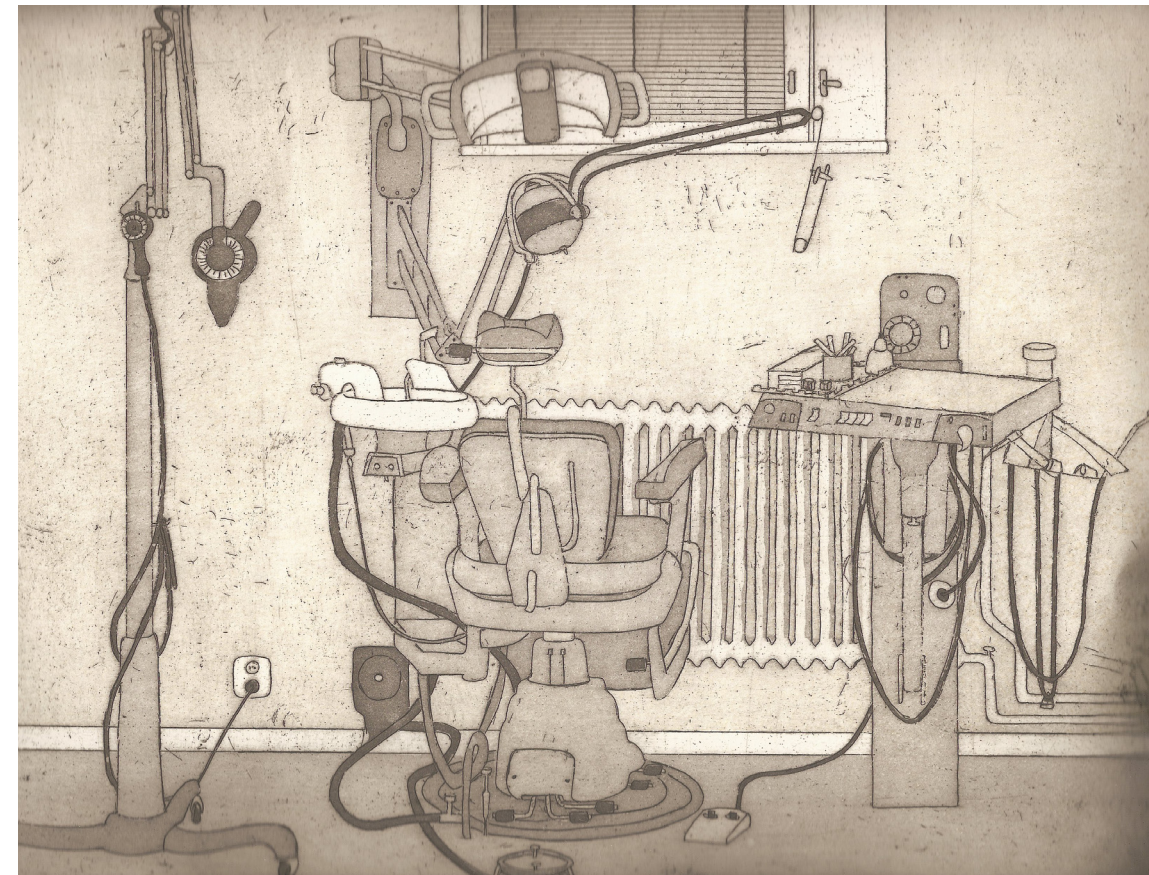


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CARBON-GRAPHITE FIBER-REINFORCED POLYMERS FOR IMPLANT SUPRASTRUCTURES



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ABSTRACT

Carbon-graphite fiber-reinforced polymers (CGFR) can be used as the core material for implant-retained prostheses as an alternative to metal frameworks. The purpose was to formulate and develop carbon-graphite fiber-reinforced polymers intended for implant suprastructures and to determine physicochemical, mechanical properties and possible cytotoxic effects. The adhesion strength between CGFR polymer to a titanium surface or CGFR polymer to opaquer layer/denture base polymer were evaluated.

The resin mixtures, based on methyl methacrylate (MMA), poly(methyl methacrylate) and poly(vinyl chloride-co-vinyl acetate), were produced with two different cross-linking agent systems: 1,4-butanediol dimethacrylate and ethylene glycol dimethacrylate or diethylene glycol dimethacrylate. The matrix resins were reinforced with tubes of braided CG fibers, cleaned and treated with a size, with fiber loadings 24-58 wt%.

Water uptake and water sorption/solubility was determined and dilatometric analysis was performed. Mechanical properties, adhesion, residual monomer and cytotoxicity were evaluated. Basic requirements regarding water sorption, water solubility, water uptake, residual MMA monomer, coefficient of linear thermal expansion were met and were similar for the two resin matrices. However, flexural properties and fracture toughness were higher for the matrix resin containing the cross linker diethylene glycol dimethacrylate, making it a more suitable resin binder.

Flexural properties increased with fiber loadings up to and including 47 wt% (38 vol%) when tested in dry and wet condition. The combination of the described fiber surface treatment, the sizing resin and the developed resin matrix contributed to good adhesion between the carbon-graphite fibers and the polymer matrix.

Hydrothermal cycling did not decrease flexural strength of the CGFR polymers with 24 and 36 wt% fiber loadings, when compared to dry and water stored specimens. However, more porosity was observed with higher fiber loadings; flexural strength decreased after thermal cycling for fiber loadings of 47 wt% and 58 wt% in relation to composites tested in dry and wet condition.

There was no evidence of cytotoxicity for the CGFR polymer and residual monomer content was within the international standard limits.

Good adhesion with a cohesive fracture type was achieved between the layers of the silicized titanium/CGFR polymer/ opaquer/denture base polymers. The combination of these materials in an implant-retained supraconstruction is promising for *in vivo* evaluation.

Key words: Implant prostheses; Matrix; MMA; PMMA nanoparticles; Copolymer; Surface treatment, Size; Adhesion; SEM; Mechanical properties, Physicochemical properties.

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LIST OF ABBREVIATIONS

BPO	Benzoyl peroxide
BDMA	Butanediol dimethacrylate,
CG	Carbon-graphite
CGFR	Carbon-graphite fiber-reinforced
DEGDMA	Diethylene glycol dimethacrylate
EGDMA	Ethylene glycol dimethacrylate
FPD	Fixed partial denture
FRC	Fiber reinforced composites
IPN	Interpenetrating polymer network
HPLC	High Performance Liquid Chromatography
LCTE	Linear coefficient of thermal expansion
MMA	Methyl methacrylate
PMMA	Poly(methylmethacrylate)
PVCAC	Poly(vinyl chloride-co-vinyl acetate)
SEM	Scanning electron microscopy
TC	Thermal cycling
VCM	Vinyl chloride monomer

1 INTRODUCTION

1.1 BACKGROUND

In 1982, P-I Brånemark presented osseointegration and its experimental and clinical background (Brånemark 1983). This started an evolution of implant treatments that changed clinical dentistry and initiated a new prosthodontic therapy for completely and partially edentulous patients. The fabrication of the implant-fixed prosthesis resembles that of a conventional partial denture and the construction is usually made as a metal framework with attached polymer teeth or porcelain (Gotfredsen & Gunne, 2000). Metal frameworks usually involve advanced technology; the process is costly in both time and price of the materials involved. Dental implants can dramatically change a patient's self-esteem and quality of life; however, too few people receive implants because of the cost (Schnitman, 1993), which is the most commonly cited reason for declining implant treatment (Narby et al., 2008). Less costly alternatives are needed.

Composite materials are made of two or more distinct materials, where the properties are superior to those of the individual components (Anusavice, 1996). Such a material should have a higher modulus of elasticity than the matrix material itself (Nielsen, 1974). The fiber-reinforced polymer is a composite material where the fibers are embedded in a continuous matrix phase (binder) (Nielsen, 1974, Carley, 1993). Fiber reinforced composites (FRC) have been investigated in different dental applications and their use is growing, including the use in implant-supported prostheses (Duncan et al., 2000; Behr et al., 2001b; Freilich et al., 2002a). An alternative to metal in implant-supported suprastructures is fiber-reinforced polymer composites (Ruyter et al., 1986; Behr et al., 2000; Freilich et al., 2002). Glass FRC for implant supported fixed prostheses have been suggested (Behr et al., 2001a). Carbon-graphite fiber-reinforced (CGFR) poly(methyl methacrylate) (PMMA) for implant supported prostheses has been previously presented (Ruyter et al., 1986; Björk et al., 1986; Ekstrand et al., 1987; Bergendal et al., 1995; Ekstrand and Hirsch, 2008). The use of fiber composite technology for implant-retained fixed partial dentures may offer a cost-effective alternative to metal suprastructures (Ruyter et al., 1986).

1.2 POLYMERS

Polymer-based materials are commonly used in prosthetic dentistry, and their good clinical performance and satisfactory handling properties are well documented (Ruyter & Øysaet, 1982; Phoenix, 2003). The most commonly used denture base polymers are based on poly(methylmethacrylate)/methyl methacrylate (PMMA/MMA) mixtures. A resin mixture of polymer powder and monomer liquid leads to reduced polymerization shrinkage when compared with polymerization of the monomer methyl methacrylate (MMA). Activation of the polymerization, by heat or chemically, initiates free radical formation from benzoyl peroxide (BPO) and an exothermic free radical addition polymerization takes place. The polymerization leads to interpenetrating polymer network (IPN) formation by combining the PMMA beads and monomer-based polymer matrix (Vallittu and Ruyter, 1997a; Øysaet and Ruyter, 1989), because PMMA becomes partly (large PMMA beads) or totally (small beads) dissolved in the monomer. The addition of cross-linking agents may improve many of the physical properties of polymers (Øysaet and Ruyter, 1989). When a fractured polymer is repaired, adequate wetting of the repair surface, with MMA dissolving the surface layer of PMMA, results in increased transverse strength (Vallittu et al., 1994a; Vallittu and Ruyter, 1997a).

1.3 FIBER-REINFORCED POLYMERS

Heat-polymerized denture base polymers are relatively brittle materials. A traditional method of reinforcing polymers is to use metal wires or other metal inclusions (Schwickerath, 1965; Carroll and von Fraunhofer, 1984; Ruffino, 1985; Vallittu and Lassila, 1992; Vallittu et al., 1995). The strength of polymers can be improved by adding reinforcing fibers (Schreiber, 1971; Delmonte, 1981; Cogswell, 1992). By combining two or more materials to make a composite, better mechanical properties than those obtained by the polymers alone can be achieved. The use of fiber reinforcement in dentistry is reported as early as the 1960s (Schwickerath, 1965). Many different kinds of fibers are suggested for fiber reinforcing dental polymers (Yazdanie and Mahood, 1985; Vallittu et al., 1994b; Björk et al., 1986; Chow et al., 1998; Kanie et al., 2003). Ultra high molecular weight polyethylene (UHMWPE) fibers have been used for reinforcement of dentures (Chow et al., 1998). In dentistry, glass fiber reinforcement is frequently used for crowns (Behr et al., 2001b); fixed partial dentures (FPD) (Nohrström et al., 2000; Meiers and Freilich, 2001; Tezvegil et al., 2003a); implant prostheses (Freilich et al., 2002a, 2002b); facial prosthesis (Kurumäki et al., 2008); splinting teeth (Giancotti et al., 2005); root canal posts (Le Bell et al., 2003);

and orthodontic retention devices (Kargul et al., 2005; Cacciafesta et al., 2005). Improved strength of denture base polymers with addition of continuous unidirectional glass fibers (Goldberg and Burstone, 1992; Vallittu et al., 1994b; Dyer et al., 2004) and woven glass fibers (Kim and Watts, 2004a) is reported. Special attention has been paid to E-glass fiber reinforcement (Vallittu, 1998). By optimizing the fiber volume fraction (for unidirectional E-glass fibers), flexural strength values are comparable to cobalt-chromium alloy (1200 MPa) (Lassila et al., 2004; Vallittu, 1997). Fatigue resistance of a glass fiber reinforced composite is superior to unreinforced or metal wire reinforced polymer (Vallittu and Lassila, 1992; Rantala et al., 2003). The aesthetic quality of glass fiber composites is an important feature partly explaining the wide use of these composites. There is good initial bonding of glass fibers to polymers when silane-coupling agents are used (Vallittu, 1993). Long-term stability in a wet environment is an important quality for the longevity of a fiber-reinforced polymer. Silica glass fiber surfaces are more stable to hydrolytic degradation than those of E-glass fibers are, as they have minimal quantities of oxides of elements (other than silicon) such as alkali and earth alkali ions compared to E-glass fibers (Meriç et al., 2005). Such oxides greatly increase water adsorption (e.g. B_2O_3) (Pantano et al., 1992) resulting in destruction of the E-glass fiber polymer matrix interface due to the formation of e.g. basic calcium hydroxide.

1.3.1 Resin matrix

Special considerations are required for developing a resin material for fiber reinforcement. A resin material intended for incorporation of fibers must possess mechanical properties that tolerate masticatory forces. The material should be biocompatible, be able to resist degradation, have low water sorption and solubility, and a low residual monomer concentration (Ekstrand et al., 1987). Thermophysical properties, such as mechanical and thermal properties, must be considered and the polymerization contraction be low. Mechanical properties can be changed by choice of components (Øysaet and Ruyter, 1989). Appropriate consistency of the unpolymerized resin is a prerequisite for ensuring adequate wetting of the fibers and good handling properties. Thus, matrix materials intended for fiber reinforcement should differ from denture base polymers in consistency and possess lower viscosity. A binder or matrix material remaining in a relatively low viscous, fluid state is preferential for ensuring adequate wetting of the fibers (Ekstrand, et al., 1987). Other factors that need considering, are handling and storing properties. Certain matrix systems have the

ability to remain in the plastic state during storage and handling before polymerization is initiated (Eichner, 1981), such as a resin system based on a vinyl chloride-vinyl acetate copolymer, PMMA and methyl methacrylate (MMA) (Eichner, 1981). MMA-based resin systems work well in sandwich structures and have the ability to bond to polymer teeth (Büyükyilmaz and Ruyter, 1997; Vallittu and Ruyter, 1997a; Vallittu and Ruyter, 1997 b).

1.3.2 CG fiber reinforcement

Polymer based materials are commonly used in prosthetic dentistry and their strength can be improved with reinforcing fibers (Schreiber, 1971; Ruyter et al., 1986; Ekstrand et al., 1987; Vallittu and Lassila, 1992; Cogswell, 1992;). Different types of fibers are added to polymer materials to improve mechanical properties; carbon-graphite (CG) fibers are the most common high strength and high modulus reinforcing fibers used in composites for high performance applications (Delmonte, 1981). In order for fibers to have a reinforcing effect, their modulus must be higher than the modulus of the matrix polymer (Murphy, 1998); the flexural modulus of CG fibers exceeds that of glass fibers (Delmonte, 1981). CG fibers contribute to stiffness and strength, improve fatigue strength, and at the same time reduce thermal expansion and polymerisation shrinkage (Delmonte, 1981).

Carbon-graphite fibers are produced by carbonization and graphitization of carbon-rich organic precursors, which are already in fiber form. The most common precursor is polyacrylonitrile (PAN) giving good carbon-fiber properties. Carbon fiber has the highest stiffness among commercially available fibers, high strength in tension and compression and high resistance to corrosion, creep, and fatigue (Delmonte, 1981). However, the impact strength is lower than that of glass fiber (Murphy, 1998).

Reinforcement with CG fibers improves fatigue and tensile strength, transverse deflection properties and modulus of elasticity of PMMA materials (Kilfoil et al., 1983; DeBoer et al., 1984; Yasdanie and Mahood, 1985; Malquarti et al., 1990).

The first dental application of carbon fibers was as a reinforcing denture base polymer of poly (methyl methacrylate) (PMMA) (Schreiber, 1971) and the fiber reinforcement resulted in a 100 % increase in flexural strength. Since then, carbon-graphite fiber-reinforced polymers have been investigated for different dental applications (Bowman and Manley, 1984; Yazdanie and Mahood, 1985; Ruyter et al., 1986; Ekstrand et al., 1987; Larson et al., 1991; Bergendal et al., 1995; Torbjörner et al., 1996; Ekstrand and Hirsch, 2008). Prefabricated carbon-graphite fiber reinforced fiber posts embedded in

epoxy resin have been used for several years (Purton and Payne 1996; Torbjörner et al., 1996).

Difficulties in handling the early generations of CGFR polymers when introducing longitudinal fibers into the matrix resin was avoided when tubes of braided CG fibers were used instead (Ruyter et al., 1986; Ekstrand et al., 1987).

The carbon-graphite fibers are black in appearance and a polymer framework with CG fibers needs to be masked (Björk et al., 1986). This is mastered by covering the framework composite with an opaquer, in a similar manner as metallic frameworks are covered (Ekstrand et al., 1987).

1.3.3 Orientation of fibers

Mechanical and physical properties are related to the orientation of the reinforcement (Nielsen, 1974). Fiber orientation can influence the strength, modulus and coefficient of thermal expansion (Nielsen, 1974). Fiber orientation can change the properties of a fiber-reinforced polymer from isotropic to anisotropic and even orthotropic (Dyer et al., 2004). Continuous unidirectional fiber-reinforced polymers give anisotropic properties to the composite, continuous bidirectional fibers (weaves) give orthotropic properties in a plane and random-oriented fibers give isotropic properties (Nielsen, 1974; Vallittu 1999). Unidirectional longitudinal fibers exhibit superior mechanical properties along their long axes (Vallittu, 1999).

1.3.4 Quantity of fibers

Fiber quantity in a polymer matrix can be given in weight percent (wt%) or in volume percent (vol%). Due to the differences in the density of fibers, presentation in volume percent is recommended (Vallittu, 1998a).

