodontic bracket and tooth, and the possible variations in the magnitude of debonding force and strain when the bracket is removed. This question was found to be important for a deeper understanding of the mechanisms that underlie bracket failures during orthodontic treatment, or an intentional removal of a bracket. The study was encouraged by the increasing use of light-curing flowable composite resins for orthodontic bonding (Scribante *et al.*, 2006; Ryou *et al.*, 2008; Pick *et al.*, 2010). Addition of a glass-fiber-reinforced resin composite significantly increased the bond strength and load necessary to debond brackets from the enamel. The composite, with a bidirectional orientation of fibers, had a thickness of 60  $\mu\text{m}$ , which affected the thickness of the interface layer more than the other interface materials (Shinya *et al.*, 2009). A shortcoming of the experimental part of this work was the fact that the thickness of the adhesive interface was not the same in all the groups. However, the study followed standard clinical procedures. The results of the present study showed that the incorporation of a bidirectional glass-fiber-reinforced composite (GFI-F and GAU-F) increased the debonding force and strain compared with non-reinforced composite resins (GFI and GAU). The working hypothesis that there was no significant difference in the

debonding stress of an orthodontic bracket bonded with resin systems of different visco-elasticity is rejected.

The nanoindentation study demonstrated varying elastic modulus of the polymeric matrix of the test materials (Figure 19). It should be noted that the nanoindentation tests were performed for the polymeric matrix of the composite resin (either flowable particulate composite or a fiber-reinforced composite), that on the average, made up half the volume of the material. Therefore, the test values of elastic modulus only partly reflect the elastic properties of the composite material. A significant correlation between the debonding force and strain and elastic modulus of the polymeric matrix of the composite was found. This suggests that the interface with a lower elastic modulus behaves as a stress absorber allowing strain to develop during debonding before actual break of the attachment.

The analysis of Adhesive Remnant Index (ARI) scores (Table 3) revealed that more remnants of the adhesive material were left on the bracket surface when polymeric matrix adhesives with a low modulus of elasticity were used. In the groups with glass fibers, the fracture occurred near the bracket surface and this fracture mode suggests that the chance of enamel fracture during debonding was low. No instance of enamel fractures were observed during the debonding process. It is known that the resin matrix of the ESN glass-fiber-reinforced composite has a high viscosity before the cure and polymer formation (Lastumaki *et al.*, 2002). The high viscosity is due to the presence of PMMA macromolecules in the resin of BisGMA monomer liquid. The values of debonding load found in the present study are in accordance with the results of previous studies (Newman *et al.*, 1995; Carvalho *et al.*, 2000). Bond strengths of 6-8 MPa are reported to be enough for clinical orthodontic needs (Reynolds, 1975; Turgut *et al.*, 2011). According to Newman *et al.*, (1995) the shear bond strength should be less than 21 MPa to avoid the enamel damage. However, the maximum bond strength should be lower than the tensile strength of enamel, which ranges between 11-25 MPa, depending on the prismatic orientation of enamel (Carvalho *et al.*, 2000). The groups with glass fibers showed comparatively higher bond strengths than the non-fiber reinforced groups, but they were low enough to prevent undue effect on the enamel. It is important to emphasize that the so-called shear bond strength tests are sensitive to many sources of inaccuracies, and the obtained stress values cannot be considered as exact estimates of the maximum shear stress that is necessary for debonding. Therefore, the shear stress values cannot directly be compared with bond strength results of other studies. Our recommendation is that the debonding force should be used in comparisons instead of the shear bond strength.

Clinically, the results of the study suggest that the probability of bracket failure during orthodontic therapy can be made lower by selecting an adhesive

material with low elasticity. The load necessary to debond a bracket was high for all groups incorporating glass fibers. However, a higher debonding force does not necessarily make an intentional removal of a bracket more difficult. The force exerted by orthodontic wires is static and long-term. Therefore, an understanding of possible viscoelastic properties of the interface of the IPN-type resin under constant load is important when considering undesired debonding of brackets due to forces caused by orthodontic wires. Thus, an insight into the elastic and viscoelastic properties of the resin under long-term static forces would be beneficial to better understand how properties of the adhesive interface of cross-linked semi-IPN polymer systems contribute to the bonding strength.

## **6.2 Effect of continuous E-glass fiber orientation on degree of conversion (DC%) and irradiance power (Study II)**

The DC% of light-curing monomer systems under orthodontic brackets is very important for successful bonding. The DC% of the resin composites has been measured by direct or indirect methods such as optic and electron microscopy, high performance liquid chromatography (HPLC), differential thermo gravimetric analyses (DTA), and vibratory methods, such as fourier transformation infrared spectrometry (FTIR), ultraviolet visible spectrometry (UV-Vis) and Raman spectroscopy (Ozturk *et al.*, 2013). In the present study, the DC% was measured using FT-IR spectroscopy because it enables monitoring of the curing process during light irradiation under a metal bracket (Shinya *et al.*, 2009). Additionally, FT-IR method provides a direct measurement of unreacted methacrylate groups, and it has been shown to be a reliable technique for detecting C=C bond stretching vibrations directly before and after curing of resin composite (Eliades *et al.*, 1987; Imazato *et al.*, 1995; Alshaafi and Alqahtani, 2013). The top surface of the adhesive test material in this setup was covered with a metal bracket, which protected the resin from light. The bottom surface was in contact with the ATR sensor and simulated the contact surface of enamel.

The curing efficiency of the adhesive resins beneath the metal bracket depends on the ability of the light to penetrate the resin material and on the amount of light scattered from the background surface (Fan *et al.*, 1984). In the present study, the control group had a DC% value of 38% was low compared to the generally accepted values for light curing resins and resin composites. A lower DC% indicates that energy of the curing light under the bracket did not allow for sufficient polymerization with the regular curing time. Obviously, the total energy from the irradiation is dependent on the curing time, and the DC% would have been greater if the curing time was longer. Regardless, if improved biocompatibility of materials is desired, more emphasis should be placed on higher DC% values.

The addition of glass fibers under the bracket in the other groups of the study, namely groups GFV, GFH, and GFB, showed increased DC% values (Figure 21). This is probably due to the glass fibers, which are capable of transmitting light and, in certain circumstances, also to scatter light from the fibers (Shinya *et al.*, 2009). The main objective of this study was to find out whether the fiber orientation could influence light transmission and scattering and enhance the curing of the adhesive resin. It should be noted that two photo curing monomer systems to be polymerized were studied: adhesive resin Transbond XT and the BisGMA-TEGDMA resin matrix of the FRC. There were minor differences between the resin matrix composition of the groups with unidirectional fibers (GFV and GFH) and bidirectional fibers (GFB). The latter also contained small quantities of poly-methyl-methacrylate in the dimethacrylate matrix (semi-IPN). This is known to have an influence on the polymerization rate but affect less the final DC%.

