

E-Glass Fiber Reinforced Composites in Dental Applications

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Abstract Fiber reinforced composites (FRCs) are more and more widely applied in dentistry to substitute for metallic restorations: periodontal splints, fixed partial dentures, endodontic posts, orthodontic appliances, and some other indirect restorations. In general in FRCs, the fiber reinforcement provides the composite structure with better biomechanical performance due to their superior properties in tension and flexure. Nowadays, the E-glass fiber is most frequently used because of its chemical resistance and relatively low cost. Growing interest is being paid to enhance its clinical performance. Moreover, various techniques are utilized to reinforce the adhesion between the fiber and the matrix. Oral conditions set special requirements and challenges for the clinical applications of FRCs. The biomechanical properties of dental materials are of high importance in dentistry, and given this, there is on-going scientific interest to develop E-glass fiber reinforced composite systems. FRCs are generally biocompatible and their toxicity is not a concern.

Keywords Fiber reinforced composite · Resin matrix · E-glass fiber · Biomechanical properties · Biomaterial · Dental material

1 Fiber Reinforced Composite

Fiber reinforced composites (FRCs) are universally used materials in aircraft and in space applications, in the marine and automotive industries, infrastructure and building con-

struction, inner house decoration and furniture, medical applications (eg. bone plates for fracture fixation, implants, and prosthetics), sports equipment, electronics (eg. printed circuit boards) and other industrial products (eg. step ladders, oxygen tanks, and power transmission shafts) [1]. A FRC is a typical composite material made of a plastic matrix that is reinforced by fine thin fibers, which have high tensile strength and a high flexural modulus. It is also called in the literature fiber-reinforced polymer (FRP) or glass-reinforced plastic (GRP) [2].

From the microscopic point of view, the reinforcing fibers prevent crack propagation by chemically bonding to the polymer matrix with covalent bonds [3]. Some previously published research reports showed that some commercial FRCs had flexural moduli and strengths seven times those of composite resins with particulate fillers [4].

Typical FRC characteristics are as follows [5]: high strength-weight and modulus-weight ratios, high fatigue strength and fatigue damage tolerance, and anisotropic properties. In addition to that, in unidirectional FRCs, tensile strength and modulus, impact strength, the coefficient of thermal expansion, and thermal conductivity differ if they are measured in different directions to the fiber reinforcement. This means that in bi-directional or multi-directional FRCs, the above mentioned parametric value differences are smaller. These above mentioned properties give FRCs almost reinforcement capacity.

FRCs can be classified into two main types [1, 6]:

- a) a continuous/aligned fiber reinforced composite, which can confer anisotropism to various degrees, according to how many directions are involved and to the amount of fibers oriented along each direction, and
- b) a discontinuous/short fiber reinforced composite, which type includes the aligned and randomly oriented,

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discontinuous fiber reinforced composites and in the randomly oriented discontinuous FRC, isotropic properties can be obtained.

2 The Matrix in FRCs

The polymeric plastic matrix, consisting of polymerised monomers, has the function of holding the fibers together in the composite structure. It also transfers stresses between fibers and protects the fibers from the outside environment such as chemicals, moisture and mechanical shocks. Thus the matrix may influence the compressive strength, interlaminar shear and in-plate shear properties, interaction between the matrix and the fiber and defects in the composite [5]. Two types of resins, the cross-linked or linear, are used in FRCs. The cross-linking polymer is also called a thermoset polymer, referring to multifunctional or dimethacrylate resins. The linear polymer is also called a thermoplastic polymer, referring to monofunctional methacrylate polymers [1].

In FRCs with an IPN, so-called interpenetrating polymer network structure, the matrix consists of a cross-linking polymer, a linear polymer and a photo-initiator [7].

Setting reactions in the resin matrix are polymerization reactions and cross-linking reactions. A polymerization reaction is the formation of a polymer by sequential addition of monomeric units. Typical polymerization reactions are addition (including free-radical addition polymerisation) and condensation polymerizations [8]. The cross-linking reaction in a polymer refers to the formation of a cross-link where chains are bonded together either through direct connection or an intermediary atom, ion, molecule or chain. This produces a 3D strongly cross-linked system [9].

3 Fiber

A fiber may be described as an elongated uniform material with a more or less equiaxed and uniform transverse cross-sectional diameter or thickness less than 250 μm , and with an aspect ratio, i.e. length to cross-sectional diameter or thickness ratio, which is usually greater than about 100. However, in some cases, such as short fibers, chopped fibers, whiskers or staple fibers, the fibers' aspect ratio can be smaller than 100 [10]. The fiber orientation, content, distribution and the ability to maintain these parameters are significant for the reinforcement and thereby clinical success. The fiber's type, length, orientation and volume fraction influence the following properties of the FRC [5]: their tensile strength and modulus, compressive strength and modulus, fatigue strength and fatigue failure mecha-

nism, density, electrical and thermal conductivity, and finally their cost. Some typical fibers used are glass, PE (polyethylene), polyester, carbon/graphite (C/G), aramid, quartz and ceramic fibers [1].