Increasing the content of fiber-reinforcement improves flexural properties (Schreiber, 1971; Knoell et al., 1975; Yazdanie and Mahood, 1985; Ekstrand et al., 1987; Vallittu and Lassila, 1992; Murphy, 1998). However, higher fiber content does not always result in higher mechanical properties. With a controlled manufacturing process a volume fraction of glass fiber incorporation into matrix can be 45-65% (Frelich et al., 2000; Lassila et al., 2005). Maximum flexural strength in dry condition for glass fiber with 65% fibers is 1230 MPa (Vallittu, 2001).

Increasing the fiber content also reduces water sorption as the relative portion of water-absorbing polymer matrix decreases (Øysaet and Ruyter, 1986).

1.3.5 Adhesion of fibers to the polymer matrix

The adherence of fibers to the resin matrix is an important quality for good mechanical properties (Beech and Brown, 1972). Fiber reinforcement is effective only when a given load can be transferred from the matrix to the reinforcement, and this can be accomplished when there is complete adhesion between resin matrix and fibers (Bae et al., 2001). Insufficient adhesion of fibers by resin matrix results in voids and porosities in the fiber-reinforced composite that are susceptible to water sorption (Vallittu et al., 1998a; Miettinen et al., 1999; Behr et al., 2000). Voids and porosities in the fiber-reinforced composite may lower flexural properties and enhance degradation (Bouillaguet et al., 2006).

Silane coupling agents can optimize chemical and physical bonding between different components in composite materials (Matinlinna et al., 2004). However, the mechanical properties of the composite can be compromised after hydrothermal aging (Lassila et al., 2002; Bouillaguet et al., 2006). Hydrolysis of the silane bonds between glass fibers and the matrix may explain the lowering of mechanical properties after hydrothermal aging (Lassila et al., 2002).

1.3.6 Fiber-reinforced polymers in implant prostheses

Different fiber-reinforced composites for implant-retained prostheses are suggested (Duncan et al., 2002; Freilich et al., 2002a), including carbon-graphite fiber-reinforced (CGFR) poly(methyl methacrylate) (PMMA) (Ruyter et al., 1986; Björk et al., 1986; Ekstrand et al., 1987). However, clinical evaluation of CGFR polymer in screw-retained implant supported fixed prostheses after 3.5 years had a survival rate of 70 % (Bergendal et al., 1995), and it was concluded that the mechanical properties of the CGFR polymer framework were unsatisfactory and that the mechanical properties needed improving (Bergendal et al., 1995).

1.3.7 Biomechanical aspects of implant suprastructures

Implants in the oral environment are subject to multidirectional forces (Rangert et al., 1995; Richter, 1998). Forces can be vertical, horizontal or inclined, and torsional forces may exist (Rangert et al., 1995; Dirtoft and Jansson, 1986). The magnitude of occlusal forces in the mouth varies. The maximal occlusal forces in the incisal area range from 264 N to 370 N (Laurell, 1985; Paphangkorakit and Osborn, 1997) and in the posterior area from 430 N to 800 N (van der Bilt et al., 2008; van Eijden, 1991).

1.4 PHYSICOCHEMICAL AND MECHANICAL PROPERTIES

1.4.1 Water sorption

Water sorption of a material includes both water adsorbed on the surface and water absorbed into the body of the material during preparation and while the material is in service (Craig, 1997). Polymers absorb water in an aqueous environment (Øysaet and Ruyter, 1986; Kazanjii and Watkinson, 1988; Buyukyilmaz and Ruyter, 1994; Ferracane et al., 1998; Martin et al., 2003; Ferracane, 2006). Poly(methyl methacrylate) absorbs water because of the polarity of the water molecule and because it is smaller than the interchain distance in the polymer (Miettinen et al., 1999). Over time, water molecules penetrate into the spaces between polymer chains, and occupy positions between the chains and force the chains apart (swelling). Water molecules function as a plasticizer and the polymer chains become more flexible, resulting in reduced flexural modulus and strength (Anusavice, 1996). As water molecules ingress into a polymer, unreacted monomer molecules and other small-sized constituents egress until equilibrium is achieved and the weight of the polymer becomes essentially constant (Øysaet and Ruyter, 1986; Ruyter, 1995; Örtengren et al., 2001). Many factors influence diffusion of water into a polymer-based material. The volume of water uptake by a polymeric material is determined by polymer structure, content of various polar and hydrophilic groups in the polymer structure, temperature, concentration of various additives, and the presence of voids within the matrix (Kalachandra and Turner, 1989; Söderholm et al., 1996; Vallittu et al., 1998a; Miettinen et al., 1999; Behr et al., 2000; Vallittu, 2000). Cross-linking agents lower water sorption of autopolymerized relining polymers (Arima et al., 1995) but no effect of cross-linking agents on the water sorption of heat-polymerized denture base polymers has been determined (Jagger and Huggett, 1990). For denture base polymers, water uptake varies with time, and water saturation is usually obtained after 2-3 months, depending on size and shape (Bates et al., 1977).

Physicochemical and mechanical properties can be affected by absorbed water (Barsby and Braden, 1979; Ruyter and Svendsen, 1980; Øysaet and Ruyter, 1986; Barsby, 1992; Ferracane et al., 1998). Water sorption can cause a reduction in strength of both the unreinforced polymer (Ruyter and Svendsen, 1980) and the fiber reinforced polymer materials (Behr et al., 2000; Ekstrand et al., 1987; Ruyter, 1995; Vallittu et al., 1998a; Vallittu, 2000). If there are regions where the fibers are not completely embedded in polymer matrix, or porosities are formed during manufacturing and polymerization, there will be voids that increase water sorption (Vallittu et al., 1998a).

Theoretically, composites with well-impregnated fibers have lower water sorption than composites with poorly impregnated fibers (Miettinen et al., 1999). In composites, water sorption increases with a reduction of filler content as the relative portion of water-absorbing polymer matrix increases. (Miettinen et al., 1999; Lassila et al., 2002; Chai et al., 2004; Ferracane, 2006).

1.4.2 Ultimate flexural strength and flexural modulus

Flexural strength of a material can be obtained if a load is applied in the middle of a beam or specimen, between supports. A three-point bending test is frequently used for comparing denture base polymers. Such a test provides information on the elasticity of a polymer, i.e. flexural modulus (Craig, 1997). The mechanical properties of fiber-reinforced composites are dependent on factors such as fiber type and quantity, the adhesion between matrix and fibers, the polymerization shrinkage of the resin and the individual properties of the fibers and the matrix (Vallittu, 1996). Generally, mechanical properties improve with high fiber content in the matrix material (Schreiber, 1971; Knoell et al., 1975; Yazdanie and Mahood, 1985; Ekstrand et al., 1987; Vallittu and Lassila, 1992; Vallittu, 1996; Murphy, 1998). The CG-fibers in a fiber composite contribute to stiffness, but fibers may also reduce thermal expansion (Kanayama et al., 2000). Reduced polymerisation shrinkage and improvement in fatigue strength are also obtained (Delmonte, 1981).

Flexural strength values for carbon-graphite fiber/epoxy posts in dry condition range from 900 to 1492 MPa (Torbjörner et al., 1996; Drummond and Bapna, 2003; Lassila et al., 2004).

1.4.3 Fracture toughness

The fracture toughness of a material reflects the resistance of a material to fracture and represents the energy required to propagate a crack through the material to complete fracture. Fracture toughness of polymer composites depends on the type of polymer and reinforcement. Fracture toughness of a monomethacrylate-based material is lower than in a dimethacrylate-based material (Kim and Watts 2004). Generally, “intrinsic” physical aging and/or storage in a humid environment at elevated temperatures can decrease fracture toughness, as well as other mechanical properties (Kohn, 2002). However, an increase in fracture toughness can be achieved by adding reinforcing fibers to a polymer to prevent or slow down crack growth (Kohn, 2002; Kim and Watts 2004), and by adding rubber-like substances (Rodford, 1986; Rodford, 1990; Zappini et

al., 2003). A fracture toughness test with ‘notched’ specimens appears reliable for determining the influence of variations in the material composition (Zappini et al., 2003). Fracture toughness testing (ASTM, 1999; Zappini, et al., 2003) was used to compare two polymers with different cross-linking agents.

1.4.4 Linear coefficient of thermal expansion

The linear coefficient of thermal expansion (LCTE) is defined as the change in length per unit of the original length of a material when the temperature is raised 1 °C (Anusavice, 1996). The variation of the coefficient of thermal expansion between different materials is important because a mismatch can lead to strains, resulting in stress formation and adverse effects on the interface. Therefore, thermally induced strains and stresses adversely affect long-term stability of intraoral multiphase materials (Delmonte, 1981). By adding fibers to a polymer, the coefficient of thermal expansion decreases (Kanayama et al., 2000). In general, the thermal coefficient varies with the direction of the fibers in a composite (Holliday and Robinson, 1973; Nielsen, 1974; Craft and Christensen, 1981; Tezvegil et al., 2003b): rigid fibers appear to prevent expansion of the matrix in the longitudinal direction so the matrix is forced to expand in the transverse direction (Nielsen, 1974; Tezvegil et al., 2003b).

1.4.5 Fatigue

One of the major concerns in the development of dental materials is physical and chemical durability. Fatigue is weakening of a material caused by repeated loading at a stress level below the fracture strength (Ferracane, 2001). Thermal cycling *in vitro* is a common way of testing dental materials for establishing suitability for *in vivo* use (Palmer et al., 1992). Hydrothermal cycling is one way of exposing a composite material to fatigue testing and provides an indication of how well the material functions in the humid oral environment (Stinchcomb et al., 1975). The mechanical properties of fiber-reinforced composites decrease after hydrolytic aging (Ruyter et al., 1986; Ekstrand et al., 1987; Vallittu et al., 1998a; Miettinen et al., 1999; Behr et al., 2000). Thermally induced strains and stresses can influence long-term intraoral stability of the materials. Cracking within the composite structure may arise because of thermal cycling (Stinchcomb et al., 1975). Fatigue damage such as various combinations of matrix cracking, debonding, delamination, void growth and fiber breakage, can be seen (Stinchcomb et al., 1975). Thermal cycling is reported to lower mechanical properties

(Torbjörner et al., 1996; Drummond and Bapna, 2003; Lassila et al., 2004; Lehmann et al., 2004).

1.5 BIOCOMPATIBILITY

1.5.1 Solubility

Water sorption and solubility may create a biological concern as hydrolytic degradation affects long-term stability of polymeric materials (Ruyter, 1995; Ferracane, 2006).

Over time, components such as stabilizers, plasticizers, monomers, residuals of initiators and degradation products may be released to the oral environment (Knott et al., 1988; Lygre et al., 1993; Ruyter, 1995; Michelsen et al., 2007). Thus, the quantity of such components should be as small as possible, ensuring that the polymer retains its characteristic properties and that no components adversely influence biocompatibility (van Noort, 2007). The soluble fraction of a polymer can be assessed by monitoring weight change of a sample when immersed in water (van Noort, 2007).

1.5.2 Residual monomer

Biological features, as well as mechanical properties, of polymeric materials are highly influenced by the monomer-polymer conversion. Regardless of the method for initiating the polymerization process, the conversion is not complete and some unreacted monomers remain in the polymer, which may leach out into water (Ruyter and Øysaet, 1982; Vallittu et al., 1998a). The various processes by which polymeric materials are produced may affect the content of the residual monomer methyl methacrylate (MMA) (Shim and Watts, 1999). For instance, by increasing polymerization temperature and polymerization time, the residual MMA content in polymers can be decreased (Giunta et al., 1979). Residual monomer levels in correctly heat-polymerized denture base polymers are below 1 wt% (Vallittu et al., 1998b). The residual MMA content in polymers can be affected by the polymerization temperature and polymerization time: levels of 0.07 wt% of residual MMA content has been registered after polymerization of a heat-cured denture base at 100 °C for 12 h (Vallittu et al., 1998b).

1.5.3 Cytotoxicity

Some substances released from materials are cytotoxic and residual monomers leached out into the oral environment may induce toxic and allergic reactions (McCabe and Basker, 1976; Giunta et al., 1979; Hensten-Pettersen and Wictorin, 1981; Vallittu et al., 1998b, Huang et al., 2001). Pre-clinical evaluation of the biocompatibility of new

materials in dentistry is necessary and *in vitro* cytotoxicity tests are necessary before *in vivo* use (Vajrabhaya and Sithisarn, 1997).

Generally, the cytotoxic effect diminishes as water immersion time increases: water storage reduces the level of residual monomer and other leachable substances in the material (Sheridan et al., 1997; Jorge et al., 2003). Cleaned and sized CG fibers for reinforcing PMMA based composites reveal no signs of toxicity after water storage, even though the presence of slightly cytotoxic substances is indicated in dry condition (Ekstrand et al., 1987). Carbon-graphite fibers *per se* exhibit no carcinogenicity (Tayton et al., 1982) and no cytotoxicity (Ekstrand et al., 1987).

1.6 TITANIUM

1.6.1 Surface treatment

For long-term stability, the adhering interfaces of an implant-retained suprastructure of titanium/opaquer layer/polymer must function as a unity. Besides macro- and micromechanical retention, different surface pre-treatment methods for enhancing retention of PMMA polymer to machined titanium surfaces have been proposed (Özcan et al., 1998; Hansson and Moberg, 1993; Kourtis, 1997). Bond strength increase of 68% between titanium and PMMA is reported when the Rocatec surface treatment is compared with a surface without any particular treatment (May et al., 1995). However, adhesion of PMMA to a polished titanium surface (without sandblasting, silicoating or Rocatec treatment) can be established when the surface is merely silanized (Ekstrand et al., 1988).

2 AIMS OF THE THESIS

The purpose of the in vitro studies was to formulate and develop carbon-graphite fiber-reinforced polymers intended for implant suprastructures and to determine physicochemical and mechanical properties of the matrices and CGFR polymers.

The specific aims were:

- To design and evaluate matrix materials for fiber-reinforced polymers (Paper I).
- To design poly(methyl methacrylate) (PMMA)-based materials, reinforced with carbon-graphite (CG) fibers for implant suprastructures and to evaluate physicochemical and mechanical properties of these composites in dry and wet condition (Paper II).
- To evaluate the effect of hydrothermal cycling on flexural strength and modulus for carbon-graphite fiber-reinforced (CGFR) polymers based on poly(methylmethacrylate) and a copolymer matrix (Paper III).
- To examine the adhesion between CG-fibers and matrix (Papers II and III).
- To evaluate the adhesion properties in systems of laminated pigmented polymers, carbon-graphite fiber composite framework and titanium surfaces (Paper IV).
- To determine water sorption, water solubility, dimensional changes due to water storage, residual monomers of heat-polymerized resin matrices (Paper I) and carbon-graphite fiber-reinforced composites (Paper V).
- To determine possible cytotoxic effects of a carbon-graphite fiber-reinforced composite (Paper V).

3 MATERIALS AND METHODS

This thesis was based on *in vitro* studies. In Paper I, two matrix materials intended for fiber-reinforced polymers were evaluated. In Papers II-V the properties of CGFR polymers were investigated. The chemicals and materials used are presented in Table 1 and a summary of the test methods in Table 2. Detailed description of the materials and methods are presented in the original papers (Papers I-V).

3.1 CHEMICALS AND MATERIALS USED

Table 1. Chemicals and materials used.

Substance	Code	Manufacturer
Methyl methacrylate, 99%	MMA	Aldrich, Steinheim, Germany
Ethylene glycol dimethacrylate, 98%	EGDMA	Aldrich, Steinheim, Germany
1,4-butanediol dimethacrylate, 95%	1,4-BDMA	Aldrich, Steinheim, Germany
Diethylene glycol dimethacrylate, 95%	DEGDMA	Aldrich, Steinheim, Germany
Poly(methyl methacrylate), MW 120,000	PMMA	Aldrich, Milwaukee, WI, USA
Poly(methyl methacrylate), MW 350,000	PMMA	Aldrich, Milwaukee, WI, USA
Poly(vinyl chloride-co-vinyl acetate) 90/10	PVCAC	Aldrich, Steinheim, Germany
Benzoyl peroxide, H ₂ O (25wt%)	BPO	Fluka Chemika, Buchs, Switzerland
Tubes of braided carbon-graphite fibers		Siltex Flecht- und Isoliertechnologie Holzmüller GmbH & Co.KG, Julbach, Germany
Vinyl chloride monomer, 99.9%	VCM	Supelco, Bellefonte, PA, USA
Opaquer, Ropak UV		Firma Bredent, Senden, Germany
Opaquer, Sinfony		ESPE Dental AG, Seefeld, Germany
Silane, EspeSil		3M ESPE AG, Seefeld, Germany
Probase Hot, powder, liquid		Ivoclar AG, Schaan, Liechtenstein
Lucitone 199, powder, liquid		Degudent, Dentsply, Hanau, Germany

Table 2. Summary of the test methods used in Papers I-V.

	I	II	III	IV	V
Water uptake and water sorption/solubility	x	x			x
Fracture toughness test	x				
Three-point bending test before TC	x	x			
Three-point bending test after TC			x		
Dilatometric analysis	x	x	x		
Shear test				x	
Determination of residual monomers	x				x
Determination of cytotoxicity					x
SEM		x	x		

Tubes of braided CG fibers (Figure 1) manufactured from polyacrylonitrile fibers (PAN; T300) (personal communication with manufacturer) were used for fiber reinforcement.