The DC% of the adhesive resin Transbond XT with unidirectional fibers (GFV and GFH) showed significantly higher values compared to samples with bidirectional fibers (GFB). To some extent, the higher DC% at the measuring time point could be explained by the lower viscosity of the matrix in the resin of groups GFV and GFH than in the group GFB, which contained matrix with the semi-IPN system. Lower viscosity resulted in an increased curing rate, so DC% could have been higher due to the increased mobility of the molecules (Dickens *et al.*, 2003). The lower viscosity of the monomer system in groups GFH and GFV is due to the presence of TEGDMA and the lack of polymethyl methacrylate. This has been shown to affect the rate of monomer conversion and early DC% (Asmussen, 1982; Ferracane and Greener, 1984). It is hypothesized that the orientation of glass fibers might also influence the DC% of the adhesive resin Transbond XT under the layer of FRC in groups GFV, GFH and GFB. Therefore, a distinction between DC% of the adhesive resin Transbond XT and the resin matrix of FRC needs to be made: the DC% measurement was made to show curing of Transbond XT, not that of the resin matrix of FRC. Nevertheless, the results did not show any significant change in DC% values of adhesive resin Transbond XT between the groups GFV and GFH, which suggests that with the present study design, optical anisotropy and light scattering from fibers, could not be detected, probably due to the small dimensions of the samples (bracket). Interestingly, the group GFB showed a lower DC% of the adhesive resins Transbond XT even though glass fibers were present. The orientation of the glass fibers and the diameter of the glass fibers in the group GFB differed from that of other FRC groups; fibers were bidirectionally oriented in the group GFB, and the diameter of the glass fibers was 6 micrometers in group GFB and 16 micrometers in groups GFV and GFH. Both of these aspects could have influenced the differences in the DC% between the groups. It is also possible that although the glass

fibers in the groups GFH, GFV and GFB were of the E-glass type, there could have been some variation in the glass composition, which could have influenced the refraction index and scattering of light from the fibers.

The Elipar Free Light 2 curing device reached a radiance of 1505 mW/cm<sup>2</sup> with standard irradiation mode when measured with a MARC device. As to irradiation power under the FRC layer, it was found that the values obtained in the present study varied significantly between the groups, except between GFH and GFV (Figure 22). The measured mean irradiance power was found to be higher in the groups where glass fibers were incorporated into the test setup. As expected, there was a clear correlation between the light irradiation power and corresponding DC% (Figure 23). The amount of light transmitted through a resin based composite is dependent on the amount of scattered and absorbed light (Musanje and Darvell, 2006). Irradiance, also called “light intensity” or “power density”, i.e., power (mW) divided by area (cm<sup>2</sup>), may vary depending on how it is measured. Beam profiles of light curing units are often inhomogeneous, the power being unequally distributed across the tip end (Flury *et al.*, 2013). The actual irradiance underneath the bracket is limited by the metal bracket and the thickness of the adhesive resin. The power of irradiance (mW/cm<sup>2</sup>) and the curing time (s) are called radiant exposure (“energy density” or “energy dose”; J/cm<sup>2</sup>), and it consequently describes a simple reciprocal relationship: if irradiance is decreased, the light curing time must be increased (Halvorson *et al.*, 2002; Musanje and Darvell, 2003; Hadis *et al.*, 2011). Some researchers maintain that similar radiant exposures with varying combinations of irradiance and light curing time lead to similar material properties (Halvorson *et al.*, 2002; Emami and Soderholm, 2003), while others have argued that irradiance and light curing time independently influence the curing process and consequently the material properties (Asmussen and Peutzfeldt, 2005; Peutzfeldt and Asmussen, 2005; Musanje and Darvell, 2006). Nonetheless, it can be assumed that certain threshold energy is needed to initiate photo curing.

The working hypothesis that the glass fiber orientation did not significantly affect the DC% and the total irradiance under the bracket in the present study is rejected. Further studies are required to determine the relationship between the threshold energy, which initiates photo curing, and the propagation energy of polymerization.

### **6.3 Creep behavior of resin composite interfaces of dimethacrylate resin composites with particulate fillers and glass fiber fillers (Study III)**

This study evaluated the creep behavior of the adhesive resins at the tooth-bracket interface subjected to static loading. The specimens were loaded with a minimal load of 20 N which is less than typical debonding force of the bracket that varies between 20-40 N (Valletta *et al.*, 2007). The load used in this study

was considerably higher than the loads used in orthodontic aligning of teeth (Weinstein, 1967; Matarese *et al.*, 2008; Baccetti *et al.*, 2009; Montasser *et al.*, 2013). There are some aspects that have to be considered when interpreting the magnitude of load and the stress that were used in this study. From a practical perspective, loads considerably lower than those used in the study would have required longer laboratory and instrument time, making the study more challenging to perform. Therefore, the load selected were higher than used in orthodontic tooth alignment, but lower than average debonding force to provoke the creep to occur at the resin composite adhesive interface. On the other hand, the load was applied to the resin composite interface, close to the bracket's bonding surface. This means, that the stress was predominantly of shear type rather than having tensile stress component, which would be the case when the load is transmitted to the interface from the arch wire slot of a bracket. With the type of bracket used in the study, the distance from the slot to the bonding surface was 1.56 mm, which would have been the momentum if the loading would have taken place with a cantilever beam. A cantilever beam deflection approach is complex because it involves materials with different physical properties from the metal bracket's arch wire slot to the surface of enamel. Therefore, a simpler type of stress, namely shear stress, applied directly to the resin composite interface, was selected for this test.

The results of the present study showed interesting variation of materials on the strain percentage of the bonding interface and time required to debond the bracket from the surface of enamel (Table 5). First of all, when pooling all the material, high linear correlation was found between the strain percentage and the loading time required to debond the bracket when the glass fiber containing and non-glass fiber containing groups were compared separately, the correlation coefficients remained high but their statistical significance became lower (Figure 25). This is likely due to the lower number of test specimens in the regression model. When looking at the resin composite materials and their values of modulus of elasticity it can be seen that regardless of the presence of glass fibers, the materials with higher modulus of elasticity (e.g. material GU: 9 GPa) of elasticity, required less time for debonding than material with lower modulus of elasticity (material GF: 2.6 GPa). This reflects higher creeping of the materials during the test event. Addition of glass fibers resulted in a tendency to increase creeping even more. Glass fibers were continuous unidirectional in type and they were oriented vertically. It is known that vertical orientation of glass fibers in relation to an axially directed force is the most effective fiber orientation to increase bonding strength of fiber-reinforced composites to tooth surface (Tezvergil *et al.*, 2005; Tezvergil *et al.*, 2006; Lassila *et al.*, 2007; Vallittu, 2015).