4 Glass Fiber

Thin strands of silica-based, SiO_2 , or other formulation glasses are extruded into many fibers with small diameters suitable for example textile manufacturing and they are manufactured as staples, in other words, naturally formed clusters or locks of wool fibers [11]. Commonly applied glass fibers for FRCs are E-glass and S-glass fiber. E-glass fiber consists of about 54.5 wt% SiO_2 , 14.5 wt% Al_2O_3 , 17 wt% CaO , 4.5 wt% MgO , 8.5 wt% B_2O_3 , 0.5 wt% Na_2O , S-glass fiber consists of 64 wt% SiO_2 , 26 wt% Al_2O_3 , 10 wt% MgO respectively [1]. Different glass fiber types are listed in Table 1.

Commercially available glass fibers are formed in the form of strands, chopped strands, woven rovings or woven cloth (or veil). In strands, the fibers can form bundles consisting of 200 or more parallel individual filaments. The chopped strand is the resulting form after cutting the continuous strands into a short length. Woven roving is a fabric in which continuous rovings are woven in two mutually perpendicular directions. Woven cloth and veil refer to a fabric in which twisted continuous strands are woven [1].

5 E-Glass Fiber

E-Glass fiber ("E" stands for electric) is made of aluminoborosilicate glass with less than 1 wt% alkali oxides. Some other elements may also be present at low impurity levels. A typical nominal chemical composition of E-glass fibers is SiO_2 54 wt%, Al_2O_3 14 wt%, $\text{CaO} + \text{MgO}$ 22 wt%, B_2O_3 10 wt% and $\text{Na}_2\text{O} + \text{K}_2\text{O}$ less than 2 wt% [1]. Some reported advantages and disadvantages of E-glass fibers are listed in Table 2.

6 Adhesion Between Fiber and Matrix

Silanes are hybrid inorganic-organic chemical compound in which a carbon is directly attached to silicon, eg. $\equiv\text{Si}-\text{C}\equiv$. These compounds are silicon esters and used as coupling agents in silanization treatment, sometimes called a silanation. This refers to the surface treatment aiming at promotion of bonding dissimilar matrices together [12–15].

Preimpregnation means that the fibers are impregnated with the matrix resin before further steps in the fabrication

Table 1 Types of glass fiber [1]

Type	Manufacturing	Composition	Characteristics	Application
A-glass	Produced from cullet glass (often bottle) to fiber	Alkali-lime with little or no boron oxide	Not very resistant to alkali	When alkali resistance is not a requirement
AR-glass			Resistant to alkali	When alkali-resistance is required
C-glass (T-glass)	From used glass staple fibers	Alkali-lime with high boron oxide content	Resistant to chemical attack and most acids which dissolve E-glass	When higher chemical resistance to acid is required, for example for glass staple fibers
D-glass		Borosilicate	High dielectric constant	When high dielectric constant is preferred
E-glass		Alumino-borosilicate with less than 1 wt% alkali oxides	Not chloride-ion resistant; E-glass surface is soluble	Mainly for glass-reinforced plastics; originally for electrical applications
E-CR-glass		Alumino-lime silicate with less than 1 wt% alkali oxides	High acid resistance	When high acid resistance is required
R-glass		Alumino silicate without MgO or CaO	Good mechanical properties	With high mechanical requirements
S-glass		Alumino silicate without CaO but with high MgO content	Highest tensile strength among all types of fiber	Aircraft components and missile casings, when high tensile strength required

of the final restoration in dentistry. One current fiber reinforcement system based on preimpregnation utilizes highly porous linear polymers to preimpregnate the fibers. Given this, the high-viscous denture base resin is subjected to further impregnation [16].

It is noteworthy that the use of natural rubber and thereafter synthetic polymers as denture base polymers had already started in the 1860s. The introduction of a denture base polymer of poly(methyl methacrylate) (PMMA) occurred in the late 1930s. With the introduction of cross-linking thermoset monomers in dentistry by Bowen, cross-linking dimethacrylate monomers became available also for monomer liquids of denture base resins and, thus, in multiphase denture base polymers—the start of the use of interpenetrating polymer network (IPN)-like structures in dentistry. As a concept, an IPN is a combination of two or

more polymers in network form that are synthesized in juxtaposition. IPNs are composed of finely divided phases with a thickness of appr. 5–10 nm. They differ from polymer blends which are rougher in structure, and also differ from copolymers which are based on chemical reactions of monomer units and polymer backbones [17].