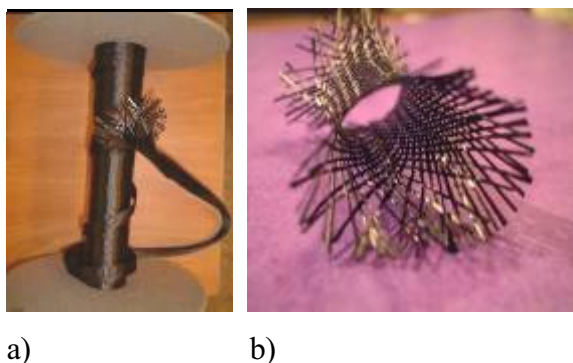


Figure 1. a) A reel of tubular braided carbon-graphite fibers for reinforcement, b) An “opened” tube showing diagonal arrangement of fiber strands.

3.2 PREPARATION OF SPECIMENS

3.2.1 Preparation of base materials

Two different resin mixtures, resin A and resin B, stable in the fluid state, were made by mixing a solution of PMMA (MW 120,000) in MMA with different cross-linking agents. Resin A solution contained the cross-linking agents ethylene glycol dimethacrylate (EGDMA) (10 wt%) and 1,4-butanediol dimethacrylate (1,4-BDMA) (3 wt%) and contained 23 wt% PMMA; resin B contained diethylene glycol dimethacrylate (DEGDMA) (14 wt%) and contained 33 wt% PMMA.

The solutions of resin A and B and the size (see below), in a glass tube, were exposed to a light source from below. The phenomenon of light scattering in all directions occurs if light passes through an inhomogeneous medium of small particles in a continuous medium.

Nine parts of solution (A or B) were mixed with one part of the copolymer powder, poly(vinyl chloride-co-vinylacetate), containing dispersed 3 wt% benzoyl peroxide (BPO).

3.2.2 Fiber treatment

The tubes of braided CG fibers were cleaned from coating and impurities for 48 hours by continuous liquid/solid extraction with tetrahydrofuran (Soxhlet-extraction). After treatment, the fibers were vacuum dried (133 mPa) at 130 °C for 10 min. Immediately after evaporation, the fibers were treated with a resin system, i.e. sizing. The size solution contained 20 g PMMA (MW 350,000), 20 g 1,4-BDMA and 160 g MMA.

3.2.3 Test specimens (Papers I-V)

Test specimens with five different shapes and sizes were prepared.

The specimens, made of polymer A and B, for fracture toughness testing were polymerized slightly oversized in gypsum moulds. The specimens were wet ground to the dimensions (40.0 ± 1.0) mm, (8.0 ± 0.2) mm and (4.0 ± 0.2) mm. An initial notch of (3.2 ± 0.2) mm depth was cut in the centre of each specimen. The notch was wetted with one drop of glycerol and was then sharpened with a specially made sharp blade to extend the notch with a small pre-crack of $(0.1-0.2)$ mm (Paper I) (Figure 2).

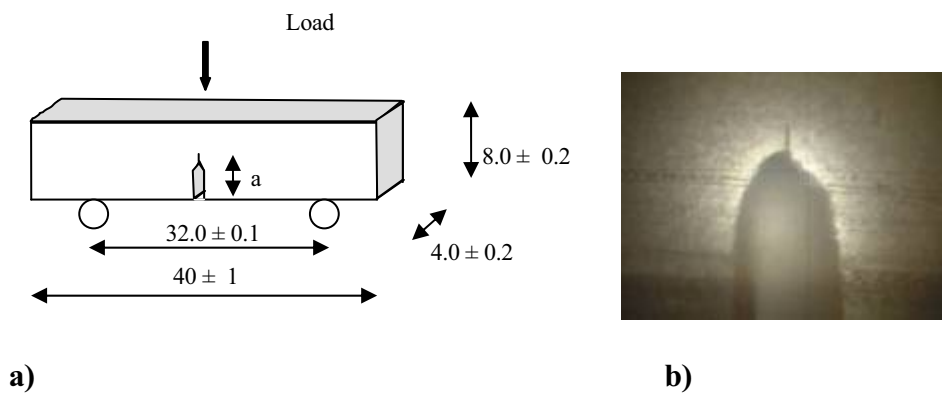


Figure 2. a) Schematic illustration of a specimen used for fracture toughness test. Dimensions in mm. Total notch depth a ranged between $(3.1 - 3.6)$ mm, b) photographic image of a tip of the notch with the pre-crack (Paper I).

Resin mixture (A or B) was placed in a steel mould under a pressure of 30 MPa before heat polymerization. The specimens for three-point bend testing obtained the dimensions (3.3 ± 0.2) mm, (10.0 ± 0.2) mm, and (64.0 ± 1) mm (ISO 1567:1999) (Paper I).

CGFR test specimens for three point bend testing (Papers II, III) and water uptake, sorption/solubility (Paper V), were made with different fiber loadings. Different numbers of the sized CG fiber tubes were embedded in a mould in either resin A or resin B. Specimens with two, three, four and five tubes, resulting in twice as many fiber-reinforcing layers, were made. The filler loadings corresponded to 24 wt% (20 vol%), 36 wt% (29 vol%), and 47 wt% (38 vol%) fiber-reinforcement for both resins A and B. In addition, specimens with filler loading of 58 wt% (47 vol%) were made with resin B. The fiber tubes were placed parallel to the long axis of the specimens (Figure 3). The samples in the steel mould were placed under a pressure of 30 MPa before heat polymerization. The specimens obtained the dimensions (3.3 ± 0.2) mm, (10.0 ± 0.2) mm and (64.0 ± 1) mm (Papers II-IV). From these specimens, CGFR polymer

specimens with the dimensions (9 ± 0.2) mm, (9 ± 0.2) mm and thickness (3.3 ± 0.2) were cut for the filter diffusions test (Paper V).

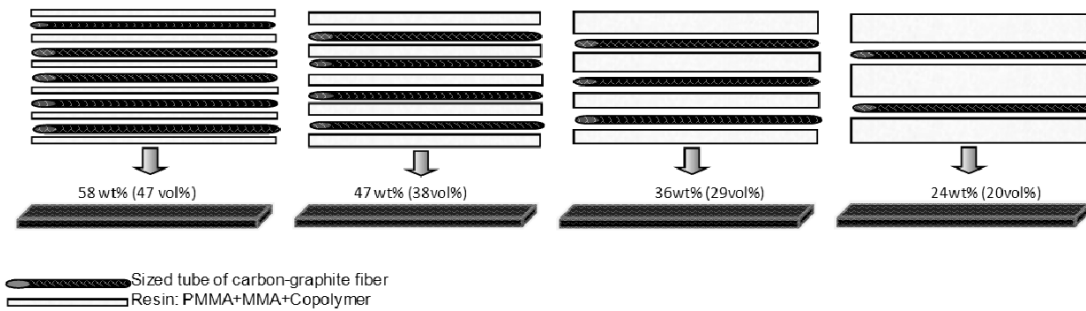


Figure 3. Schematic illustration of specimen fabrication with 24, 36, 47 and 58 wt% CG fiber reinforcement, where tubes of CG fibers are layered with resin (Papers II-IV).

Specimens for shear bond testing were prepared with the dimensions (3.3 ± 0.2) , (10.0 ± 0.2) , and (21 ± 1) mm from a titanium plate and a bolt of CGFR polymer (with the fiber tubes parallel to the contact surface) and denture base polymer were attached (Figure 4). In addition, test specimens with an unreinforced matrix polymer plate and a CGFR polymer plate with the same dimensions as the titanium plates were prepared. The polymer plates were opaquer layered (Ropak or Sinfony) and a bolt of denture base polymer (Probase Hot or Lucitone) was attached (Paper IV).



Figure 4. Illustration of specimen for shear bond tests (Paper IV).

Specimens for dilatometric analysis were prepared (Figure 5) from both unreinforced matrix polymers and reinforced polymers (47 wt% fiber loading), and were cut from the previously prepared larger specimens (see above), to the dimensions (3.3 ± 0.2) , (3.3 ± 0.2) and (10 ± 0.2) mm (Papers I-III).

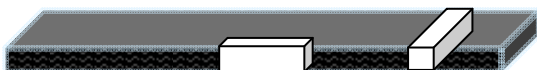


Figure 5. Specimens for TMA analyses were cut either **a)** longitudinally or **b)** transversely (in the laminar plane and perpendicular (90°) to the tubular direction) (Papers I-III).

3.2.4 Polymerization procedure

After an applied pressure of 30 MPa on the steel mould containing the specimens, the mould was placed in a water bath and heated to $(70 \pm 1) ^\circ\text{C}$, and maintained at this temperature for 90 minutes. Thereafter, the temperature was increased during 20 minutes to $100 ^\circ\text{C}$ and the water kept boiling for 1 hour. After heat polymerization, the mould was allowed to cool on the bench to room temperature before the test specimens were removed from the mould. The excess material was removed from the specimens by wet grinding.

3.3 TEST METHODS

3.3.1 Calculation of the fiber content (Paper II).

For formulation of the mixtures, wt% was used for practical reasons. In addition, the fiber content was calculated as percentage by volume (Vg) with the following equation:

$$V_g = 100 \times (W_p/\rho_g)/[(W_g/\rho_g) + (W_r/\rho_r)]$$

where W_g is the mass fraction of reinforcement, ρ_g is the density of the fibers, W_r is the mass fraction of polymer and ρ_r is the density of the polymer. The density of polymer A was 1.20 g/cm^3 , and polymer B was 1.19 g/cm^3 (Meriç et al., 2005). The density of the CG fibers was, according to manufacturer's information, 1.76 g/cm^3 .

3.3.2 Water uptake and water sorption/solubility (Papers I, II, V)

After storing the polymer specimens in a desiccator at $(37 \pm 1) ^\circ\text{C}$, the “conditioned mass”, m_0 , was determined with an analytical balance. The conditioned specimens were immersed in water until saturated and with constant mass to an accuracy of 0.2 mg. This mass was recorded as m_1 . Water uptake was registered intermittently until water saturation over a period of time. After water saturation, the specimens were dried in a desiccator: the “reconditioned” mass was recorded as m_2 . Water sorption (W_{sp}) and water solubility (W_{sol}), given in wt%, were measured and calculated from the equations (Papers I, II, V):

$$W_{sp} = (m_1 - m_2) \times 100 / m_2$$

$$W_{sol} = (m_0 - m_2) \times 100 / m_0$$

Linear expansion due to water uptake was measured with a micrometer in all three directions of the specimens: height, width, and length. The volume of each specimen was calculated with the mean of nine thickness measurements, three width measurements, and two length measurements. Volumetric change was calculated (Papers I, V).

3.3.3 Fracture toughness testing (Paper I)

Notched specimens (Figure 2) were fabricated and stored in water for 7 days. The specimens were placed with the notch opposite the load plunger (Figure 6). The three-point bending test was in air at $(23 \pm 1) ^\circ\text{C}$ with a constant displacement rate of $(1.0 \pm 0.2) \text{ mm/min}$ until maximal load was exceeded, and the test was considered finished when the load was less than $(1.0 \pm 0.2) \text{ N}$.

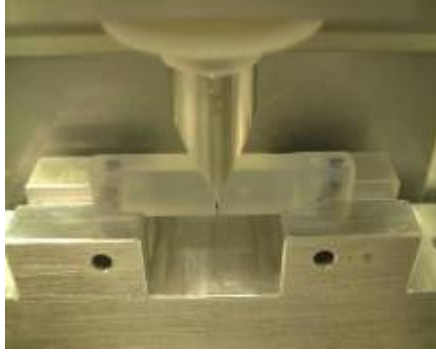


Figure 6. Set up of fracture toughness test (Paper I).

Maximum stress intensity factor ($\text{MPa} \cdot \text{m}^{1/2}$) was calculated from the following equation:

$$K_{I,\max} = \frac{f(x) P_{\max} L \times \sqrt{10^{-3}} [\text{MPa} \cdot \text{m}^{1/2}]}{(b h^{3/2})}$$

Where f is a geometrical function dependent on x

$$f(x) = 3x^{1/2} [1,99 - x(1-x)(2,15 - 3,93x + 2,7x^2)] / [2(1+2x)(1-x)^{3/2}]$$

x is given by $x = a/h$

P_{\max} is the maximum load, in Newton, exerted on the specimen

L is the distance, in mm, between the supports, accurate to $\pm 0.01 \text{ mm}$

b is the width, in mm, of the specimen, accuracy 0.01 mm

h is the height, in mm, of the specimen, accuracy 0.01 mm

a is the total notch length, in mm, of the specimen, accuracy 0.002 mm

Fracture work (J/m^2) was calculated from the following equation:

$$\text{FW} = \frac{U \cdot 1000}{[2b(h-a)]}$$

Where U is the recorded area under the load/deflection curve in [N·mm] given by the following function $U = \int Pdv$, where v is the deflection in mm, P is the load in N. The area under the load/displacement curve represents the energy required to fracture the specimen. Dividing this energy by twice the surface area of the fracture, a surface energy expressed in J/m^2 was obtained: this was fracture work.

3.3.4 Bend testing before and after thermal cycling (TC) (Papers I-III)

Flexural strength and modulus were determined for unreinforced specimens (Paper I), fiber-reinforced specimens in dry condition and after water saturation (Paper II) and thermally cycled fiber-reinforced specimens (Paper III). Specimens for thermal cycling were stored in water for 90 days prior to being subjected to thermal cycling (12,000 thermal cycles in water baths of $(5 \pm 1)^\circ\text{C}$ and $(55 \pm 1)^\circ\text{C}$ with a 30 s immersion at each temperature and with a 2 s transfer between the temperature baths). Three-point flexural test, according to ISO 1567:1999, was with a Lloyd LRX testing machine and a Nexygen software computer program. The testing was in water at $(37 \pm 1)^\circ\text{C}$ with a constant displacement rate of 5 mm/min. The distance between supports was (50 ± 0.1) mm. The ultimate transverse strength (σ) and flexural modulus (E) of the specimens were calculated.

3.3.5 Dilatometric analysis (Papers I-III)

Dimensional changes with temperature were measured for unreinforced matrix polymers A and B (Paper I), for fiber-reinforced polymer (47 wt% fiber loading) in dry condition (Paper II) and for unreinforced matrix polymer B and fiber-reinforced polymer (47 wt% fiber loading) in water saturated condition (Paper III). The linear coefficient of thermal expansion (LCTE) was measured with a thermomechanical analyzer (TMA) (Perkin Elmer TMA 7, Perkin Elmer Inc, Norwalk, CT, USA). The probe was stabilized on the specimen surface by a low constant load of 10 mN. The temperature was increased to 180°C and maintained for one minute before it was decreased to 5°C . The heating and cooling rate was $2^\circ\text{C}/\text{min}$. The TMA software system (Pyris Software v. 4.0, Perkin Elmer) plotted dimensional changes as a function of temperature at different temperatures. The LCTE values were calculated in the temperature range of 20 - 50°C .

3.3.6 Shear testing (Paper IV)

Shear bond strengths of differently treated titanium surfaces to CGFR polymer and denture base polymers, as well as shear bond strengths of controls (sandblasted titanium plates) after water saturation and thermal cycling (5000 cycles, 5-55 °C) were determined. All specimens were water saturated for 200 days before exposure to thermal cycling of 30-35 s immersion time in water at $(5 \pm 1) ^\circ\text{C}$ and $(55 \pm 1) ^\circ\text{C}$, prior to shear testing according to ISO 10477:2004(E). The specimens were mounted in the shear testing apparatus and loaded with a constant displacement rate of (1 ± 0.3) mm/min (Figure 7). The load F (N) was recorded when the polymer bolt fractured from the plate. The bond strength B was calculated in MPa from the equation $B=F/A$. A is the adhesive surface area, in mm^2 .

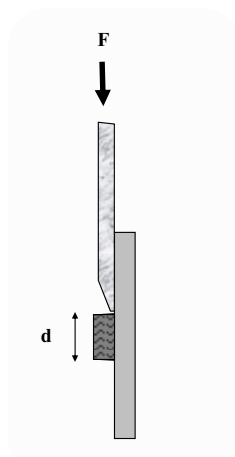


Figure 7. Schematic illustration of set up of shear bond strength test. The specimen was loaded with a force, F , d is the diameter of the bolt (Paper IV).

The type of fracture between the adhering polymer and the titanium plates or CGFR polymer plates was evaluated by visual inspection and microscopy. The fracture sites were classified as adhesive when the fracture was at the interface, and cohesive, when the fracture was in the polymeric phases or in the opaquer layers or both.

3.3.7 Determination of residual monomers (Papers I, V)

High Performance Liquid Chromatography (HPLC) was used to analyze the presence of cross-linking agents and vinyl chloride monomer (VCM) and residual MMA monomer. One third (four polymer A and four polymer B) of the 24 unreinforced specimens received an additional heat treatment at 130 °C for 30 min directly after polymerization, and another third received the additional heat treatment after 2 weeks. The remaining third of the test specimens did not receive any additional heat treatment (Paper I).

Half of the CG fiber-reinforced polymer A and B test specimens with different fiber loadings (24, 36 and 47 wt%) received additional heat treatment (Paper V).

The specimens were broken into small pieces, dispersed, and partly dissolved in acetone before HPLC analysis for residual MMA monomer and the presence of the cross-linking agents and VCM (Papers I and V). For the quantitative determination of residual MMA, standard calibration curves were established from peak area or heights at 205 nm obtained from injection of known concentrations of MMA reference substance: a wavelength of 190 nm was used for the detection of VCM and 205 nm for detection of the cross-linking agents. The quantitative analytical method (including sampling) of residual MMA monomer is an accredited test method with an uncertainty $\pm 10\%$ of value.

3.3.8 Determination of cytotoxicity (Paper V)

Cytotoxicity was evaluated by MTT assay and filter diffusion test.

3.3.8.1 MTT assay

MTT assay is a spectrophotometric test for determining cell viability. Extracts were prepared from the polymer A and B specimens produced with 47 wt% fiber loading that had been stored dry. Cytotoxicity was rated based on cell viability relative to controls: extracts were rated as severely ($< 30\%$), moderately (30-60%), slightly (60-90%), or non-cytotoxic ($> 90\%$) based on the activity relative to the values obtained for controls. The whole test was duplicated with the same extracts.