In the present creep testing, the shear stress was actually directed to the interface of single glass fibers and the polymer matrix. Based on the observations

of higher strain percentage and time, it can be assumed that the interfacial region of glass fibers and the polymer matrix can absorb the energy and make the interface between the bracket and tooth more elastic. Whether horizontal orientation of glass fibers or the use of woven bidirectional glass fibers would have resulted in similar or different strain percentage remains unclear. Creep properties of the interface relate also to the curing of the resin composite at the interface which is known to depend on the type of fillers (particulate fillers or fiber fillers) of the resin composite. In the present study, the curing characteristics were not investigated. Therefore it cannot be concluded whether variation in degree of cure (monomer conversion) of the resin composite was related to the effects of the fibers or to the presence of glass fibers as such.

Creep is the time-dependent change in strain under constant stress, and as a result, creep tests usually measure dimensional change as a function of time at a pre-selected stress. The deformation occurring at each time point is expressed as compliance ( $J$ ) which is calculated by estimating the ratio of strain at any given time. Time-dependent compliance is defined by recoverable and non-recoverable deformation during a stress application segment in a creep-recovery test. Time-dependent viscoelastic contributions to creep occur simultaneously during stress application over a selected time period (Vaidyanathan and Vaidyanathan, 2001). The creep behavior was tested also by the dynamic mechanical analysis. For this, test specimens of rectangular shape were prepared with similar material combinations that were used in the tooth-bracket test setup. In non-reinforced test specimen groups, the resin composite GF specimen showed the highest elastic and creep deformation. This is in line with the low modulus of elasticity of the material and agrees well with the results of the tooth-bracket model. The specimens with higher modulus of elasticity, groups GU and TB, had lower creep deformation. In the glass fiber reinforced groups, the creeping was somewhat less than with the non-reinforced specimens. This result is not in line with the results from the tooth-bracket model (Figure 24). When testing specimens by three point bending model, considerable magnitude of tensile stress was present on the lower surface of the test specimens and this may be the cause for the different results obtained when testing creep in the test setup of tooth-bracket model *versus* rectangular test specimens. The GF specimen showed the highest elastic and creep deformation, with the other two groups (TBF and GUF) presenting almost similar elastic and creep deformation. GFF specimens showed the highest recovery followed by TBF and GUF. Recovering phase of the DMA analysis showed variation between the resin composites of GU and GUF. These materials had the highest modulus of elasticity, and it is likely that it was the most brittle material that failed by internal cracking during the loading time of 7500 s. This in turn caused the permanent deformation of the test specimen, shown by the lower stress level after recovering compared to the initial stress of the creeping test.

Considering the outcome of the study, the working hypothesis that there was no significant difference in the shear stress creep behavior between particulate filler resin composite and glass fiber reinforced resin composite is rejected.

Clinically, this study provides an insight to the material behavior when glass fibers are used at the interface of enamel and bracket. Due to differences in magnitude of load and type of stress, the results cannot be clinically interpreted precisely. However, when considering the length of the time brackets are in place, and that the maximum creeping occurs within six hours with higher levels of stress, it is likely that the creeping behavior of interfacial composites has clinical relevance.

#### **6.4 Creep behavior of resin composite interfaces reinforced with FRC of unidirectional or bidirectional continuous fiber and conventional particle-filled composite (PFC) (Study IV)**

Creep behavior of interfacial adhesive resin was investigated in two different test models, shear creep with bracket-tooth model under shear stress, and bending creep with three point bending test where the predominant type of stress was tensile. In addition, the time required to debond the bracket from the tooth surface was determined.

The results demonstrated interesting differences of the interface adhesive materials in the strain percentage of the bonding interface and time required for bracket debonding. The test setups, one adopted from the clinical context and the other modified from the conventional material testing setup, provided information how the materials' composition and fiber orientation influenced the shear behavior of the material. The creep of polymers, which are viscoelastic materials, demonstrates a time-dependent increase in strain. Both testing models in the present study confirmed that the behavior of the studied materials is viscoelastic creep. Polymer visco-elasticity is known to be related to the polymer structure, *e.g.*, cross-linking density and molecular weight (Rao *et al.*, 2016). This study used three different polymer matrices in the resin composites at the interface. The polymer matrix of composite Transbond XT and that of unidirectional FRC were cross-linked in nature, whereas the polymer matrix of bidirectional FRC was a less cross-linked semi-interpenetrating polymer network (semi-IPN) (Sperling, 1994; Tezvergil *et al.*, 2005). The IPN matrix demonstrated lower creep than its cross-linked counterpart (Figure 26). The molecular basis of creeping of these two types of polymer matrices is in the chain structure of the cross-linked polymer under constant stress, and rearrangement of the partially linear polymer chain structure of the semi-IPN. Segmental motion of the linear polymer chains of the polymer matrix results in macroscopic creep strain, as described earlier for resin composites with fiber reinforcement (Raghavan and Meshii, 1998). The stress between the bracket base and tooth was less than 0.5 MPa, which is a low

level in relation to dimethacrylate properties. However, the stress of this magnitude was selected for the present experiments because it is similar to the forces exerted by orthodontic arch wires in clinical use. On the other hand, the tested resin composite materials differed not only in terms of fillers, but also in their polymer matrix. One of the polymer matrices was plasticized via its IPN structure. The creep of this material at low stress levels was within the scope of the study, and the complex stress distribution simulated clinical conditions.

The nanohardness, elastic modulus, and indenter penetration depth confirmed differences in the properties of the polymer matrices (Table 7). We used a very low indentation depth to provide comparable values for the properties of the resin composite polymer matrices (cross-linked *versus* IPN), not of the actual composite materials themselves, which would have required a larger-scale test. Thus, the study focused on the influence of filler/fiber systems on the macroscopic creep properties, and compared the polymer matrix properties by nanomechanical means. The highest nanohardness of the polymer matrix was found for Transbond XT, which suggests that photoinitiated polymerization of the monomer is effective, as has been previously demonstrated experimentally (Dickens *et al.*, 2003; Papakonstantinou *et al.*, 2013; Kilponen *et al.*, 2016). In addition, the presence of TEGDMA in the polymer matrix of unidirectional fibers could have affected the degree of conversion of BisGMA-based resin, although tested nanomechanical properties were somewhat lower than for the Transbond XT (Asmussen, 1982; Ferracane and Greener, 1984). The small quantities of polymethyl-methacrylate in the IPN could have influenced the DC% of the groups; this in turn could explain why the time required for bracket debonding was less compared to groups with cross-linked matrices (Vallittu, 2015). A minor increase in the penetration depth of TBH and TBV specimens was observed during unloading (Figure 27). This could be explained by the anisotropic properties of cross-linked matrices with continuous fibers in groups TBH and TBV, which could also be the reason for the minor time-dependent properties of such materials. In contrast, groups TBC with particulate fillers and TBE with bidirectionally oriented fibers, showed isotropic or orthotropic properties for the composite. The elastic modulus measurement in the present study provided additional information on polymer matrix characteristics and compositions used in the composites at the interface. This information has relevance in selection of resin matrix materials for future studies.