Today in dental materials, IPN-like nanostructures are formed and they are formed in denture base polymers, denture teeth and fiber-reinforced composites and very recently in some novel restorative composite resins. In adhesive interfaces, IPN polymers and composites provide good interfacial adhesion to resin composites based on the secondary-IPN bonding due to swelling of the IPN nanostructure. Several adhesive interfaces between natural and synthetic biomaterials and adhesive resins by means of primers or coupling agents can also be considered as IPNs.

Table 2 Advantages and disadvantages of E-glass fibers [1]

Advantages	Disadvantages
Low cost and high production rates	
Relatively low density	Higher density compared to carbon and organic fibers
	Low tensile modulus
Able to maintain strength properties over a wide range of conditions	Self-abrasive if not treated and the tensile modulus decreases if abraded
Relatively insensitive to moisture	Relatively low fatigue resistance
Chemical-resistant	Chloride ions attack and dissolve E-glass surface
Non-flammable and heat-resistant	

Some other interfaces are a dentine bonding hybrid layer, silane promoted adhesive interphases between metal and ceramics and adhesive resins. On the other hand, the so-called semi-IPN refers to the impregnation methods based on using a combination of thermoset and thermoplastic types of resins. Here, the polymer matrix is a multiphase material. The semi-IPN is formed during the polymerization of the dimethacrylate monomers with a swelled linear polymer, PMMA [7].

In addition to the above methods, plasma-etching has also been applied to enhance polyalkane fiber's adhesion to the matrix [18].

It is also noteworthy that durable adhesion between fiber and matrix provides good load transfer between the two, which ensures that the load is transferred to the stronger fiber and this is how the fiber actually works as a reinforcement. However, if the adhesion is not so durable and if any voids appear between the fiber and the matrix, these voids may act as initial fracture sites in the composite and facilitate the breakdown of the material [19]. Given this, durable adhesion between the fiber and the matrix is significant for the mechanical performance and the longevity of restoration in dental applications [20].

7 Oral Conditions

The oral cavity can be considered a hostile environment with cyclic masticatory loads, pH variation, temperature variation, saliva, proteins and blood [21].

Maximum occlusal forces can be up to 900 N in the molar region in young adults and chewing forces in the range of 100–300 N. According to a DIN standard, a fixed partial denture should withstand more than 1000 N occlusal force in a static fracture resistance test. The maximum occlusal force may be applied 3000 times per day. Combining all these considerations together, a fixed partial denture has to meet great cyclic loads for a long time in everyday use [22].

Commonly applied artificial aging of test specimens *in vitro* is based on cyclic thermal fluctuation that takes place at 5 °C to 55 °C and is repeated for 6000 times to simulate the oral conditions [23]. The literature also suggests some other regimens for scientific research: 35 °C (for 28 s), 15 °C (for 2 s), 35 °C (for 28 s), 45 °C (for 2 s) and even 10000 cycles per year [24].

Left alone, the saliva and blood in oral conditions might have an influence on the water sorption and the general dimensional stability (incl. solubility) of dental materials.

8 Mechanical Properties of FRC

The term “hardness” refers to resistance to deformation, indentation, scratching and wear of a body material.

Hardness is a surface phenomenon influenced by yield strength, true tensile strength, work hardening, elastic modulus and so on [9, 25]. There are various standard testing methods for hardness, such as Brinell, Vickers, Knoop, Rockwell, Rockwell superficial and Shore scleroscope [26].

Flexural strength refers to the maximum stress and strain at the surface of the specimen [8]. Now, flexural modulus is a measure of the stiffness during the first or initial step of bending a body (material). It is calculated according to an ASTM D-790 standard: mathematically it is the slope of the initial straight line portion on the stress–strain curve [27]. In laboratory experiments, several factors have effects on the flexural properties. According to some previous research, thermo-cycling, the brand of the FRC material and diameter of the specimen may have a significant effect ($p < 0.001$) on flexural strength of FRC root canal posts [28]. Furthermore, fatigue strength refers to the stress that causes failure after some specified number of loading cycles [9]. In the aspect of fatigue strength, FRCs are considerably stronger than typical cast metal alloys used in dentistry [29]. In clinical use, biomechanical properties of dental materials vary depending on which application the material is utilized. For instance, in a direct fibre-reinforced resin-bonded dental bridge, the weakest region exists across the pontic–abutment interface [30].