3.3.8.2 Filter diffusion test

Specimens from polymer A and B produced with 47 wt% fiber loading were prepared: to assure absence of sharp edges, the specimens were ground. The test specimens were stored dry prior to testing. The filter diffusion test was performed twice. Mouse fibroblasts were cultured and after 24 hours inverted to Petri dishes with agar nutrient medium. Test specimens were placed on the upper surface of the filter and both negative and positive controls disks were used. After 24-hour incubation the specimens were carefully removed from the filter and the filter was then separated from the agar surface. The cytotoxic effects were thereafter determined with a stain procedure where succinate dehydrogenase activity was present when the cells were viable, the cells turned blue, and dead cells without enzyme activity were uncolored.

3.3.9 SEM evaluation (Papers II, III)

Cross sections of specimens were examined by scanning electron microscopy (SEM) (Paper II). The CG fibers *per se* were examined by SEM (Paper III). The surface of the CG fibers and the adhesion between fibers and matrix from fractured specimens with fiber loadings of 24, 36, 47 and 58 wt% before (Paper II) and after thermal cycling (Paper III) were also evaluated by SEM.

3.4 STATISTICAL ANALYSIS

The results of the fracture toughness testing, three-point bend testing and water sorption and solubility were investigated with t-tests and paired t-tests, as appropriate, through the Statistica system for Windows, release 6.1 (Paper I).

The measurements of ultimate flexural strength, flexural modulus, water sorption, and solubility were investigated by t-tests and paired t-tests, as appropriate, with Statistical Analysis System software (Paper II).

The results of the measurements of ultimate flexural strength and flexural modulus for the thermally cycled specimens were tested by two-sided ANOVA and t-tests with Statistical Analysis System software. T-tests were used where appropriate (Paper III).

The results of the measurements from shear bond testing were tested by ANOVA and t-tests with Statistical Analysis System software (Paper IV).

Two-way and three-way ANOVAs were also used to determine if fiber load (24, 36 and 47 wt%) and polymer type (A and B) influenced the resulting water sorption, water solubility, volumetric expansion and residual monomer content with or without additional heat treatment. Pair wise comparisons were calculated with t-tests (Paper V). A p-value less or equal to 0.05 denoted statistical significance.

4 RESULTS

4.1 BASE MATERIAL

The solutions of A and B and the size were verified as inhomogeneous solutions due to the presence of light scattering phenomena when illuminated with a visible light source.

4.2 DETERMINATION OF THE FIBER CONTENT (PAPER II).

Two, three, four and five tubes resulted in twice as many fiber-reinforcing layers. The filler loadings corresponded to 24 wt% (20 vol%), 36 wt% (29 vol%), and 47 wt% (38 vol%) fiber-reinforcement for both resins A and B. In addition, specimens with filler loading of 58 wt% (47 vol%) were made with resin B.

4.3 WATER UPTAKE AND WATER SORPTION/SOLUBILITY (PAPERS I, II, V)

Cumulated water sorption (without solutes), solubility for polymers A and B, and volumetric expansion after 3 months in water are presented in Table 3.

Table 3. Evaluation of properties of two matrix polymers intended for fiber composites (Paper I).

	Polymer A		Polymer B		p-value	
	Mean	SD	Mean	SD		
Water sorption (wt%)	2.26	0.06	2.28	0.04	0.47	NS
Water solubility (wt%)	0.023	0.020	0.025	0.003	0.84	NS
Volumetric expansion (vol%)	1.04	0.12	0.98	0.14	0.46	NS

SD, standard deviation. NS, not significant

Mass increase due to water uptake increased with time in a similar manner for both unreinforced polymers (Paper I). Water uptake for both polymers A and B was (2.2 ± 0.2) wt% after 3 months water saturation (Paper I).

Linear expansion due to water uptake ranged from 0.24-0.41% depending on which dimension (height, width or length) was measured. The lengthwise expansion was lower than height and width expansion.

Volumetric expansion was (1.04 ± 0.12) vol% for polymer A and (0.98 ± 0.14) vol% for polymer B. When the polymer was reinforced with CG fibers, the volumetric increase was equal to or below (0.013 ± 0.0053) vol%.

Mass increase with time due to water uptake for specimens with 36 wt% fiber reinforcement was obtained at 90 days with polymer A and at 200 days with polymer B

(Paper II). Water sorption results are displayed in Figure 8. Water sorption was equal to or below (3.3 ± 1.18) wt% for fiber loadings of 24, 36 and 47 wt%. There was no significant effect of either polymer type (two-way ANOVA, $p = 0.161$) or fiber loading (fiber loading 24, 36 and 47 wt%: two-way ANOVA, $p = 0.127$). For polymer B, there was a significant effect of different fiber loadings when 58 wt% was added (ANOVA $p < 0.001$). The highest fiber loading with polymer B revealed considerably higher water sorption (5.3 ± 1.22) wt% than with fiber loadings 47 wt% ($p = 0.007$), 36 wt% ($p < 0.001$) and 24 wt% ($p = 0.006$).

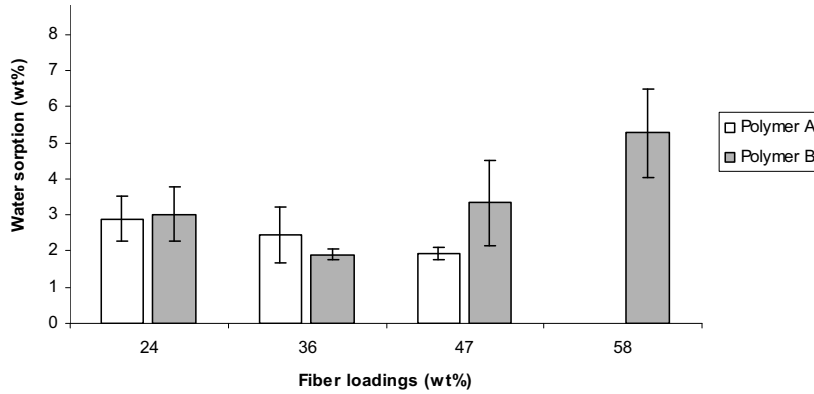


Figure 8. Water sorption calculated as mass fraction for polymers A and B with increasing CG fiber loadings (Paper V).

Water solubility was equal to or below (0.04 ± 0.02) wt% for all fiber loadings, except for polymer B with fiber loadings of 47 and 58-wt% (Figure 9).

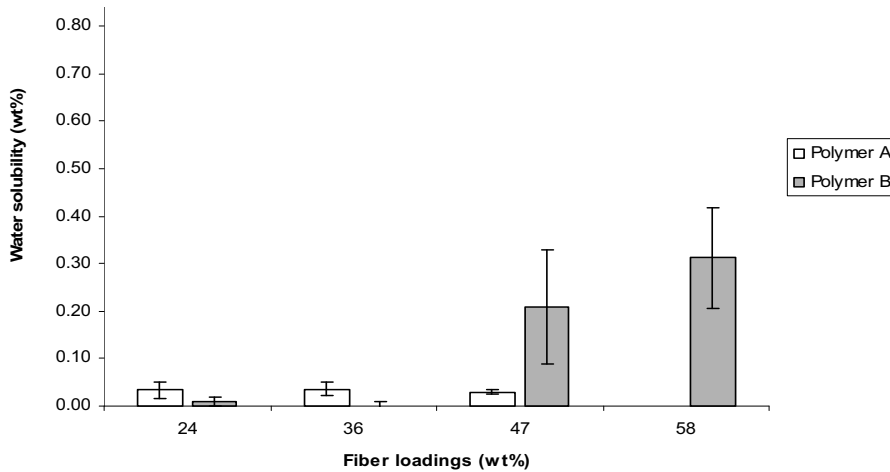


Figure 9. Water solubility calculated as mass fraction for polymers A and B with increasing CG fiber loadings (Paper V).

Volumetric increase was similar for all composites tested and equal to or below (0.013 ± 0.0053) vol%. No difference between composites A and B were determined with

two-way ANOVA ($p = 0.454$), but there was a minor difference in means for composite B between fiber loadings ($p = 0.049$).

4.4 FRACTURE TOUGHNESS TESTING (PAPER I)

Polymer B showed increased maximum stress intensity factor and higher fracture work value than polymer A, when tested both dry and water saturated (Table 4).

Table 4. Evaluation of fracture toughness for polymers A and B (Paper I).

	Polymer A		Polymer B		p-value
	Mean	SD	Mean	SD	
Maximum stress intensity factor ($\text{MPa}\cdot\text{m}^{1/2}$)	0.55	0.12	0.75	0.17	0.04
Fracture work (J/m^2)	44	13	63	17	0.06

SD, standard deviation. NS, not significant

4.5 BEND TESTING BEFORE AND AFTER TC (PAPERS I-III)

Ultimate flexural strength and flexural modulus by three-point bend testing for the two tested matrix materials are presented in Tables 5 and 6. Ultimate flexural strength values were higher for Polymer B than for polymer A, tested both dry and after 90 days in water. Polymer B had higher values, compared to polymer A, for flexural modulus when tested dry but not when tested water saturated. Flexural modulus remained stable for polymer A after 90 d storage in water ($p=0.23$), but the flexural modulus decreased for polymer B ($p=0.006$).

Table 5. Ultimate flexural strength (MPa) in dry condition, after water storage and after thermal cycling (12,000 cycles), $n=5$. Mean values (SD). Significance ($p < 0.05$). Standard deviations are given within parentheses (Papers I-III).

Type of polymer	CG Fiber Wt%	Dry (37 ± 0.2)°C		Wet (37 ± 0.2)°C 90 d		TC
Polymer A	-	56.0	(13.3)	54.0	(3.3)	-
Polymer B	-	68.7	(9.8)	64.0	(6.1)	-
Polymer A	24	234.4	(42.69)	263.3	(38.77)	-
Polymer A	36	478.4	(43.88)	399.6	(38.50)	-
Polymer A	47	540.6	(49.62)	547.7	(28.12)	-
Polymer B	24	273.5	(62.75)	280.9	(45.01)	244.8 (32.33)
Polymer B	36	411.0	(51.80)	399.5	(47.11)	441.3 (68.96)
Polymer B	47	549.4	(14.34)	563.3	(89.24)	459.2 (45.32)*
Polymer B	58	589.7	(58.79)	419.9	(55.62)	310.4 (52.79)*

Table 6. Flexural modulus (GPa) in dry condition, after water storage and after thermal cycling, (12,000 cycles). Significance ($P < 0.05$). Standard deviations are given within parentheses (Papers I-III).

Type of polymer	CG Fiber Wt%	Dry (37 ± 0.2)°C	Wet (37 ± 0.2)°C	TC
			90 d	
Polymer A	-	2.65 (0.34)	2.43 (0.19)	-
Polymer B	-	2.97 (0.31)	2.48 (0.09)	-
Polymer A	24	13.50 (1.341)	12.86 (2.166)	-
Polymer A	36	24.25 (1.166)	18.91 (2.329)	-
Polymer A	47	31.36 (1.960)	31.40 (0.949)	-
Polymer B	24	13.92 (2.708)	14.24 (2.096)	12.80 (2.017)
Polymer B	36	20.01 (2.059)	19.20 (3.751)	23.24 (2.758)
Polymer B	47	30.62 (2.264)	29.53 (4.699)	29.69 (2.183)
Polymer B	58	36.41 (1.965)	36.12 (2.139)	30.30 (4.149)*

Polymer A, without fiber-reinforcement, tended to brittle fracture into multiple pieces, whereas, unreinforced polymer B exhibited less brittle fracture, mainly into two pieces. All unreinforced test specimens broke into at least two pieces after three-point bend testing; this was in contrast to the CG fiber-reinforced specimens, where the fibers kept the fractured specimen in one piece (Figure 10).

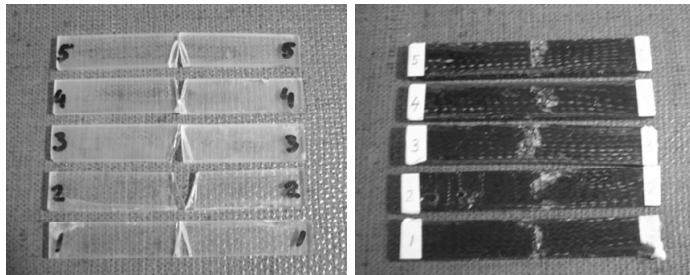


Figure 10. Illustration of fracture type after three-point bend testing for (a) unreinforced Polymer B specimens (Paper I) and (b) 36 wt% CG fiber-reinforced test specimens (Paper II).

Ultimate flexural strength and flexural modulus for the CGFR polymers tested dry, water stored and thermally cycled are presented in Tables 5 and 6. With increased fiber loading, flexural strength and modulus increased, both when tested dry and after water storage ($p < 0.05$). With higher fiber contents (58 wt%), when tested dry and water stored, ultimate flexural strength after water saturation decreased ($p = 0.04$). Flexural strength after thermal cycling increased with increasing fiber loading from 24 wt% to 36 wt% (t-test, $p < 0.001$). There was no increase between 36 and 47 wt% fiber ($p =$

0.642) but between 47 and 58 wt% there was a decrease ($p = 0.001$). When compared to water stored specimens (90 days), hydrothermal cycling did not decrease flexural strength of the carbon-graphite fiber-reinforced polymer with 24 and 36 wt% fiber loading ($p > 0.05$); however, flexural strengths decreased for fiber loadings of 47 wt% ($p = 0.040$) and 58 wt% ($p = 0.026$) (Table 6).

There was no statistically significant difference in the measured ultimate flexural strength and flexural modulus, either in dry or wet condition, for the 24, 36 and 47 wt% CG fiber-reinforced A and B polymers ($p > 0.05$).

Flexural modulus increased with increasing fiber loading. Differences in means between fiber loadings were identified in the thermally cycled group (ANOVA, $p < 0.001$). There was a significant increase between 24 and 36 wt% fiber loadings, ($p < 0.001$) and between 36 and 47 wt% fiber loadings ($p = 0.003$). No difference was noted between 47 and 58 wt% fiber loadings ($p = 0.778$). When compared with water-stored specimens, flexural modulus was reduced only for the composite with the highest fiber loading (Table 6).

4.6 DILATOMETRIC ANALYSIS (PAPERS I-III)

Linear dimensional changes with temperature for unreinforced polymers A and B were similar. LCTE was negative between 110-130 °C. Linear expansion for polymer A was $(77 \pm 1)/^{\circ}\text{C}$ and $(78 \pm 1)/^{\circ}\text{C}$ for polymer B. Within the temperature interval from 5 °C to 70 °C, the polymers had a uniform and linear expansion as a function of temperature, indicating that the polymeric materials were stable without a glass transition. The cooling curves indicated a glass transition at approximately 100°C.

The LCTE values for CGFR polymers A and B with a fiber loading of 47 wt% were similar and determined to be $-2.5 \times 10^{-6}/^{\circ}\text{C}$ longitudinally (Figure 11a) and $62.4 \times 10^{-6}/^{\circ}\text{C}$ transversely (Figure 11b). The longitudinal LCTE specimens, i.e. parallel to the long axis of the flexural test specimens, had a negative LCTE (Figure 11a), whereas, the transverse LCTE, i.e. perpendicular to the long axis of the flexural test specimens, were positive (Figure 11b) and had a similar appearance to the unreinforced polymers.

The linear coefficients of thermal expansion for the CG-fiber, the matrix polymer in wet and dry condition and the longitudinal and transverse CGFR composite are presented in Table 7.

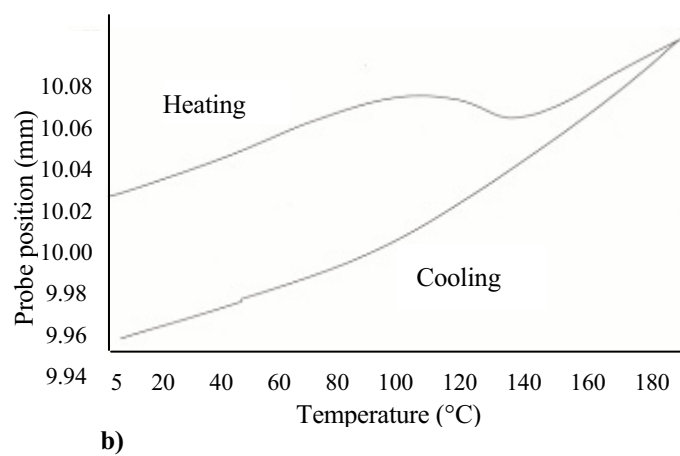
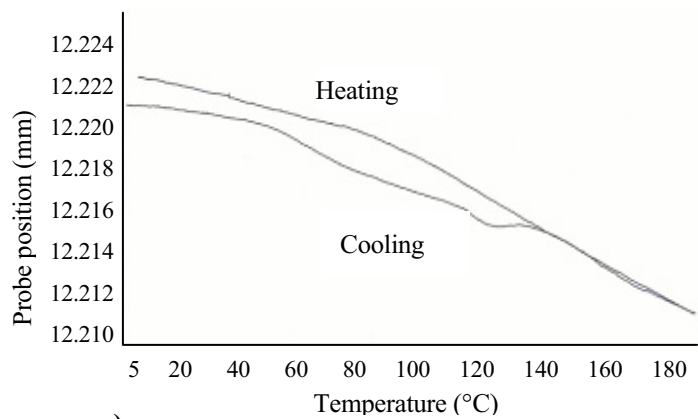


Figure 11. Representative graphs of the linear dimensional change as a function of temperature for polymers A and B with 47 wt% CGFR polymer when the specimens were **a)** longitudinal to the direction of fiber tubes, displaying a negative LCTE and **b)** in the transverse direction of fiber tubes, displaying a positive LCTE. Heating and cooling rate was 2 °C/min. The temperature was held at 180 °C for one minute before it was decreased to 5 °C (Paper II).