Another factor that has an impact on the creep behavior of the resin composites at the interface is the type of the fillers. The fillers used in the present study were particulate fillers (Transbond XT), continuous unidirectional fibers, or bidirectional fiber weaves, responsible for the isotropic, anisotropic, and orthotropic physical properties of the composite, respectively. The bending creep test was carried out to investigate the effects of fiber direction and the fiber-

reinforcing efficiency (Krenchel's factor) (Krenchel, 1963; Vallittu PK, 2017). Indeed, fiber direction considerably influenced the creep of the materials. Fiber direction perpendicular to the long axis of the specimen yielded the highest creep for the composite, due to the fact that the stress was not directed axially to the fibers. When the adhesive interface between the glass fibers and the polymer matrix was stressed, and a failure most frequently occurred at the fiber-matrix interface. The lowest creep was seen with the control material, *i.e.*, Transbond XT with particle fillers as well as with unidirectional fibers, which were oriented along the long axis of the specimen. It seems that although there were two kinds of polymer matrices in the specimens with unidirectional fibers (stick resin was used to impregnate the fiber weave and Transbond XT resin to fill the mold), the mechanical properties of the Transbond XT matrix mostly affected the final creep behavior of the material with unidirectional fibers. Test specimens with bidirectional fibers were made of Transbond XT and fibers of semi-IPN matrix. Unlike the unidirectional fiber specimens, the semi-IPN matrix, due to its higher elasticity, had the greatest effect on creep behavior. In general, the creep of the study materials was in line with that reported in the recent literature (Mortazavian and Fatemi, 2015). In the shear creeping test the brackets bonded with different kind of resin composite interfaces behaved similarly as did the materials in the bending creep test. However, in the shear test, differences in the fiber orientation resulted in some differences. Unidirectional fibers that were oriented along the long axis of the tooth (vertically) yielded the highest strain; somewhat lower strain was found with horizontally oriented fibers. Effects of fiber orientation in the adhesive interface of restorative resin composite and enamel has been described previously (Vallittu, 1999). Vertical orientation of fibers is the most efficient in relation to axially directed force to increase the bond between fiber composite and tooth surface (Tezvergil *et al.*, 2005; Lassila *et al.*, 2007). This could be due to the ability of the vertically oriented fibers to carry the stress in the direction of the applied load. In contrast, the stresses in horizontally oriented fibers are not spread evenly among all fibers, leading to sequential breakage of fiber interfaces, one fiber after another, causing entire fiber breakage along the margins (Lassila *et al.*, 2007). Similar phenomena could also have been the reason for the creep behavior. The lowest creep was found for the control material and bidirectional fiber-reinforced interface. Direction and magnitude of stress at the bracket-enamel interface may differ considerably from the levels of stresses used in this study. Therefore, the results of this study cannot be directly applied to clinical context. However, the present study provides an understanding of the creep behavior when fiber-reinforced composites with different fiber orientation are used at the interface of enamel and orthodontic bracket. The long-term use of orthodontic bracket could benefit from the anisotropic

behavior and orientation of the FRC, as illustrated by bracket debonding times of the various groups.

Based on the present results, fiber orientation at the interface had an impact on the creep properties; thus, the working hypothesis was rejected.

## 7 CONCLUSIONS

- a) The present *in vitro* study showed that incorporation of a FRC with a low elastic modulus between the bracket and enamel increased the debonding force and strain before debonding more than adhesive systems with a higher elastic modulus. A correlation was found between the elastic modulus of the polymer matrix of the adhesive composite material and the debonding force of the bracket.
- b) A layer of E-glass fibers under a metal bracket improved the degree of conversion of light curing adhesive resin by enhancing the transmittance of curing light. No difference was found if unidirectional fibers were parallel or perpendicular to the direction of irradiance of the curing light. Unidirectional fibers enabled better curing of adhesive than bidirectional fiber weave under the bracket.
- c) Incorporation of continuous glass fibers at the interface between orthodontic bracket and enamel increased the creeping and debonding time of the bracket. Attachment of orthodontic brackets could benefit from the increased creeping time provided by the glass fibers incorporated in the interface adhesive materials.
- d) The creep of the interface adhesive and the time required for bracket debonding increased with the incorporation of glass fibers in the interface between bracket and enamel. Orientation of the fibers and the resin matrix type also affected the creep behavior.
- e) Overall, the procedures of bonding orthodontic brackets to the tooth are technique sensitive and involve many steps. The insertion of glass fibers at the interface between the bracket and tooth could add to the number of existing steps and would be time consuming for the clinician. However, the incorporation of the glass fibers at the interface has a promising advantage that could dominate the additional steps involved.

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**REFERENCES**

- Agarwal B, Broutman L. *Analysis and Performance of Fiber Composites*. 2nd ed. New York; Chichester Wiley 1990.
- Al-Haddad AA. *Characterisation and Performance of Fiber-Reinforced Composite Restorations*. Manchester, UK: Faculty of Medical and Human Sciences, School of Dentistry, The University of Manchester; 2015.
- Alkire RG, Bagby MD, Gladwin MA, Kim H. Torsional creep of polycarbonate orthodontic brackets. *Dent Mater*. 1997; 13 (1):2-6.
- Alshaafi MM, Alqahtani MQ. Effects of Different Porcelains on Polymerization of Light- and Dual-Cured Resin Cements. *J Biomat Tissue Eng*. 2013;3(5):564-569.
- Amirouche-Korichi A, Mouzali M, Watts DC. Effects of monomer ratios and highly radiopaque fillers on degree of conversion and shrinkage-strain of dental resin composites. *Dent Mater*. 2009;25(11):1411-1418.
- Artun J, Bergland S. Clinical trials with crystal growth conditioning as an alternative to acid-etch enamel pretreatment. *Am J Orthod*. 1984;85(4):333-340.
- Asmussen E, Peutzfeldt A. Polymerization contraction of resin composite vs. energy and power density of light-cure. *Eur J Oral Sci*. 2005;113(5):417-421.
- Asmussen E. Factors affecting the quantity of remaining double bonds in restorative resin polymers. *Eur J Oral Sci*. 1982;90(6):490-496.
- Azzopardi N, Moharamzadeh K, Wood DJ, Martin N, van Noort R. Effect of resin matrix composition on the translucency of experimental dental composite resins. *Dent Mater*. 2009;25(12):1564-1568.
- Baccetti T, Franchi L, Camporesi M, Defraia E, Barbato E. Forces Produced by Different Nonconventional Bracket or Ligature Systems during Alignment of Apically Displaced Teeth. *Angle Orthod*. 2009; 79 (3) :533-539.
- Bahramian N, Atai M, Naimi-Jamal MR. Ultra-high-molecular-weight polyethylene fiber reinforced dental composites: Effect of fiber surface treatment on mechanical properties of the composites. *Dent Mater*. 2015;31(9):1022-1029.
- Bales J. Deformation of reinforced polycarbonate orthodontic brackets stressed by a labiolingual moment, *Thesis*: University of Manitoba; 1998.
- Ballo A, Närhi T. Biocompatibility of fiber-reinforced composites for dental applications. In: Shelton R, *Biocompatibility of Dental Biomaterials*: Woodhead Publishing ; 2017 :23-39.