9 Biocompatibility and Toxicity

Polymerization shrinkage, residual monomers and short fibers and nano-particles may cause incompatibility. In general, the initial resin monomers in FRC may reach a conversion rate between 35% and 77% through polymerization, when cured [8]. The accompanying polymerization shrinkage indirectly influences tissue compatibility. The volume change may cause a marginal gap between the restorations and tooth tissues, which induces the bacterial penetration and thus advance pulpitis [31].

The residual monomers may directly cause some adverse biological reactions. These residual monomers include principally benzoyl peroxide and acrylic monomers. Some common residual monomers and their abbreviations are listed in Table 3. Besides, formaldehyde and glutaraldehyde can also be found as residual monomers after polymerization [32].

Filler content also influences cytotoxicity. For instance, so-called flowable resin-based composites that are intended for luting agents and metal facings to endodontic posts and cores, have been reported to be significantly more cytotoxic over a longer period of time compared with similar types of resin composites for posterior region restoration with lower filler content [33]. Mutagenicity and carcinogenicity may

Table 3 Some monomers and their abbreviations [33]

Monomer	Abbreviation	Role in FRCs
<i>bis</i> -phenol-A-diglycidylmethacrylate	<i>bis</i> -GMA	Cross-linking monomer in matrix
Methyl methacrylate	MMA	Linear monomer
Urethane dimethacrylate	UEDMA	Cross-linking monomer
Triethylene glycol dimethacrylate	TEGDMA	Cross-linking monomer
Ethylene glycol dimethacrylate	EGDMA	Cross-linking monomer
Hydroxyethyl methacrylate	HEMA	Linear monomer
Camphorquinone	CQ	Photo-sensitizer
<i>N, N</i> -cyanoethyl methylaniline	CEMA	Reducing agent

be caused by the chemicals, such as *bis*-GMA and TEGDMA, or the 450 nm-wavelength light involved in photo-polymerization of light-cured FRCs. The ‘no-touch’ technique, i.e. using leather or common gloves and neoprene gloves may prevent these two adverse effects [34].

Resin-based composites may also promote bacterial growth in an oral environment. These bacteria include *Streptococcus sobrinus*, *Lactobacillus acidophilus* and so on. Since marginal adaptation is an important aspect in the restoration design, some antibacterial monomers may become less effective after polymerization. In clinical service, resin-based composites induce more significant inflammation than amalgams or gold alloys do. This is probably due to the increased plaque accumulation on the surface of resin-based composites [35].

10 Dental Use of FRC

In general, the current dental use of FRCs’ falls into three categories: direct-placement splints, endodontic posts, fixed partial dentures and indirect restorations, such as bridges and crowns [36]. Arch-wires in orthodontic brackets are usually made of stainless steel or Cr-Co alloy, but also of Ti and its alloys. Nowadays, FRCs are more and more substituting metallic biomaterials because metallic biomaterials are always accompanied with aesthetic problems. By optimizing the fiber-to-matrix ratio, a range of elastic stiffness could be obtained [37]. As a splinting of two-tooth segments, the FRC support could withstand chewing forces within the experimental period of 8.5 years as has been reported [38]. With a FRC as a splinting material, the aesthetics are not a concern. However, the biggest challenge has been considered to be the contact of the splinting material to all the teeth to be splinted [39]. In some other applications, porcelain and FRC may be combined together to build up a 3-unit bridge, which may satisfy the demands of strength, resilience and aesthetics [40]. In another study, a fixed bridge was composed of a preimpregnated and unidirectional FRC substructure and a hybrid particulate

composite veneer. Since the substructure occupied a sufficiently large volume, the fixed bridge could serve for up to four or more years [41]. According to a published clinical report, FRC fixed partial dentures could serve for 5–10 years [42]. Moreover, FRCs have become a choice of material for immediate tooth replacement because of the convenience of this technique that can be carried out at the dentist’s office [43]. A FRC has also been applied for molar crown fabrication and these crowns demonstrated satisfying long-term performance [44].

In a recent patent, a FRC post was composed of an inner core rod and an outer fiber mesh. The inner core rod was fibers impregnated in the resin matrix. As for the outer fiber mesh, its inner surface was attached to and embedded in the resin matrix of the inner core section and its outer surface was dry, unimpregnated fibers [45].

11 Conclusion

In contemporary dentistry, better adhesion and biomaterials with superior biocompatibility are continuously sought. By fulfilling well the clinical and in general biomechanical requirements, FRCs would develop as important biomaterials also in the future. Given this, long term reports are still necessary and challenges exist: would FRCs remain as temporary or develop to be permanent restorative materials. As one of the current hot spots in research, the chemical composition of the matrix merits much attention to ensure its biocompatibility.

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