Table 7. Linear coefficient of thermal expansion

Substance	LCTE value	Reference
CG-fiber, longitudinal	$0.3 \times 10^{-6}/^{\circ}\text{C}$	Siltex, Technisches Datenblatt: Carbon/Flechtschlauch
CG-fiber, transverse	$36.5 \times 10^{-6}/^{\circ}\text{C}$	Siltex, Technisches Datenblatt: Carbon/Flechtschlauch
Matrix polymer B, dry	$78 \times 10^{-6}/^{\circ}\text{C}$	Segerström et al 2005, Paper I
Matrix polymer B, wet	$84 \times 10^{-6}/^{\circ}\text{C}$	Segerström & Ruyter 2009, Paper III
CG-fiber composite, longitudinal	$-2.5 \times 10^{-6}/^{\circ}\text{C}$	Segerström & Ruyter 2007, Paper II
CG-fiber composite, transverse	$62.4 \times 10^{-6}/^{\circ}\text{C}$	Segerström & Ruyter 2007, Paper II

4.7 SHEAR TESTING (PAPER IV)

The shear bond strengths of differently treated titanium surfaces to CGFR polymer and denture base polymer, and the shear bond strengths of controls (sandblasted titanium

plates) after water saturation and thermal cycling (5000 cycles, 5-55 °C) are displayed in Figure 12.

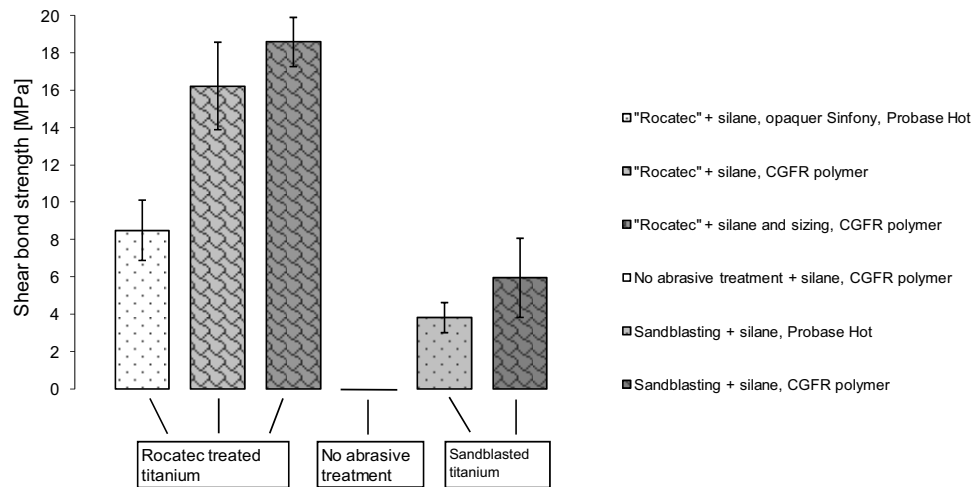


Figure 12. Shear bond strength values of differently treated titanium surfaces (Rocatec treatment or sandblasting) to CGFR polymer and denture base polymer (Probase Hot) and shear bond strength values of controls consisting of titanium without abrasive surface treatments. Vertical lines represent standard deviations (Paper IV).

Sandblasting and silanization, compared to no abrasive surface treatment, increased shear bond values but with apparently adhesive fracture type. For polished titanium plates that received solely silane treatment, i.e. no abrasive surface treatment, no bond strength to the CGFR polymer was registered. Rocatec treatment improved bond strength compared to specimens that were merely sandblasted ($p < 0.0001$). The combination of Rocatec treatment, silanization, opaquer Sinfony and denture base polymer revealed an apparently adhesive fracture combined with minor regions of cohesive fracture in the opaquer. The combination of Rocatec treatment, silanization and CGFR polymer revealed a partly cohesive fracture in the CGFR polymer combined with minor regions of apparently adhesive fracture. When Rocatec treated surfaces were combined with the size, shear bond strength increased. Shear bond strength values for CGFR polymer adhering to Rocatec treated and silanized titanium were higher than those for Probase Hot combined with opaquer ($p < 0.0001$). Shear bond strength values for CGFR polymer adhering to sandblasted silanized titanium were also higher than those for Probase Hot ($p = 0.02$).

Results from shear bond testing, after thermal cycling of the roughened and polished carbon-graphite fiber-reinforced polymer and the controls of polished unreinforced matrix polymer are presented in Figure 13.

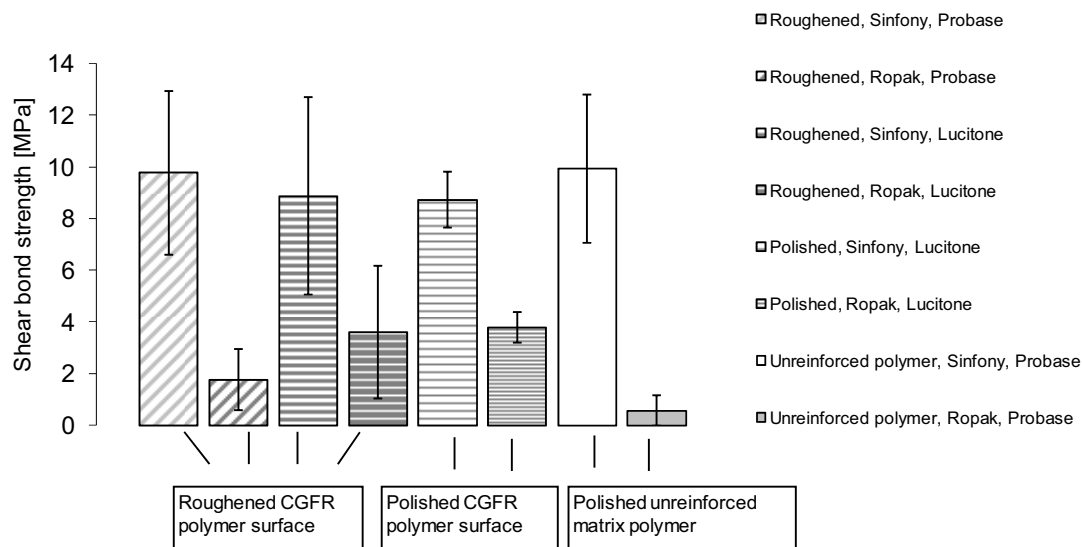


Figure13. Shear bond strength values of polymer B specimens, carbon-graphite fiber-reinforced framework polymer to two different opaques (Sinfony or Ropak) and denture base polymers (Probase Hot or Lucitone 199) and shear bond strength values of controls consisting of unreinforced matrix polymer after thermal cycling (5000 cycles, 5-55 °C). Vertical lines represent standard deviations (Paper IV).

The application of opaquer Sinfony produced higher bond strengths than the application of opaquer Ropak for all groups ($p < 0.0001$), and cohesive fracture in the opaquer layer was the dominating fracture type. Mainly adhesive fractures with minor regions of cohesive fractures were observed with the opaquer Ropak. When the opaquer Sinfony was used there was no difference regarding whether the surface was roughened or polished (ANOVA $p = 0.86$).

4.8 DETERMINATION OF RESIDUAL MONOMERS (PAPERS I, V)

In the matrix polymer, residual cross-linking agents and residual vinyl chloride monomer were not quantifiable or detectable by HPLC. The content of the released residual MMA monomer is presented in Figure 14. Additional heat treatment resulted in an increase of residual MMA, regardless of whether the heat treatment was given immediately after polymerization or 2 weeks after polymerization.

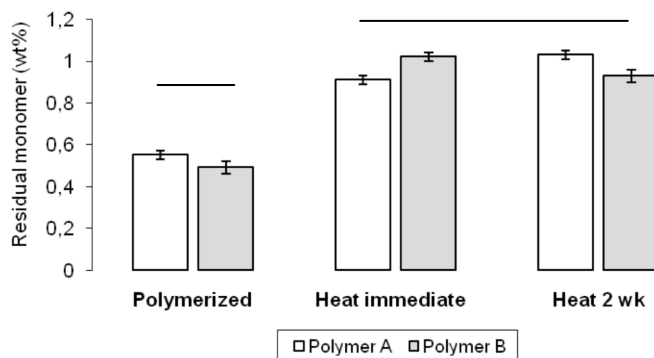


Figure 14. Residual monomer for polymers A and B in wt%. “*Polymerized*” stands for heat polymerized specimens and no additional heat treatment. “*Heat immediate*” stands for heat polymerized with immediate additional 30 min heat treatment at $(130 \pm 2)^\circ\text{C}$. “*Heat 2 wk*” means heat polymerized and after 2 weeks with an additional 30 min heat treatment at $(130 \pm 2)^\circ\text{C}$. Vertical lines represent standard deviations. Horizontal lines above bars indicate groups that do not differ statistically from each other (Paper I).

Residual MMA monomer content (mean) for all CG fiber-reinforced specimens was equal to or below (0.68 ± 0.05) wt% (Figure 15). The fiber content affected residual monomer levels ($p < 0.001$). Specimens with fiber loading of 47 wt% had relatively low residual MMA. Composites of polymer B contained higher levels of residual monomer than those of polymer A (three-way ANOVA, $p < 0.001$). Composites with polymer B (24 and 36 wt%) contained higher levels of residual monomer than the comparative composites with polymer A (one-way ANOVA, $p = 0.015$ for 24 wt% and $p < 0.001$ for 36 wt%), except for 47 wt% ($p = 0.325$). Additional heat treatment (130°C) increased residual monomer content (three-way ANOVA, $p = 0.046$) and was evident for the composites with fiber loading of 24 wt% (two-way ANOVA, $p < 0.001$). The cross-linking agents EGDMA, 1,4-BDMA and DEGDMA, and VCM, were neither quantifiable nor detectable. By “detectable” is meant that the signal (S) from MMA is at least twice the noise (N) signal ($S/N \geq 2/1$).

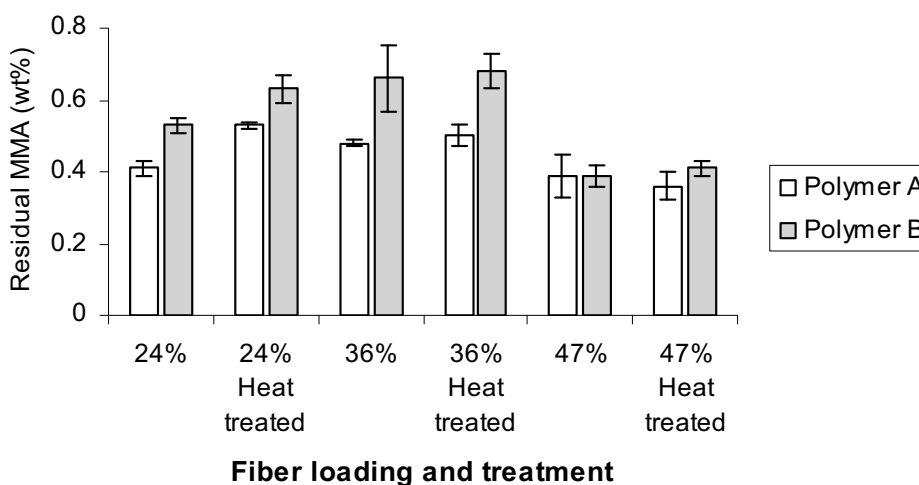


Figure 15. Residual MMA monomer in the fiber composites with different CG fiber loadings before and after additional heat treatment (Paper V).

4.9 DETERMINATION OF CYTOTOXICITY (PAPER V)

The MTT-test and filter-diffusion test both indicated biocompatibility for fiber-reinforced polymers A and B; the MTT-test revealed mitochondrial enzyme activity and the filter diffusion test did not display cytotoxicity (Figure 16).

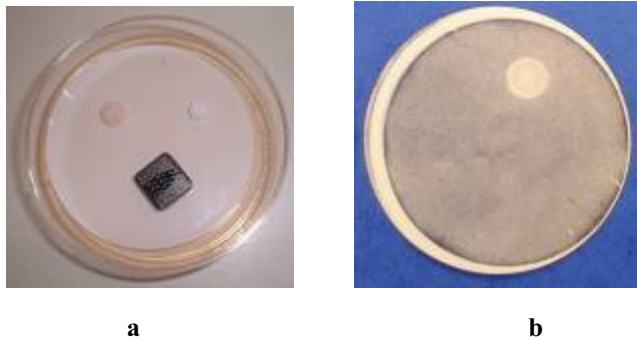


Figure 16. The results of the filter diffusion test. Cells adjacent to the negative control disk and the square test specimen (see placement of the disk and test specimen to the left in **a**) had no color change indicating cell viability. The cells which had contact with the positive control disk were decolorized revealing cell death as displayed in **b**.

4.10 SEM EVALUATION (PAPERS II, III)

SEM revealed that CG fibers in the polymer matrix were well embedded in binder material. After 90 days in water, the micrographs displayed matrix-embedded fibers at the fractured surfaces and continuity between CG fibers and matrix was observed (Figure 17 a). SEM of thermally cycled fractured composite specimens, after flexural testing, revealed carbon-graphite fibers embedded in polymer matrix (Figure 17b) and continuity between carbon-graphite fibers and matrix, regardless of fiber loading.

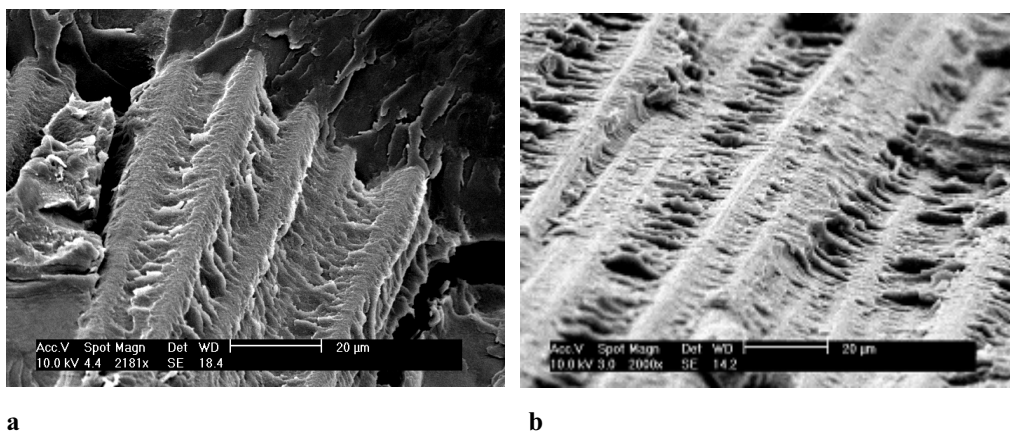


Figure 17. Good adhesion between fibers seen on SEM of a fractured surface of **a**) a water saturated (90 days in water) CGFR polymer A with a fiber loading of 24 wt%, (Paper II) and **b**) of water stored (90 days in water) and thermally cycled carbon-graphite fiber reinforced polymer with fiber loading of 36 wt% (Paper III).

The effect of low and high fiber content is presented in Figure 18; the number of voids increased in a composite with 58 wt% compared to a composite with 24 wt% carbon-graphite fibers.

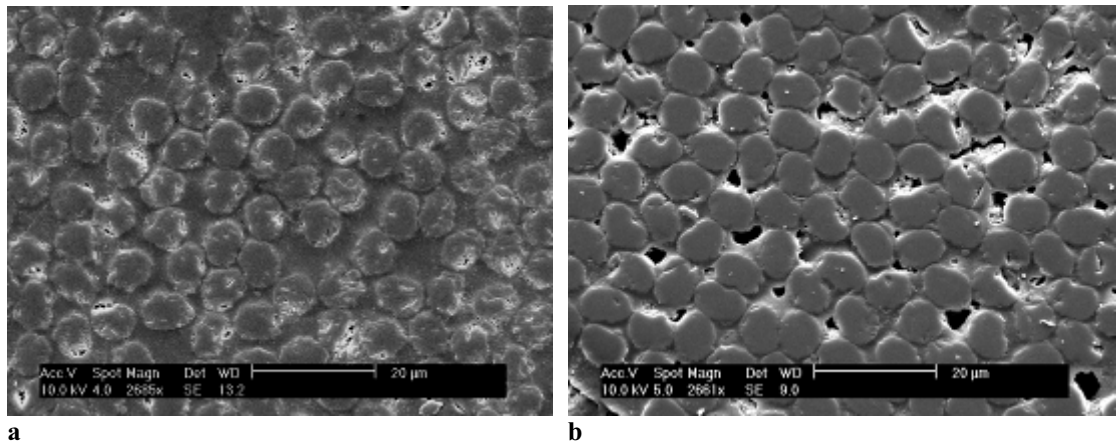


Figure 18. Increasing number of voids within the resin matrix and gaps along the interface between fibers and matrix when comparing fiber loading of **a)** 24 wt% (to the left) with fiber loading of **b)** 58 wt% (to the right) (Paper II).

The topography of the carbon-graphite fiber surface is displayed in Figure 19.