- Barbero E. *Introduction to Composite Materials Design*. 2nd ed. USA: CRC press; 2010.
- Barbucci R. *Integrated Biomaterials Science*. New York ; London: Kluwer Academic/Plenum; 2002.
- Beun S, Glorieux T, Devaux J, Vreven J, Leloup G. Characterization of nanofilled compared to universal and microfilled composites. *Dent Mater*. 2007; 23(1):51-59.
- Bishara SE, Soliman MMA, Oonsombat C, Laffoon JF, Ajlouni R. 2004. The Effect of Variation in Mesh-Base Design on the Shear Bond Strength of Orthodontic Brackets. *Angle Orthod* 74:400-4
- Bouillaguet S, Schutt A, Alander P, et al. Hydrothermal and mechanical stresses degrade fiber-matrix interfacial bond strength in dental fiber-reinforced composites. *J Biomed Mater Res B Appl Biomater*. 2006;76(1):98-105.
- Bowman AJ, Manley TR. The elimination of breakages in upper dentures by reinforcement with carbon fiber. *Br Dent J*. 1984; 156(3):87-89.
- Brunharo IHVP, Fernandes DJ, Miranda MSd, Artese F. Influence of surface treatment on shear bond strength of orthodontic brackets. *Dental Press J. Orthod*. 2013;18:54-62.
- Butterworth C, Ellakwa AE, Shortall A. Fiber-reinforced composites in restorative dentistry. *Dent Update*. 2003 ;30(6):300-306.
- Callister W. *Materials Science and Engineering: An Introduction*. 7th ed. New York.: John Wiley & Sons; 2007.
- Carvalho RM, Santiago SL, Fernandes CA, Suh BI, Pashley DH. Effects of prism orientation on tensile strength of enamel. *J Adhes Dent*. 2000;2(4):251-257.
- Cheng TH, Jones FR, Wang D. Effect of fiber conditioning on the interfacial shear strength of glass-fiber composites. *Compos Sci Technol*. 1993;48(1):89-96.
- Cogswell FN. An introduction to thermoplastic composite materials. In: Cogswell FN, ed. *Thermoplastic Aromatic Polymer Composites*: Butterworth-Heinemann; 1992:1-10.
- D'Attilio M, Traini T, Di Iorio D, Varvara G, Festa F, Tecco S. Shear Bond Strength, Bond Failure, and Scanning Electron Microscopy Analysis of a New Flowable Composite for Orthodontic Use. *Angle Orthod*. 2005;75(3):410-415.
- Dean JP, Jeansonne BG, Sarkar N. In vitro evaluation of a carbon fiber post. *J Endod*. 1998;24(12):807-810.
- Debnath S, Wunder SL, McCool JI, Baran GR. Silane treatment effects on glass/resin interfacial shear strengths. *Dent Mater*. 2003;19(5):441-448.
- DeBoer J, Vermilyea SG, Brady RE. The effect of carbon fiber

- orientation on the fatigue resistance and bending properties of two denture resins. *J Prosthet Dent.* 1984;51(1):119-121.
- DiBenedetto AT. Tailoring of interfaces in glass fiber reinforced polymer composites: a review. *Mat Sci Eng:A.* 2001; 302 (1):74-82.
- Dickens SH, Stansbury JW, Choi KM, Floyd CJE. Photopolymerization Kinetics of Methacrylate Dental Resins. *Macromolecules.* 2003; 36 (16): 6043-6053.
- Eliades GC, Vougiouklakis GJ, Caputo AA. Degree of double bond conversion in light-cured composites. *Dent Mater.* 1987; 3(1):19-25.
- Eliades T, Kakaboura A, Eliades G, Bradley TG. Comparison of enamel colour changes associated with orthodontic bonding using two different adhesives. *Eur J Orthod.* 2001;23(1):85-90.
- El-Safty S, Akhtar R, Silikas N, Watts DC. Nanomechanical properties of dental resin-composites. *Dent Mater.* 2012; 28(12):1292-1300.
- Emami N, Soderholm KJ. How light irradiance and curing time affect monomer conversion in light-cured resin composites. *Eur J Oral Sci.* 2003;111(6):536-542.
- Evans LB, Powers JM. Factors affecting in vitro bond strength of no-mix orthodontic cements. *Am J Orthod.* 1985;87(6):508-512.
- Faltermeier A, Rosentritt M, Faltermeier R, Reicheneder C, Müßig D. Influence of Filler Level on the Bond Strength of Orthodontic Adhesives. *Angle Orthod.* 2007;77(3):494-498.
- Fan PL, Stanford CM, Stanford WB, Leung R, Stanford JW. Effects of backing reflectance and mold size on polymerization of photo-activated composite resin. *J Dent Res.* 1984;63(10):1245-1247.
- Ferracane JL, Greener EH. Fourier Transform Infrared Analysis of Degree of Polymerization in Unfilled Resins—Methods Comparison. *J Dent Res.* 1984; 63(8):1093-1095.
- Flury S, Lussi A, Hickel R, Ilie N. Light curing through glass ceramics with a second- and a third-generation LED curing unit: effect of curing mode on the degree of conversion of dual-curing resin cements. *Clin Oral Investig.* 2013;17(9):2127-2137.
- Fraunhofer J. Adhesion and Cohesion. *Int J Dent.* vol. 2012, Article ID 951324
- Fujisawa N, Swain MV. On the indentation contact area of a creeping solid during constant-strain-rate loading by a sharp indenter. *J Mater Res* 2007; 22(4):893-899.
- Galan D, Lynch E. The effect of reinforcing fibers in denture acrylics. *J Ir Dent Assoc.* 1989; 35(3):109-113.
- Galvão MR, Costa SXS, Victorino KR, et al. Influence of light guide

- tip used in the photo-activation on degree of conversion and hardness of one nanofilled dental composite. *Laser Physics*. 2010; 20(12):2050-2055.
- Garoushi S, Kaleem M, Shinya A, et al. Creep of experimental short fiber-reinforced composite resin. *Dent Mater J*. 2012; 31(5):737-741.
- Garoushi S, Lassila L, Vallittu P. Fiber-reinforced Composite in Clinical Dentistry. *Chin J Dent Res*. 2009(1):7-14.
- Garoushi S, Mangoush E, Vallittu M, Lassila L. Short Fiber Reinforced Composite: a New Alternative for Direct Onlay Restorations. *Open Dent J*. 2013; 7:181-185.
- Garoushi S, Vallittu PK, Lassila LV. Short glass fiber reinforced restorative composite resin with semi-inter penetrating polymer network matrix. *Dent Mater*. 2007;23(11):1356-1362.
- Garoushi SK, Lassila LV, Tezvergil A, Vallittu PK. Fiber-reinforced composite substructure: load-bearing capacity of an onlay restoration and flexural properties of the material. *J Contemp Dent Pract*. 2006;7(4):1-8.
- Goertzen W, Kessler M. Creep behavior of carbon fiber/epoxy matrix composites. *Mat Sci Eng: A*. 2006;421(1):217-225.
- Goldberg AJ, Burstone CJ. The use of continuous fiber reinforcement in dentistry. *Dent Mater*. 1992;8(3):197-202.
- Guarita MK, Moresca AHK, Losso EM, Moro A, Moresca RC, Correr GM. Effect of Different Surface Treatments for Ceramic Bracket Base on Bond Strength of Rebonded Brackets. *Braz Dent J*. 2015;26:61-65.
- Habelitz S, Marshall SJ, Marshall GW, Jr., Balooch M. Mechanical properties of human dental enamel on the nanometre scale. *Arch Oral Biol*. 2001;46(2):173-183.
- Hadis M, Leprince JG, Shortall AC, Devaux J, Leloup G, Palin WM. High irradiance curing and anomalies of exposure reciprocity law in resin-based materials. *J Dent*. 2011;39(8):549-557.
- Halvorson RH, Erickson RL, Davidson CL. Energy dependent polymerization of resin-based composite. *Dent Mater*. 2002; 18(6):463-469.
- Halvorson RH, Erickson RL, Davidson CL. The effect of filler and silane content on conversion of resin-based composite. *Dent Mater*. 2003;19(4):327-333.
- Ilie N, Bucuta S, Draenert M. Bulk-fill resin-based composites: an in vitro assessment of their mechanical performance. *Oper Dent*. 2013; 38(6):618-625.
- Ilie N, Hickel R. Resin composite restorative materials. *Aust Dent J*. 2011;1:59-66.
- Imazato S, Tarumi H, Kobayashi K, Hiraguri H, Oda K, Tsuchitani Y. Relationship between the degree of conversion and internal

- discoloration of light-activated composite. *Dent Mater J*. 1995;14(1):23-30.
- Karaman AI, Kir N, Belli S. Four applications of reinforced polyethylene fiber material in orthodontic practice. *Am J Orthod Dentofacial Orthop*. 2002;121(6):650-654.
- Kilponen L, Uusitalo E, Tolvanen M, Varrelä J, Vallittu P. Photopolymerization of Light Curing Adhesives Used with Metal Orthodontic Brackets and Matrices. *J Biomater Tissue Eng*. 2016;6(8):659-664.
- Kim J-K, Mai Y-W. Chapter 5 - Surface treatments of fibers and effects on composite properties. In: Kim J-K, Mai Y-W, eds. *Engineered Interfaces in Fiber Reinforced Composites*. Oxford: Elsevier Science Ltd; 1998:171-237.
- Knox J, Hubsch P, Jones ML, Middleton J. The influence of bracket base design on the strength of the bracket-cement interface. *Journal of Orthodontics*. 2000;27(3):249-254.
- Krenchel H. *Fiber reinforcement*. Copenhagen Technical University of Denmark; 1963.
- Larson WR, Dixon DL, Aquilino SA, Clancy JM. The effect of carbon graphite fiber reinforcement on the strength of provisional crown and fixed partial denture resins. *J Prosthet Dent* 1991;66(6):816-820.
- Lassila LV, Nohrstrom T, Vallittu PK. The influence of short-term water storage on the flexural properties of unidirectional glass fiber-reinforced composites. *Biomaterials* 2002;23(10):2221-2229.
- Lassila LVJ, Tezvergil A, Dyer SR, Vallittu PK. The bond strength of particulate-filler composite to differently oriented fiber-reinforced composite substrate. *J prosthodont* 2007; 16(1):10-17.
- Lastumäki TM, Kallio TT, Vallittu PK. The bond strength of light-curing composite resin to finally polymerized and aged glass fiber-reinforced composite substrate. *Biomaterials* 2002;23(23):4533-4539.
- Lehtinen J, Laurila T, Lassila LVJ, Tuusa S, Kienanen P, Vallittu PK, Hernberg R. Optical characterization of bisphenol-A-glycidyl dimethacrylate-triethylene glycol dimethacrylate monomers and copolymers. *Dent Mater* 2008;24(10):1324-8.
- Lovell LG, Stansbury JW, Syropes DC, Bowman CN. Effects of Composition and Reactivity on the Reaction Kinetics of Dimethacrylate/Dimethacrylate Copolymerizations. *Macromolecules* 1999;32(12):3913-3921.
- Lutz F, Phillips RW. A classification and evaluation of composite resin systems. *J Prosthet Dent*. 1983; 50(4):480-488.
- Matarese G, Nucera R, Militi A, et al. Evaluation of frictional forces during dental alignment: an