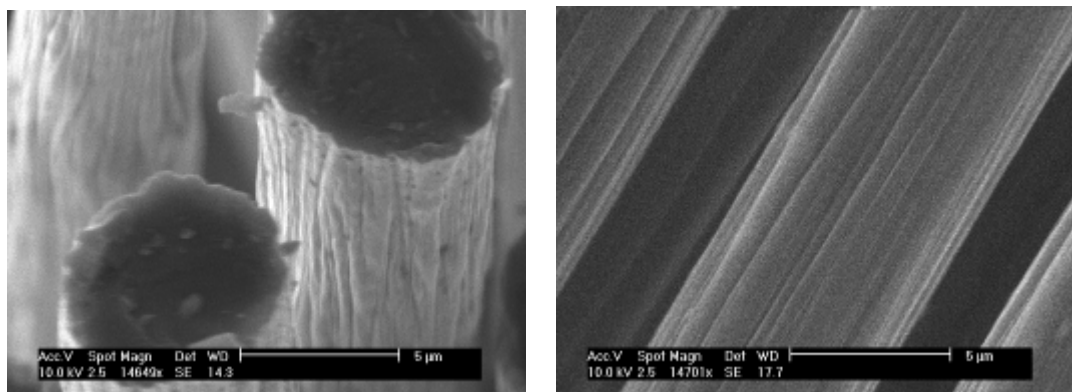


Figure 19. Magnification (x 15000) of the carbon-graphite fiber surface reveals an uneven striated surface with longitudinal furrows and ridges oriented along the filament axis.

5 DISCUSSION

5.1 POLYMER MATRIX (PAPER I)

When a resin material intended for incorporation of fibers is developed, certain factors must be considered, so that the desired properties result. For ensuring adequate wetting of the fibers, a relatively low-viscous binder or resin matrix material is preferred.

Proper viscosity combined with the ability to remain in a fluid state during storage and handling is important for optimal handling and storing properties. An MMA based resin system was chosen as it works well in laminated systems and bonds to polymer teeth (Büyükyılmaz and Ruyter, 1997; Vallittu and Ruyter, 1997a; Vallittu and Ruyter 1997b). The consistency of a resin system can be varied by varying the quantities of PMMA and by altering the molecular weight of PMMA dissolved in the monomer mixture (Kurata and Tsunashima, 1999). Solution A contained 23 wt% PMMA, and solution B contained 33 wt% PMMA. As viscosity increases with molecular weight (MW) and PMMA has a molecular weight distribution, a molecular weight of 120,000 was chosen. This molecular weight is well above the limit of 600 for the degree of polymerization (i.e. MW=60,000 for PMMA) where the strength of a polymer becomes constant with increasing molecular weight (Tager, 1978). The ability of the resin mixtures to remain in a fluid state during storage (in a refrigerator) and handling before polymerization (Eichner, 1981) was due to mixing a copolymer powder of vinyl chloride and vinyl acetate with a MMA monomer/PMMA solution of relatively low viscosity.

Two different compositions of matrix resins with different cross-linking agent systems were evaluated. The resin A solution contained the cross-linking agents EGDMA and 1,4-BDMA, and resin B contained DEGDMA. When the cross-linking agent in a polymer is altered, the mechanical properties can change (Øysaet and Ruyter, 1989). Both maximum stress intensity factor ($K_{I,max}$ value) and fracture work describe the fracture resistance of a material. High maximum stress intensity factor indicate that materials fracture less readily and the material has enhanced toughness. Fracture work value (Zappini et al., 2003) indicates how well materials can withstand the propagation of cracks (Øysaet and Ruyter, 1989). The expectation was that the polymer containing a cross-linking agent with an adequate chain length (Figure 20) would show greater fracture toughness. This expectation was confirmed when polymer B, containing the cross-linking agent DEGDMA (Figure 20), exhibited enhanced toughness; however,

this enhanced toughness is mainly attributed to DEGDMA's tendency for cyclopolymerization (Øysaetd and Ruyter, 1989).

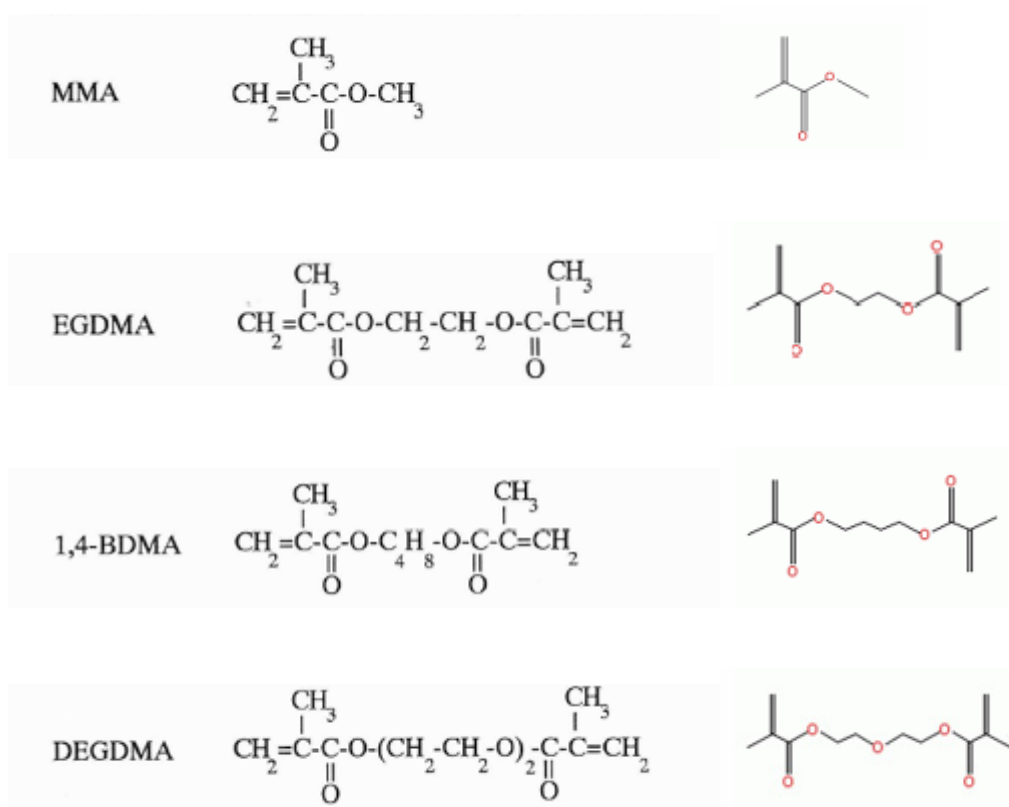


Figure 20. Molecular structures of methyl methacrylate (MMA), ethylene glycol dimethacrylate (EGDMA), 1,4-butanediol dimethacrylate (1,4-BDMA) and diethylene glycol dimethacrylate (DEGDMA).

5.2 FIBER REINFORCEMENT (PAPERS II-V)

An optimized integrated system between fibers and matrix is a requirement for durable fiber-reinforced polymers. CG fiber reinforcement was chosen partly because the flexural modulus of CG fibers exceeds that of e.g. glass fibers (Delmonte, 1981). CG fibers contribute to stiffness and strength, and improve fatigue strength, while reducing thermal expansion and polymerisation shrinkage (Delmonte, 1981). Furthermore, CG fibers are inert in an aqueous environment and resistant to chemical degradation (Delmonte, 1981). Removing impurities from commercial CG fibers by solvent cleaning ensured an active CG surface susceptible to the sizing resin, which was also compatible with the resin matrix. In addition, the sizing resin facilitated handling properties and storage of the sized fibers. Even though processing with CG fibers has previously resulted in difficult handling (Bowman and Manley, 1984; De Boer et al., 1984), the present techniques and materials improved handling characteristics.

Numerous types of CG fibers are available for reinforcement of polymers (chopped, continuous, woven, braided and tubular); however, the tubes of braided fibers provide a more even distribution of reinforcement than other fiber types. Braided fibers “in tubes” are advantageous as they allow high fiber content and offer comfortable handling properties and are easy to introduce into a monomer/polymer mixture (Ekstrand et al., 1987). An earlier clinical investigation also claimed that mechanical properties needed improving (Bergendal et al., 1995). The tubes and braided nature of the fibers result in multi directional orientation; thus a more balanced stress distribution is obtained, as fiber bundles at different angles are advantageous when load is present on more than one axis (Ekstrand et al., 1987; Ko, 1986; Ma et al., 1986). As prosthetic replacements, such as implant-retained suprastructures, are exposed to more than one direction of forces (Dirtoft and Jansson, 1986a and 1986b), it is beneficial to place a fiber arrangement offering reinforcement to multi-axial forces, such as combined bending and torsion forces. In addition, the three-dimensionally braided composites provide improved stiffness and strength in all directions, thus, preventing interlaminar failure (Ma et al., 1986; Ko, 1986).

The carbon-graphite fiber topography of longitudinal striations with ridges and furrows (Figure 19) increases surface area and surface roughness of the fibers and offers mechanical interlocking (Minford, 1983). There is also a possibility of shrink fitting of the resin matrix (Lee and Orlowsky, 1974) around the fiber itself, as well as embracement of the uneven fiber surface (ridges). These mechanisms should contribute to the enhanced strength of adhesion at the interface between the fibers and the matrix, and explain the good adhesion observed by SEM, (Papers II-III).

The combination of thorough cleaning, improved sizing resin and the developed resin matrices contributed to continuity between the CG fibers and the polymer matrix, indicating good adhesion between fibers and matrix. However, an increasing number of voids with higher fiber loading (Figure 18) were also identified by SEM (Paper II). Reduction of porosity is essential for obtaining a high strength and durable composite, and techniques for minimizing porosity and the number of voids in carbon-graphite fiber polymers intended for implant suprastructures need developing.

The disadvantage of the black appearance of the fibers is easily covered by an opaquer. The entire opaquer coated framework is embedded in the pink-pigmented denture base

polymer, a procedure similar for metal suprastructures (Figure 21), rendering good aesthetic appearance (Paper IV).

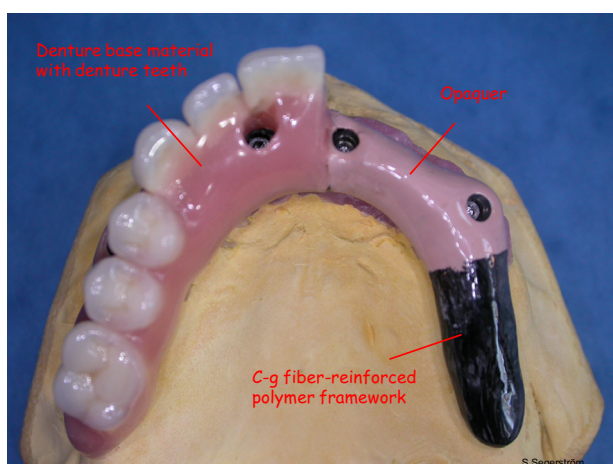


Figure 21. A model of an implant-retained supraconstruction.

5.3 FLEXURAL AND FATIGUE PROPERTIES

The mechanical properties of carbon-graphite fiber-reinforced polymers were substantially improved compared with earlier documented values for flexural strength (Ekstrand et al., 1987) when tested dry after dry storage or when tested wet after storage in water (up to 90 days). For higher CG fiber (e.g. 47 wt%) loadings flexural strength values of 500-600 MPa approximate to that of high-gold alloys (400-570 MPa) (Christian Erneklint, 2006, personal communication). Furthermore, the flexural strength of CGFR polymers with 24 and 36 wt% fiber loadings was not decreased after thermal cycling, even though thermal cycling is generally claimed to lower mechanical properties (Torbjörner et al., 1996; Drummond and Bapna, 2003; Lassila et al., 2004; Lehmann et al., 2004). The stability of flexural strength values for dry, water stored and thermally cycled CGFR specimens with fiber-loadings of 24 and 36 wt% indicated durable adhesion between fibers and polymer matrix. Intimate contact between the fibers and matrix was verified by SEM (Papers II and III).

The reason for improved mechanical properties was probably due to the solvent cleaning of the commercial CG fibers to remove impurities, combined with vacuum treatment, ensuring an active surface compatible with the sizing resin, which was also compatible with the resin matrix. The sizing system used resulted in good wetting. The matrix resin consisted of a dispersed phase of a copolymer powder in a colloidal solution of PMMA nanoparticles in a monomer solution containing a cross linker (MMA+DEGDMA). It was assumed that after polymerization the colloidal solution

resulted in a cross-linked matrix with evenly distributed interpenetrated PMMA nanoparticles, and that the copolymer particles were evenly distributed. The incorporation of PMMA nanoparticles in the sizing and matrix materials probably contribute to improved mechanical properties (Khaled et al., 2007) and reduced polymerization contraction, and internal strains and stresses. Appropriate polymerization contraction was obtained, resulting in favorable shrink fitting (Lee and Orłowsky, 1974) and giving good adhesion.

Incorporating high fiber content in the matrix material generally improves mechanical properties (Schreiber, 1971; Ekstrand et al., 1987; Murphy, 1998; Knoell et al., 1975; Yazdanie and Mahood, 1985; Vallittu and Lassila, 1992); however, higher fiber content does not always result in higher mechanical properties. For the CGFR composite materials in question (with fiber loadings of 24, 36, 47 and 58 wt%), the flexural properties increased with increasing percentage volume of fibers when tested in dry condition; however, after water storage (90 days), the flexural strength for composites with the higher fiber content of 58 wt% decreased. After thermal cycling (12,000 cycles), the flexural strength for CGFR composites with 47 and 58 wt% fiber loading decreased compared with flexural values for the same composites tested in wet conditions. A decrease in flexural property after thermal cycling of glass and carbon fiber-reinforced endodontic posts is described in several studies (Torbjörner et al., 1996; Drummond and Bapna, 2003; Lassila et al., 2004). The decrease in flexural properties of carbon fiber-reinforced epoxy resin posts after hydrothermal aging is ascribed to hydrolysis and degradation of the matrix, as well as stresses at the fiber-matrix interface leading to debonding and/or matrix cracking (Torbjörner et al., 1996). The fabrication technique may cause decreased flexural properties in CGFR composites with higher fiber loading after water sorption, with further impairment resulting from thermal cycling. Manual introduction of high quantities of fibers into the resin matrix may result in incorporation of voids and porosities. With higher quantities of CG fibers in the matrix material, porosities tend to increase; porosities in long-term water-stored fiber-reinforced specimens are assumed to contain water. With increasing quantity of porosities, water absorption increases and the strength of fiber-reinforced composites decreases: this has been ascribed to the detrimental effect of water (Vallittu et al., 1998a; Behr et al., 2000; Vallittu, 2000; Vallittu, 2001).

The results of the present investigations indicated that processing technique could be improved regarding fiber packing and embedding in the resin binder, aiming at reducing porosities and voids in the carbon-graphite fiber reinforced polymer. A refined

processing technique may improve flexural properties of the composites with high fiber loading. One technique for preventing air entrapment in the fiber-resin mixture is a combination of a vacuum technique with vibration and hydrostatic pressure, high enough to compress entrapped air to a negligible volume (Kinloch, 1983; Behr et al., 2000), however, as MMA is relatively volatile; the vacuum technique could be somewhat cumbersome.

5.4 WATER UPTAKE

In resins A and B, water sorption at saturation was similar and below the requirement for water sorption, according to the international standard for denture base polymers (ISO 1567, 1999; ISO 20795-1, 2008). The two cross-linking agent systems used did not have any substantial effect on water sorption: this is in accordance with other findings for heat-polymerized denture polymers (Jagger and Huggett, 1990). The solubility values were well below the requirement for solubility in the international standards (Paper I).

In particulate composites, water sorption increases with a reduction of filler content as the relative portion of water-absorbing polymer matrix increases (Øysaet and Ruyter, 1986; Miettinen et al., 1999; Lassila et al., 2002; Ferracane, 2006). Water sorption at water saturation was equal to or below (3.3 ± 1.18) wt% for all fiber loadings tested, except for the highest fiber loading (polymer B, 58 wt%) (Paper V). All composites, except the highest fiber loading, had water sorption of the same magnitude as the commonly used methyl methacrylate-based denture base polymers (Buyukyilmaz and Ruyter, 1994), indicating good contact and adhesion between fibers and polymer matrix (Miettinen et al., 1999).

Fiber-reinforced polymer A specimens had a tendency for decreased water sorption with increasing CG fiber loadings. This did not apply to composites containing polymer B with 47 wt% and 58 wt% CG fibers (Paper V). Current manual fabrication techniques result in an increasing number of voids with higher fiber loadings. The reduction of porosities is essential for obtaining durable composites with low water sorption. A stable fiber-matrix interface, without gaps along the interface between fibers and matrix, as well as lack of voids and porosities within the resin matrix, assures lower sorption (Miettinen et al., 1999).

The time of water saturation between the two types of fiber-reinforced polymers differed: polymer B needed longer for water saturation (Paper II). Water sorption depends on the chemistry of the monomers and the structure of the resulting polymer system. The reason for the longer time needed for water saturation for polymer B can be explained by the more complex cyclic structures of the polymer system due to the use of dimethacrylate monomer DEGDMA (Figure 20) (Øysaet and Ruyter, 1989; Huang et al., 1995).

As water diffuses into the polymer and separates the polymer chains, uptake of water or a solvent may cause swelling that affects the dimensions of the composite resulting in expansion (Anusavice, 1996). Linear expansion in height and width due to water uptake was similar for the unreinforced polymers A and B, whereas, linear expansion in length was less than in height and width. This reduced expansion was probably due to anisotropy introduced by the preparation procedure. Volumetric expansion was similar for both tested resins. Dimensional changes were small for the unreinforced matrix polymers (Paper I) and the dimensional changes were even smaller when the resin matrices were reinforced with CG fibers (Paper V). There was a minor reduction in volume expansion with increasing CG fiber content, which was statistically significant when polymer B was used as the matrix: fillers generally reduce the overall volume of the water-absorbing polymer (Øysaet and Ruyter, 1986; Miettinen et al., 1999; Lassila et al., 2002; Ferracane, 2006). Due to the inertness of CG fibers, water was not absorbed by the fibers. However, this reduction in volume expansion was not observed for composites with polymer A and for the highest fiber content of polymer B (Paper V) and was probably due to low expansion values and measurement uncertainty of such values.