- experimental model with 3 nonleveled brackets. *Am J Orthod Dentofacial Orthop.* 2008; 133(5):708-715.
- Matinlinna JP, Lassila LV, Ozcan M, Yli-Urpo A, Vallittu PK. An introduction to silanes and their clinical applications in dentistry. *Int J Prosthodont* 2004; 17(2): 155-164.
- Matinlinna JP, Vallittu PK. Silane based concepts on bonding resin composite to metals. *J Contemp Dent Pract.* 2007;8(2):1-8.
- McCabe J, Walls A. *Applied Dental Materials.* 9th ed. Oxford: Blackwell; 2008.
- Miettinen VM, Vallittu PK, Docent DT. Water sorption and solubility of glass fiber-reinforced denture polymethyl methacrylate resin. *J Prosthet Dent.* 1997;77(5):531-534.
- Millett DT, Glenny AM, Mattick RC, Hickman J, Mandall NA. Adhesives for fixed orthodontic bands. *Cochrane Database Syst Rev.* 2016;25(10).
- Ministry of Social Affairs and Health, Finland. 2012. Change in purpose for which tissue samples will be used. In: Ministry of Social Affairs and Health, No. 101/2001 Act on the Medical Use of Human Organs Tissue and Cells, Helsinki. 2nd February 2002, Stion 20 (689/2012).
- Mitra SB, Wu D, Holmes BN. An application of nanotechnology in advanced dental materials. *J Am Dent Assoc.* 2003;134(10):1382-1390.
- Montasser MA, El-Bialy T, Keilig L, Reimann S, Jager A, Bourauel C. Force levels in complex tooth alignment with conventional and self-ligating brackets. *Am J Orthod Dentofacial Orthop.* 2013;143(4):507-514.
- Mortazavian S, Fatemi A. Effects of fiber orientation and anisotropy on tensile strength and elastic modulus of short fiber reinforced polymer composites. *Compos Part B-Eng.* 2015;72:116-129.
- Murphy J. Chapter 2 - Reinforcements. In: Murphy J, ed. *The Reinforced Plastics Handbook.* Oxford: Elsevier; 1998: 56-94.
- Musanje L, Darvell BW. Curing-light attenuation in filled-resin restorative materials. *Dent Mater.* 2006;22(9):804-817.
- Musanje L, Darvell BW. Polymerization of resin composite restorative materials: exposure reciprocity. *Dent Mater.* 2003; 19(6):531-541.
- Newman GV, Newman RA, Sun BI, Ha JL, Ozsoylu SA. Adhesion promoters, their effect on the bond strength of metal brackets. *Am J Orthod Dentofacial Orthop.* 1995;108(3):237-241.
- Nohrstrom TJ, Vallittu PK, Yli-Urpo A. The effect of placement and quantity of glass fibers on the fracture resistance of interim fixed partial dentures. *Int J Prosthodont.* 2000;13(1):72-78.

- Özcan M, Dündar M, Erhan Çömlekoğlu M. Adhesion concepts in dentistry: tooth and material aspects. *J Adhes Sci Technol.* 2012;26(24):2661-2681.
- Ozturk B, Cobanoglu N, Cetin AR, Gunduz B. Conversion degrees of resin composites using different light sources. *Eur J Oral Sci.* 2013;7(1):102-109.
- Papakonstantinou AE, Eliades T, Cellesi F, Watts DC, Silikas N. Evaluation of UDMA's potential as a substitute for BisGMA in orthodontic adhesives. *Dent Mater.* 2013;29(8):898-905.
- Park SB, Son WS, Ko CC, et al. Influence of flowable resins on the shear bond strength of orthodontic brackets. *Dent Mater J.* 2009;28(6):730-734.
- Peskersoy C, Culha O. Comparative Evaluation of Mechanical Properties of Dental Nanomaterials. *J Nanomater.* 2017: 6171578:8
- Petrie E. *Handbook of Adhesives and Sealants.* 2nd ed. Newyork: The McGraw-Hill Companies, Inc.; 2007.
- Peutzfeldt A, Asmussen E. Resin composite properties and energy density of light cure. *J Dent Res.* 2005;84(7):659-662.
- Pick B, Rosa V, Azeredo TR, Cruz Filho EA, Miranda WG, Jr. Are flowable resin-based composites a reliable material for metal orthodontic bracket bonding? *J Contemp Dent Pract.* 2010;11(4):E017-024.
- Piitulainen J, Posti JP, Aitasalo K, Vuorinen V, Vallittu P, Serlo W. Pediatric cranial defect reconstruction using bioactive fiber reinforced composite implant: Early outcomes. *Acta Neurochir* 2015; 157(4):681-7.
- Posti J, Piitulainen J, Hupa L, Fagerling S, Frantzen J, Aitasalo KJM, Vuorinen V, Syrjänen S, Vallittu PK. A glass fiber-reinforced composite – bioactive glass cranioplasty implant. A case study of an early development stage implant removed due to a late infection. *J Mech Behav Biomed Mater* 2016; 55:191-200.
- Proffit W, Fields H. *Contemporary Orthodontics.* Missouri, United States: Mosby Elsevier; 2012.
- Raghavan J, Meshii M. Creep of polymer composites. *Compos Sci Technol.* 1998;57(12):1673-1688.
- Rao KV, Ananthapadmanabha GS, Dayananda GN. Effect of Cross-linking Density on Creep and Recovery Behavior in Epoxy-Based Shape Memory Polymers (SMEPs) for Structural Applications. *J Mater Eng Perform.* 2016; 25(12) :5314-5322.
- Reynolds IR. A Review of Direct Orthodontic Bonding. *Br J Orthod.* 1975;2(3):171-178.
- Ritter A. *Sturdevant's Art and Science of Operative Dentistry.* Missouri, United States: Mosby; 2018.

- Rosato DV, Rosato DV. Chapter 2 - Reinforcements. In: Rosato DV, Rosato DV, eds. *Reinforced Plastics Handbook (Third Edition)*. Amsterdam: Elsevier Science; 2005:24-108.
- Ruyter IE, Oysaed H. Conversion in denture base polymers. *J Biomed Mater Res*. 1982;16(5):741-754.
- Ryou DB, Park HS, Kim KH, Kwon TY. Use of flowable composites for orthodontic bracket bonding. *Angle Orthod*. 2008;78(6):1105-1109.
- Sakaguchi R, Powers J. *Craig's restorative dental materials* Vol 13 ed. USA: Mosby Elsevier; 2012.
- Scribante A, Cacciafesta V, Sfondrini MF. Effect of various adhesive systems on the shear bond strength of fiber-reinforced composite. *Am J Orthod Dentofacial Orthop*. 2006;130(2): 224-227.
- Shadman N, Atai M, Ghavam M, Kermanshah H, Ebrahimi SF. Parameters affecting degree of conversion of dual-cure resin cements in the root canal: FTIR analysis. *J Can Dent Assoc*. 2012;78.
- Shinya M, Shinya A, Lassila L, Varrel J, Vallittu P. Enhanced Degree of Monomer Conversion of Orthodontic Adhesives Using a Glass-Fiber Layer under the Bracket. *Angle Orthod*. 2009;79(3):546-550.
- Sperling LH. *Interpenetrating Polymer Networks: An Overview*. *Interpenetrating Polymer Networks*. Vol 239: *J Am Chem Soc*.1994: 3-38.
- Stipho HD. Repair of acrylic resin denture base reinforced with glass fiber. *J Prosthet Dent*. 1998;80(5):546-550.
- Subramani K, Huja S, Kluemper GT, Morford L, Hartsfield JK. Chapter 11 - Nanotechnology in Orthodontics-1: The Past, Present, and a Perspective of the Future. In: Subramani K, Ahmed W, Hartsfield JK, eds. *Nanobiomaterials in Clinical Dentistry: William Andrew Publishing*; 2013:231-247.
- Sunna S, Rock WP. Clinical performance of orthodontic brackets and adhesive systems: a randomized clinical trial. *Br J Orthod*. 1998;25(4):283-287.
- Tezvergil A, Lassila LV, Vallittu PK. The effect of fiber orientation on the polymerization shrinkage strain of fiber-reinforced composites. *Dent Mater*. 2006; 22(7):610-616.
- Tezvergil A, Lassila LVJ, Vallittu PK. The effect of fiber orientation on the thermal expansion coefficients of fiber-reinforced composites. *Dent Mater*. 2003;19(6):471-477.
- Tezvergil A, Lassila LVJ, Vallittu PK. The shear bond strength of bidirectional and random-oriented fiber-reinforced composite to tooth structure. *J Dent*. 2005;33(6):509-516.

- Turgut MD, Attar N, Korkmaz Y, Gokcelik A. Comparison of shear bond strengths of orthodontic brackets bonded with flowable composites. *Dent Mater J*. 2011;30(1):66-71.
- Uysal T, Ulker M, Baysal A, Usumez S. Microleakage between composite–wire and composite–enamel interfaces of flexible spiral wire retainers. Part 2: comparison of amorphous calcium phosphate-containing adhesive with conventional lingual retainer composite. *Eur J Orthod*. 2009;31(6):652-657.
- Vaidyanathan J, Vaidyanathan TK. Flexural creep deformation and recovery in dental composites. *J Dent*. 2001;29(8):545-551.
- Valletta R, Prisco D, De Santis R, Ambrosio L, Martina R. Evaluation of the debonding strength of orthodontic brackets using three different bonding systems. *Eur J Orthod*. 2007; 29(6):571-577.
- Vallittu P. *Interpenetrating Polymer Networks (IPNs) in Dental Polymers and Composites*. In: *Adhesion Aspects in Dentistry*. Edited by Matinlinna, J; Mittal, KL. FL, USA: CRC press; 2009.
- Vallittu PK. Comparison of two different silane compounds used for improving adhesion between fibers and acrylic denture base material. *J Oral Rehabil*. 1993; 20(5):533-539.
- Vallittu PK. Impregnation of glass fibers with poly-methyl-methacrylate using a powder-coating method. *App Comp Mater*. 1995; 2(1):51-58.
- Vallittu PK. A Review of Fiber-Reinforced Denture Base Resins. *J Prosthodont*. 1996;5(4):270-276.
- Vallittu PK. Ultra-high-modulus polyethylene ribbon as reinforcement for denture polymethyl methacrylate: A Short communication. *Dent Mater* 1997; 13: 381-382.
- Vallittu PK. Bioxid Oy (Turku, FI), assignee. Polymer-fiber prepreg, a method for the preparation thereof as well as the use of said prepreg, (Patent) 1998.
- Vallittu PK. Compositional and weave pattern analyses of glass fibers in dental polymer fiber composites. *J Prosthodont*. 1998a;7(3):170-176.
- Vallittu PK. Flexural properties of acrylic resin polymers reinforced with unidirectional and woven glass fibers. *J Prosthet Dent*. 1999;81(3):318-326.
- Vallittu PK, Sevelius C. Resin-bonded, glass fiber-reinforced composite fixed partial dentures: a clinical study. *J Prosthet Dent*. 2000;84(4):413-418.
- Vallittu PK. Strength and interfacial adhesion of FRC-tooth system. *The Sond International Symposium on Fiber-Reinforced Plastics in Dentistry, Symposium Book on the Scientific Workshop on Dental Fiber-Reinforced Composite*. in Nijmegen, The Netherlands. 2001

- Vallittu PK. Interpenetrating polymer networks (IPNs) in dental polymers and composites. *J Adhes Sci Techn* 2009;23;961-972
- Vallittu PK. High aspect ratio fillers: fiber-reinforced composites and their anisotropic properties. *Dent Mater* 2014; 31:1-7
- Vallittu PK. High-aspect ratio fillers: fiber-reinforced composites and their anisotropic properties. *Dent Mater.* 2015;31(1):1-7.
- Vallittu P, Özcan M. *A Clinical Guide to Fiber Reinforced Composites (FRCs) in Dentistry*: Woodhead Publishing; 2017:11-34.
- Vallittu PK. An overview of development and status of fiber-reinforced composites as dental and medical biomaterials. *Acta Biomater Odontol Scand.* 2018; 4(1):44-55
- Van Meerbeek B, Peumans M, Poitevin A, et al. Relationship between bond-strength tests and clinical outcomes. *Dent Mater.* 2010;26(2):16.
- Viljanen EK, Skrifvars M, Vallittu PK. Degree of conversion of an experimental monomer and methyl methacrylate copolymer for dental applications. *J Appl Polym Sci* 2004;93:1908-1912.
- Viljanen EK, Lassila LVJ, Skrifvars M, Vallittu PK. Degree of conversion and flexural properties of a dendrimer/methyl methacrylate copolymer: A statistical modeling. *Dent Mater* 2005;21:172-177.
- Wang WN, Lu TC. Bond strength with various etching times on young permanent teeth. *Am J Orthod Dentofacial Orthop.* 1991;100(1):72-79.
- Wang WN, Yeh CL, Fang BD, Sun KT, Arvystas MG. Effect of H3PO4 concentration on bond strength. *Angle Orthodontist.* 1994;64(5):377-382
- Wang WN, Li CH, Chou TH, Wang DDH, Lin LH, Lin CT. Bond strength of various bracket base designs. *Am J Orthod Dentofacial Orthop.* 2004;125(1):65-70.
- Weinstein S. Minimal forces in tooth movement. *Am J Orthod.* 1967;53(12):881-903.
- Willems G, Lambrechts P, Braem M, Celis JP, Vanherle G. A classification of dental composites according to their morphological and mechanical characteristics. *Dent Mater.* 1992;8(5):310-319.
- Zachrisson B. Long-term experience with direct-bonded retainers: update and clinical advice. *J Clin Orthod.* 2007;41(12):728-737; quiz 749.
- Zachrisson YO, Zachrisson BU, Buyukyilmaz T. Surface preparation for orthodontic bonding to porcelain. *Am J Orthod Dentofacial Orthop.* 1996;109(4):420-430.
- Zhang M, Matinlinna JP. E-Glass Fiber Reinforced Composites in

Dental Applications. *Silicon*.  
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