5.5 DILATATION PROPERTIES

The variation of the coefficient of thermal expansion between different materials is important, because a mismatch leads to strains resulting in “internal” stress formation that adversely affect the interface. Therefore, thermally induced strains and stresses can adversely affect long-term stability of multiphase materials (Delmonte, 1981) used intraorally.

The addition of fibers to a polymer decreases the coefficient of thermal expansion (Kanayama et al., 2000). In general, the thermal coefficient varies with the direction of the fibers in a composite (Holliday and Robinson, 1973; Nielsen, 1974; Craft and

Christensen, 1981; Tezvergil et al., 2003b): rigid fibers appear to prevent expansion of the matrix in the longitudinal direction and the matrix is forced to expand in the transverse direction (Nielsen, 1974; Tezvergil et al., 2003b). For CG fibers, longitudinal thermal expansion is low, but in the transverse direction, it is of the same magnitude as that of an unfilled polymer. The difference in thermal expansion in relation to fiber direction was verified (Paper II). Within the temperature range of 5-55 °C used in thermal cycling, no cracking of the specimens was observed, even though there was a difference in thermal expansion values longitudinally between the CG-fiber and polymer matrix, with “near zero” LCTE in the fiber direction and the larger LCTE for the polymer matrix (Table 7). The LCTE for the CGFR polymer was in accordance with this, as specimens cut in the transverse direction had a positive LCTE of the same magnitude as the matrix materials; whereas, the LCTE of longitudinally cut specimens was negative (Paper II). In addition, the tubular structure of CG fiber reinforcement with a three-dimensional fiber arrangement resembles a squeezed coil spring, which allows flexibility in freedom of expansion and contraction to strain changes. The tubular structure of the fiber-reinforcement allowed transverse expansion (giving a positive LCTE value in the transverse direction) leading to a minor longitudinal contraction (giving a negative LCTE value longitudinally) as the least resistance for expansion was offered in the transverse direction (Figure 11). Water immersion (90 days) did not increase the LCTE value of the matrix polymer significantly (Paper III). Thus, when the ratio of LCTE of matrix and CG fibers remains of the same magnitude the flexural properties of the CGFR composites are not affected (Papers II and III).

The longitudinal thermal expansion for a CGFR polymer is low (lower than for titanium); however, in the transverse direction, the LCTE value for the matrix of the CGFR composite is of the same magnitude as CG-fibers (by a factor of 2/1) and higher than for titanium. Thermal coefficient of expansion for titanium is relatively low $8.4\text{--}8.9 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$ (Low et al., 2001). As the resulting thermal expansion coefficients for CGFR polymers and for titanium do not differ considerably, strains at the CGFR composite surface adjacent to the titanium should be tolerable.

5.6 ADHESION PROPERTIES OF THE LAMINATE MATERIALS

Good adhesion with a cohesive fracture type was achieved between the layers of the Rocatec-treated titanium/CGFR polymer/Sinfony opaquer/denture base polymers (Probase Hot and Lucitone 199) (Paper IV).

For durability, the system of Ti-metal/framework polymer/opaquer/denture base polymer/denture teeth should function as a unity when exposed to intraoral strains and stresses. Thus, the bonding between Ti-metal framework polymer/opaquer/denture base polymer/denture teeth should be optimal (Figure 22).

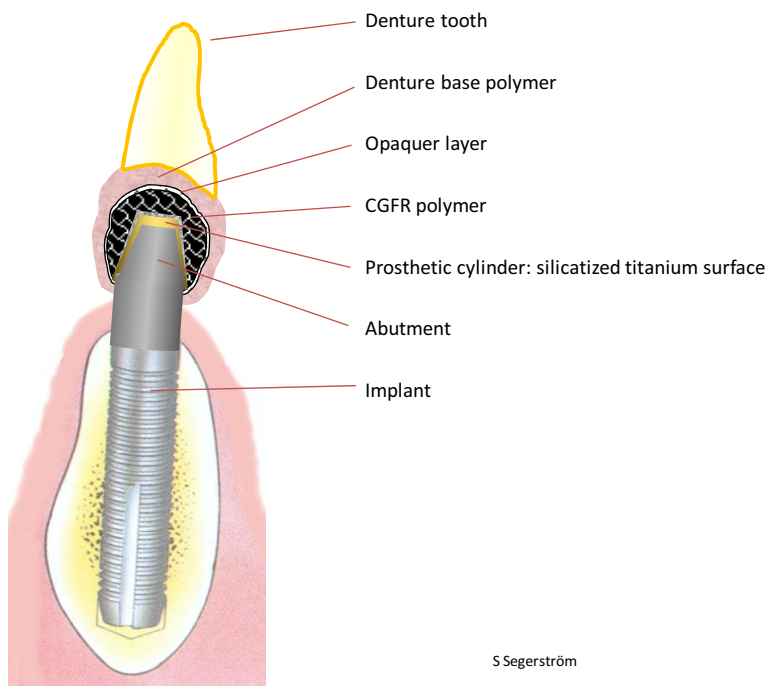


Figure 22. Cross-section of the laminates in an implant-retained supraconstruction.

The supraconstruction components in CGFR composite are MMA/PMMA based; the major monomer component of the CGFR framework polymer is MMA; and both opaques tested contain MMA: according to the manufacturers, Ropak UV-F liquid contains 40-60% MMA and Sinfony contains 30-40% MMA. Both denture bases tested are MMA/PMMA based. Thus, all components intended for CGFR supraconstruction contained the same or similar basic components, which should be advantageous. A cohesive bond between the most commonly used acrylic resin teeth and heat-cured denture base polymers is documented (Büyükyılmaz and Ruyter, 1997): the same applies for polymer teeth and an experimental composite (Meriç and Ruyter, 2007) based on the same matrix material as used in this study. MMA has good swelling properties because of diffusion and penetration of the monomer methyl methacrylate.

In the penetrated region, an interpenetrating polymer network (IPN) is formed, resulting in good bond strength (Vallittu and Ruyter, 1997b; Büyükyilmaz, 1997).

The addition of 47 wt% CG-fiber reinforcement to the resin matrix polymer did not lower shear bond values (Figure 13). Cohesive fracture in the opaquer layer was the dominating type of fracture when the opaquer Sinfony was used, and there was no difference whether the CGFR polymer surface was roughened or polished (Paper IV): this indicated adhesion did not depend on mechanical retention.

In construction of a fiber-reinforced composite framework with titanium cylinders on titanium implants, reliable adhesion between the metal and the framework is necessary. With a retentive metallic cylinder design and an increase in surface area combined with surface treatment, the probability of a durable bond between the metal and framework polymer is ensured. The type of surface treatment of the titanium surface is important and by increasing the contact surface area of the titanium plates through sandblasting, the shear-bond strength values improved compared with no abrasive surface treatment of the titanium plates (Paper IV). Rocatec-treated surfaces gave higher bond strengths than sandblasted surfaces, especially in combination with a size. The main difference between the two abrasive treatments is that the Rocatec treatment gives a “silicized” surface, resulting in higher bond strengths and increased cohesive fracture type/decreased adhesive fracture surfaces. Rocatec-treated surfaces combined with the size, produced mainly cohesive fractures, and the increasing shear bond strength indicated that with a size, wettability of the surface improves.

The shear bond strength for Rocatec-treated titanium surfaces with the opaquer Sinfony covered by the denture polymer Probase was lower than for the Rocatec treated titanium surfaces without an opaquer and with CGFR polymer. The fractures were in the opaquer layer and apparently adhesive with minor cohesive regions. One reason for the lower bond strength may be cross-linking in the opaquer layer, resulting in a higher polymerization contraction due to the high dimethacrylate content. Another reason for the lower bond strength may be the higher polymerization contraction for the polymer (denture polymer Probase), having no fiber-reinforcement, compared with the CGFR polymer with reduced contraction due to the presence of the fiber not taking part in the polymerization process.

The opaquer Sinfony had higher shear bond strength values than Ropak when tested on a roughened and a polished CGFR polymer surface and on a polished unreinforced polymer (Figure 13). The fracture type was more cohesive in the opaquer Sinfony and was mainly adhesive with the opaquer Ropak (Paper IV). The reason for this may be the content of the relatively high molecular weight monomer in Ropak (dipentaerythritol (monohydroxy)pentaacrylate) (MW = 476). This reduces the mobility of MMA (MW = 100) due to the size of the large monomer, the content of hydroxy group, and its high cross-linking ability which results in a polymer of assumed high cross-linking density. The consequences are less dissolution and swelling at the surfaces of the adherent CGFR polymer and denture base polymer. Monomers in Sinfony are lower in molecular weight, and combined with the laminate application of the materials were more compatible and effective than Ropak.

There are different test methods for investigating bond strengths. Although there are limitations in shear bond testing, it was preferred over push out testing because the push out test method is affected by polymerization shrinkage and the resulting bond strength values could be influenced (increased/decreased).

The MMA-based heat-cured “high impact” denture base polymer (Lucitone 199) gave similar bond values to the CGFR framework polymer as the heat-cured conventional denture base polymer (Probase Hot) (Paper IV). With a “high impact” denture base material in implant suprastructures, one of the most common complications, such as fractures of the acrylic part, are reduced.

5.7 BIOCOMPATIBILITY

Residual monomer content for both matrix polymers was well below the recommendations for denture base polymers (ISO 1567, 1999; ISO 20795-1, 2008). Additional heat treatment (130°C for 30 min) increased residual MMA of the unreinforced polymers A and B by a factor of two, even though a decrease was anticipated (Paper V). The reason for this increase is most likely thermal degradation and depolymerization. It has been indicated that thermal degradation and in particular depolymerization of PMMA can be initiated at temperatures above 100 °C (McNeill, 1968).

Additional heat treatment had minor effects on the residual MMA monomer content for the fiber-reinforced polymers with higher fiber loadings (36 and 47 wt%); however, in

the fiber composites with the lowest content of CG fibers (24 wt%) in both polymers A and B a slight increase of residual MMA monomer was identified (Figure 15). The absence of an increase in residual monomers after inclusion of CG fibers indicates that besides a reduction due to increased filler/decreased matrix content there could be a chemical interaction between the fibers and the matrix system. The surface of the fibers may interact with the system, and thus, the inclusion of CG fibers may prevent formation of a labile polymer fraction, or inhibit depolymerization.

Cross-linking agents and vinyl chloride monomer were not detectable by HPLC analysis.

In general *in vitro* data in and data from cytotoxicity tests are relevant yet not directly transferable to the *in vivo* situation. Nevertheless, the *in vitro* methods play an important role in analyzing the biocompatibility of polymers. For instance, solubility can be affected by the pH of the solution (Chadwick et al., 1990). However, CG-fiber *per se* exhibits no carcinogenicity (Tayton, 1982) and no cytotoxicity after water storage (Ekstrand et al., 1987). Both MTT and filter diffusion tests indicated that the CGFR polymer systems were non-cytotoxic, even though they had not been stored in water prior to testing. Accordingly, CGFR polymer systems investigated were assumed to be biocompatible and it is considered that the materials can be suitable for clinical evaluation.

5.8 CLINICAL APPLICATION

Carbon-graphite fiber-reinforced poly(methyl methacrylate) is an alternative framework material for implant-supported fixed prostheses and a method has been developed for production of such frameworks (Björk et al., 1986; Ruyter et al., 1986). In a multi-center study, Bergendal et al. (1995) evaluated 27 fixed prostheses *in vivo* over a period of 56 months and concluded that CGFR polymer prostheses of that generation fulfill the criteria for biocompatibility, high precision, acceptable aesthetics and low costs; however, the technical criterion was not fully met by that generation of CGFR composites; five prostheses fractured around the end abutment cylinders (Bergendal et al., 1995).

Since then the CGFR polymer has been improved. The MMA compatible matrix system used in the present *in vitro* investigations provided the desired adhesion between CGFR polymer “framework” and denture base polymers and the fiber distribution and content was optimized. The results of the physicochemical,

mechanical, and biological properties of the CGFR polymers (Papers I-V) inferred the materials were well suited for commencing clinical evaluation. A pilot study with 11 patients that started in 2003 has not revealed any fractures (personal communication Karl Ekstrand). Neither have any fractures occurred in a randomized multi-center study, initiated 2004 with the hypothesis that CGFR polymer framework in implant prostheses functions as well as metal frameworks (personal communication Ulf Karlsson, Johan Segerström).

Occlusal load is a critical factor in reaching and maintaining osseous integration. The restorative material used in dental implants may be one of the factors affecting the forces transmitted to peri-implant bone (Skalak, 1983). Different types of restorative prosthetic materials for implants affect stress transmission at bone-implant interface differently; ceramic crowns transmit greater forces than composite crowns (Conserva et al., 2009). Thus, shock absorbing ability for the prosthetic restorative materials may be of biological and biomechanical interest (Skalak, 1983). CGFR polymer suprastructures are expected to have more shock absorbing capacity than metal/ceramic suprastructures.

A procedure for the production of implant-retained prosthesis, presented in the Appendix (“Production of an implant-retained prosthesis with a carbon-graphite fiber-reinforced polymer framework: A dental technique”), describes a dental laboratory method for obtaining biocompatible and long lasting suprastructures. The use of fiber composite technology for implant-retained fixed partial dentures offers a cost-effective alternative to metal suprastructures. The advantages of CGFR polymer include ease of production, reduced production time and a reduced cost of materials.

CGFR polymer prostheses can be an alternative treatment when minimization of treatment cost is imperative. In prosthetic rehabilitation after treatment of trauma or oral cancer, where there is an advantage of fast rehabilitation from a quality-of-life perspective, CGFR technology may be beneficial.

6 CONCLUSION

As an alternative to metal frameworks, carbon-graphite fiber-reinforced polymers can be used as the core material for implant-retained prostheses. Ease of production including reduced production time and reduced costs may result in more edentulous patients gaining access to implant treatment.

Carbon-graphite fiber-reinforced polymers intended for implant suprastructures were formulated and developed. Physicochemical and mechanical properties of the matrices and CGFR polymers were determined in dry condition, after storage in water, and after thermal cycling.

Two resin mixtures, based on methyl methacrylate (MMA)/poly(methyl methacrylate) (PMMA) and the copolymer poly(vinyl chloride-co-vinyl acetate), were produced with two different cross-linking agent systems: 1,4-butanediol dimethacrylate (1,4 BDMA) and ethylene glycol dimethacrylate (EGDMA) or diethylene glycol dimethacrylate (DEGDMA). Both resin binders revealed an appropriate consistency while remaining in a fluid state during storage and manipulation. Basic requirements regarding water sorption, water solubility, residual MMA monomer, coefficient of linear thermal expansion were met and were similar for the two resin matrices investigated. The basic requirements regarding mechanical properties were also met. Flexural properties and fracture toughness were higher for the matrix resin containing the cross linker diethylene glycol dimethacrylate, rendering it more suitable as a resin binder.

The tubes of braided carbon-graphite fibers for reinforcement increased flexural properties of the composites. Flexural strength, flexural modulus and linear coefficient of thermal expansion were similar for both types of fiber composites. The three-dimensional distorted tubular structure of the fiber-reinforcement, resembling a squeezed coil spring with a braided diagonal fiber arrangement, offered favorable geometry in handling thermally induced strains.

Flexural properties increased with fiber loadings up to and including 47 wt% (38 vol%) when tested in dry and wet conditions. More porosity was observed with fiber loading of 58 wt%. The combination of the described fiber surface treatment, the sizing resin, and the resin matrix developed contributed to good adhesion between the carbon-graphite fibers and the polymer matrix.

At 24 and 36wt% fiber loadings, hydrothermal cycling did not decrease flexural strength of the CGFR polymers, when compared to water stored specimens. For fiber loadings of 47 wt% and 58 wt%, flexural strength decreased after thermal cycling in relation to composites that had been merely water stored. Composites with CG fiber loadings up to 36 wt% appear promising for clinical use. For fiber quantities above 36 wt%, the manufacturing process can be improved by improving embedding of the fibers in the resin binder to obtain better stability in the humid oral environment.

The CGFR polymers with fiber loadings up to 47 wt% had acceptable values for water sorption and solubility and had dimensional stability. Residual monomer content was within the limits of the international standard and was stabilized by the inclusion of CG fibers.

Cytotoxicity could not be demonstrated for the CGFR composites; cross-linking agents and vinyl chloride were not detectable by HPLC analysis.

A silicatized titanium surface gave higher bond strength to CGFR polymer and cohesive fracture than a sandblasted surface where the fracture was adhesive. The opaquer Sinfony gave mainly cohesive fractures and higher adhesion values, than the opaquer Ropak. Good adhesion with a cohesive fracture type was achieved between the layers of the Rocatec-treated titanium/CGFR polymer/Sinfony opaquer/denture base polymers (Probase Hot and Lucitone 199). The different coefficients of expansion for the materials did not prevent compatibility between the materials. The combination of these materials in an implant-retained supraconstruction is promising for *in vivo* evaluation and a randomized multi-center study has commenced.

7 SWEDISH SUMMARY

Kolfiberförstärkta polymerer kan användas i protetiska implantatkonstruktioner istället för metaller. Detta skulle kunna öka tillgängligheten för implantatbehandling vid tandlöshet då framställningen av kolfiberförstärkta akrylatbroar inte kräver så avancerad teknik.

Målet med avhandlingen var att framställa och *in vitro* utvärdera vissa fysiska och mekaniska egenskaper för såväl matrix som för kolfiberförstärkt komposit i torrt tillstånd, efter förvaring i vatten samt efter cyklisk värmebehandling. Även kompositens biokompatibla lämplighet utvärderades.

Två MMA-baserade polymermatriser med olika tvärbindare hade gynnsamma egenskaper avseende hanterbarhet, vattenlöslighet, vattenupptag, förekomst av restmonomer. Polymermatrisen som innehöll 14 vikts% av tvärbindaren dietylen glykol dimetakrylat (DEGDMA) hade högre böjhållfasthet och brottsseghet och var därmed bättre lämpad som matrispolymer än den som innehöll 1,4-butandiol dimetakrylat (1,4 BDMA) och etylen glykol dimetakrylat (EGDMA).

Polymermatriserna förstärktes med tubulär flätad kolfiberstruktur med fiberinnehåll från 24 till 58 vikts%. Böjhållfastheten ökade med ökat fiberinnehåll oavsett typ av matris. Kombinationen med ytbehandlingen av fibrer och polymermatris resulterade i god adhesion mellan polymermatris och kolfiber. Cyklisk värmebehandling minskade inte böjhållfastheten hos de kolfiberarmerade polymererna förstärkta med 24 och 36 vikts% fibrer utan var jämförbar med de vattenförvarade provkropparna. Ytterligare högre fiberinnehåll resulterade inte i högre böjhållfasthet. Förekomsten av blåsor ökade vid högre fillerhalt.

Bindningsstyrkan mellan silikatiserad titan och kolfiberförstärkt polymer var högre än för enbart sandblästrad titan. God adhesion med kohesiv frakturtyp kunde ses mellan silikatiserad (Rocatec behandlad) titan/kolfiberförstärkt polymer/opaker (Sinfony)/protesbasmaterial. Materialens expansionskoefficienter visade god kompatibilitet.

Vattenupptag och vattenlöslighet var övervägande inom gränsvärden för internationell standard. Polymerer med högst fiberinnehåll uppvisade något sämre värden.

Restmonomerinnehållet var också inom gränsvärden och stabiliserades dessutom av kolfiberinnehållet vid ytterligare värmebehandling. Inga tecken på cytotoxicitet observerades för någon av de kolfiberförstärkta polymererna.

Kombinationen av silikatiserad titan/kolfiberförstärkt polymer/opaker/protesbasmaterial verkar lovande för implantatbroar och utvärdering *in vivo*. Med den aktuella tillverkningstekniken och efter sammanfattning av resultaten verkar fiberhalter på 36 vikts% lovande för kliniskt bruk. Tekniken kan utvecklas med strävan till ökad vätbarhet för fibrerna vid högre fiberhalter för att optimera materialegenskaper genom att minska porositeter och öka hållfasthet och stabilitet ytterligare i den fuktiga orala miljön. Klinisk utvärdering i form av en randomiserad multicenter studie pågår.

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10 APPENDIX

Production of an implant-retained prosthesis with a carbon-graphite fiber-reinforced polymer framework: - A dental technique (submitted for publication).

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Abstract

As an alternative to conventional metal framework, this article describes a procedure for the production of implant-retained prostheses with a carbon-graphite fiber-reinforced polymer framework as the core material, which is surrounded with a denture base polymer. The advantages of this kind of construction include: ease of production, reduced production time and reduced cost of materials. Special emphasis is placed on describing methods in the dental laboratory for obtaining biocompatible and long lasting suprastructures.

Introduction

The most commonly used framework materials for implant prosthodontics are metallic materials such as gold, silver palladium and cobalt-chromium alloys and titanium (1-5). The metal framework is cast or milled and advanced technology is required, such as casting equipment or computerized milling and eroding equipment. The advanced techniques and time required for manufacturing can result in considerable costs, even though the costs of the materials may be low.

An alternative non-metallic material for use in implant supported fixed prostheses can be made of fiber-reinforced composites (6-11). Polymer based materials are commonly used in prosthetic dentistry and good clinical performance and satisfactory handling properties are documented (12-13). The strength of polymers can be improved by adding reinforcing fibers (14-18). The use of fiber reinforcement for denture base

acrylics is reported as early as in the 1960's (19). By adding carbon-graphite (CG) fibers to a poly(methyl methacrylate), matrix strength and stiffness increase (7, 14, 16). CG fibers are widely used in composites for high performance applications (15). Carbon-graphite fiber-reinforced poly(methyl methacrylate) (CGFRP) for implant-retained prostheses have previously been presented (6-8, 20).

Reinforcement with glass fibers is described for implant prostheses (9-11) and the case presentations are promising, and clinical trials are suggested for assessment of long-term outcomes (9-11). E-glass is the most commonly used glass fiber in dentistry, it has initial strength and the appearance makes it preferable for dental applications with high cosmetic demands. In comparison with carbon-graphite fibers, E-glass fibers exhibit relatively low tensile modulus (15); however, the hydrolytic stability of E-glass fiber is questionable, as its composition is based on a calcium-boroaluminosilicate (21).

For early versions of CGFRP in screw-retained prostheses, a success rate of 70%, after a mean functioning time of 3.5 years, was determined by Bergendal et al (22), in the longest documented clinical trial. Fractures occurred in the framework adjacent to the penetrating distal abutments and propagated through the acrylic resin and carbon-graphite fibers. A chemical bonding was not obtained between implant cylinders and framework material and the fabrication of the frame material was produced with a preliminary technique not permitting optimal fiber content throughout the framework. In addition, the fracture sites revealed incomplete wetting of the fibers. Bergendal et al's longitudinal multi-center study (22) concludes that a CGFRP framework can be used to form a biocompatible suprastructure of implant-retained prostheses with high precision, at low material costs, and with good aesthetic results; however, it was assumed that the mechanical properties were unsatisfactory and required improvement.

Mechanical properties for acrylic polymers attached to and surrounding the metallic framework material in implant-retained prostheses are, in most cases, sufficient, although, a considerable degree of mechanical failures occurs in clinical trials (23-27). Complications in association with both implants and suprastructures are common, but the most frequent complications concern fractures of the acrylic resin part of the prostheses, including artificial acrylic resin teeth (24, 27): time is needed for supplementary and maintenance treatment (23, 25). The high percentage of fractures is due to both inadequate laboratory technique and patients with increased bite force (23, 26).

With carbon-graphite fiber-reinforced polymer technology, a well functioning implant-retained suprastructures can be offered, rendering minimal health risk to the patient and the need for expensive advanced equipment is minimized.

The following laboratory procedure describes an uncomplicated method of preparing an implant-retained prosthesis with a carbon-graphite fiber-reinforced polymer framework. Heat-polymerization ensures good bonding between the fiber-reinforced framework, base polymer and polymer teeth and the low residual monomer content results in good biocompatibility. The procedure describes the production of an implant-retained prosthesis for the lower jaw: the equivalent procedure can be applied to the upper jaw.

Technique

1. Take an impression at the abutment level of the four implants in the mandible and make a gypsum cast (Figure 1).
2. Perform the bite registration (dentist), with wax rims attached to a rigid light-cured frame, and make a tooth set up with polymer teeth (dental technician) (Figure 2). Try the tooth set up clinically.



Figure 1. Gypsum cast of the four implants in the mandible



Figure 2. Tooth set up with polymer teeth.

3. Fix the abutment replicas to the tooth set up (Figure 3). Make a new gypsum cast with the abutment replicas in place.



Figure 3. Abutment replicas fixed to the tooth set up.

4. Embed the abutment replicas in the tooth set up with gypsum in a flask (Figure 4).



Figure 4. Abutment replicas in the tooth set up embedded in gypsum in a flask.

After the flask is separated into two halves, the embedded abutment replicas are in the lower gypsum flask (Figure 5). After wax removal the denture teeth remain in the upper part of the flask and the cervical part of the denture teeth are exposed in the upper half of the flask (Figure 6).



Figure 5. Abutment replicas visible in the lower gypsum flask.



Figure 6. Cervical part of the denture teeth exposed in the upper part of the flask.

5. With putty laboratory A-silicone (e.g. Lab-Putty, Coltène AG, Altstätten, Switzerland), carefully block the area buccally below the teeth and at the cervical margins of the teeth (Figures 6 and 7). Ensure that enough space is available for the covering opaquer and the pink-colored acrylic resin; thereby, obtaining a good aesthetic result.



Figure 7. Putty laboratory A-silicone is used to block the area buccally below the teeth and at the cervical margins of the teeth.

6. Treat the prosthetic cylinders with a “silicating” procedure (e.g. Rocatec® (3M-ESPE) (tribochemical silica coating, 110-µm grain-sized silica coated particles (Rocatec Pre and Rocatec Plus)) and EspeSil silane coupling agent)) and sizing material (consisting of MMA, PMMA and cross-linking agent) (20), to ensure good wetting ability and contact with the framework resin. Fix the cylinders to the abutment replicas, (the lower half of the flask), with gold screws (Figure 8). Block the screw holes with putty laboratory A-silicone.



Figure 8. The treated prosthetic cylinders are fixed to the abutment replicas with gold screws.

7. Put the carbon-graphite fiber reinforced resin dough, with putty consistency, in the mould in the space for the framework around the prosthetic cylinders, allowing the cylinders to perforate the fiber containing resin. Preform the “holes” in the fiber-containing dough at the site of the penetrating cylinders with a sharp-pointed PTFE, poly(tetrafluoroethylene) or wooden instrument (stick). Then tightly squeeze the doughy resin on to the pre-treated cylinders, thus surrounding them and providing a tight seal (Figure 9). During this procedure, use “rubber” gloves for handling the doughy unpolymerized polymer material. A flow cabinet with good ventilation assures non-inhalation of monomer vapors.



Figure 9. Carbon-graphite fiber-reinforced resin dough is squeezed into the mould allowing the cylinders to perforate the dough.

8. Clamp together the two denture flask halves with a hydraulic force of 200 N. Place the flask in a water bath and heat to 70 °C: maintain this temperature for 90 minutes before increasing to boiling temperature (100 °C) and boiling for 1 hour. Remove the clamped flask from the hot water and allow cooling on the laboratory bench to room temperature. As the halves are separated, the polymerized carbon-graphite fiber polymer framework with excess material is visible (Figure 10).



Figure 10. The polymerized carbon-graphite fiber polymer framework with excess materials visible in the mould.

9. Locate the screw holes and unscrew the framework. Remove the construction from the mould and then remove the excess material: grind the framework into shape with a laboratory hand piece and bur (Figure 11). This procedure should be conducted in a well-ventilated area.



Figure 11. The framework removed from the mould and cut into shape.

10. Cover the entire framework with a light cured methyl methacrylate containing opaquer (e.g. Ropak® UV-F opaquer liquid and powder, Bredent, Senden, Germany) compatible with PMMA (Polymethylmethacrylate) (Figure 12).



Figure 12. Fiber-reinforced framework re-attached in the mould and covered with a PMMA compatible opaquer layer.

11. Cover the fiber-reinforced framework with a pink acrylic (e.g. Probase) to a thickness of at least 0.5 mm and reattach it to the abutment replicas in the mould. Provide the prosthetic teeth with grooves and treat the ridge laps with methyl(methacrylate) (Figure 13). Block the access holes to the prosthetic cylinders with putty lab silicone. Reclamp the flask, and heat-polymerize the implant prosthesis by placing it in a water bath and bringing the temperature up to 70 °C, maintain this temperature for 90 minutes before increasing the temperature to boiling point (100 °C) and boil for 1 hour. Remove the clamped flask from the hot water.



Figure 13. Before the framework is covered with pink acrylic grooves are made in the prosthetic teeth and the ridge laps are treated with methyl(methacrylate).

12. Allow the flask to cool at room temperature on the laboratory bench. Locate the screw channels through the denture base material and/or denture teeth and ensure access by drilling to the silicone material placed above the gold screws. Control the access screw channels and if necessary shape them (Figure 14).



Figure 14. Post heat-polymerization, the implant prosthesis with shaped and cleaned access screw channels.

13. Finish the prosthesis and polish in the customary manner for dentures (Figure 15).



Figure 15. The polished carbon-graphite fiber-reinforced implant prosthesis.

Discussion

To ensure sufficient mechanical properties for the CGFRP framework, high fiber content must be present in the matrix material. The flexural properties increase with incorporation of higher quantities of braided CG fibers (16). The recent method of producing the CG fiber-reinforced polymer framework beam allows increased fiber content with an even distribution in the base material (20). For optimal mechanical properties, the fibers must be well adhered to and well impregnated with the resin (28). Surface sizing treatment of the fibers improves the bonding of the fiber composite to the polymer matrix material (16, 20).

The adhesion between the prosthetic cylinders (titanium) and the fiber-reinforced polymers is important. The interphase of the framework and metallic cylinder is exposed to occlusal forces and bonding problems between machined metallic surfaces and PMMA have been described (22, 29-30). The adhesion between metallic materials and resin materials can be improved (31). Besides macro- and micromechanical retention, various additional methods of adhesion have been developed (32-37). Not only gaining, but also

maintaining an improved bond is possible (38-39). Surface treatment methods such as Silicoater (32-34), Silicoater MD (35-36) and Rocatec (37) increase bond strengths: May et al (40) report bond strength increases of 68% between titanium and PMMA with the Rocatec surface treatment, compared with no surface treatment. The advantage of the Rocatec method is the absence of heat treatment with a flame, which can alter the crystal structure of the metallic construction (37).

The most commonly used polymer matrix material for industrial application is epoxy based; however, as low-molecular-weight epoxy fractions are active sensitizers, individuals manufacturing or using epoxy resins can become sensitized to the uncured resin (41-42). Avoiding sensitizing substances in dental applications is preferable. The most common denture base materials are based on poly(methylmethacrylate) (PMMA) and methylmethacrylate (MMA): these types of polymer matrices has also been used in fiber-reinforced composites (11, 16, 22). However, MMA must be handled with caution, especially for dentists and dental technicians (43), because skin contact with monomers can cause hand eczema (44). Development of ergonomic procedures and practices for safe handling are recommended (44). Gloves offer a limited degree of protection against MMA and cross-linking agents (44-47), but better protection is obtained with double gloves, a synthetic rubber or polyethylene inner glove without texture, wet with water, before a natural rubber (latex) glove is placed on top (46-47). The expensive laminate 4H gloves (AB Alfort & Cronholm, Bromma, Sweden) offer the best protection against methacrylates (46-48), but are inconvenient to use due to thickness and lack of flexibility (45).

Local irritation or allergic reactions are not only caused by MMA but by formaldehyde produced in low quantities from residual MMA monomer (49). Every effort should be made to eliminate residual monomer or reduce it to low levels. The quantity of residual MMA monomer in correctly treated heat polymerized denture base polymers is low and the time spent at 100 °C during heat-polymerization is important for minimizing residual MMA monomer (50). Curing cycles at a temperature below 100 °C produce denture base polymers with a higher residual MMA content than those produced with a prolonged curing period at 100 °C (50). Heat-polymerized materials have a lower content of residual monomers than autopolymerized denture base materials (13) and release less formaldehyde (49). Carbon-graphite fibers *per se* exhibit good biocompatibility (16, 51-52) and recent cytotoxicity testing of the present CGFRP exhibited no cytotoxicity (Segerström et al 2008 submitted).

Great stress is exerted on a cantilever construction, especially at the areas around

the distal abutments. A fiber-reinforced polymer with even distribution of fibers and high content of fiber loading is advantageous as the mechanical properties improve (14, 16, 18). With tubes of braided fibers, a high fiber loading and an even distribution of reinforcement can be provided throughout the reinforced polymer; resulting in easy handling properties (20). With higher fiber loadings, flexural strength values can approximate that of gold (20, personal communication C Ernekli 2006). The main disadvantage of the carbon-graphite fiber is aesthetic appearance, as it is black. One way of successfully mastering this drawback is by covering the framework composite with an opaquer, in a similar manner as metallic surfaces are covered.

Good laboratory technique is important for obtaining a long lasting construction. Special considerations should be taken when making implant-retained prostheses for reducing frequent complications involving acrylic resin fracture and tooth fracture/debonding. The polymerization temperature is crucial for the bonding between polymer base and polymer teeth: with increasing temperature, higher bond strengths are achieved (53). Poor adhesion to the teeth occurs with autopolymerized denture base-materials. As heat-polymerized denture base materials provide the best bond strength between polymer teeth and base polymer (53) they should be selected.

There are conflicting recommendations regarding the treatment of polymer teeth and whether to treat with monomer liquid or not. Some claim that by treating the denture teeth with monomer liquid, bond strength increases (54-55), whereas others claim the opposite (56-58). An increase in bond strength can be achieved with bonding agents (59). Conflicting results over whether to grind the polymer teeth or not are also presented: in some studies, grinding of the ridge lap surface increases the bond strength (53, 60-61), whereas, in other studies, there is no improvement in adhesion (54-57). Another cause of tooth bond failure can be ineffectual wax elimination (62): wax retention is evident up to 90 °C and wax solvent is recommended for complete removal (63). With the same substances in the framework material and in the acrylic part of the suprastructure, the chemical bond between the two can be improved. Two important steps in obtaining a high value of tooth bond are through thorough dewaxing of tooth surfaces and through heat-polymerization.

For coating the framework and attachment of synthetic teeth, denture base polymers with improved impact resistance (containing rubber particles) are proposed, as they have better fracture toughness than conventional denture base polymers (64). The coating of CGFRP framework with such a denture base polymer provides a tougher (less brittle) suprastructure than if coated with conventional denture base polymer.

The outcome of an ongoing randomized prospective clinical study with implant-retained CGFRP frameworks appears promising, as there have been no fractures since the study started 2004.

Summary

The laboratory procedure for creating a carbon-graphite fiber-reinforced polymer framework requires less time and less expensive equipment than conventional metallic frameworks. The use of carbon-graphite fiber-reinforced polymer technology offers a biocompatible and functional alternative to conventional techniques with metallic materials as frameworks and production procedures are less complex and costs are lower. By strictly following the recommendations in the laboratory, biocompatible and long lasting suprastructures can be produced.

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