# TEXTILE PREFORMS FOR DENTAL APPLICATIONS

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## *Abstract:*

*Dentistry has advanced to the use of FRCs, which helps patients to live their lifetime with their dentition intact. A large number of developments in the field of fibrous composite implants and devices for orthopaedic and dental applications have taken place. The present paper discusses the applications of fibre- and textile-reinforced composites in dental practices, mainly focussing on periodontal splinting. The conventional methods of splinting and the design & use of fibre-reinforced composites as restoratives to stabilise and splint teeth have been discussed in detail. The current controversy of incorporating implants in patients requiring splinting is discussed in relation to the various fibres applied as reinforcement for the splinting material.*

## *Key words:*

*Dental materials, fibre-reinforced composites, periodontal splinting, splinting materials.*

## Introduction

Composite materials have enabled significant advances in the medical field. Their range of applications is wide, and includes well-publicised uses in orthopaedic & prosthetic devices and components for large-scale medical resonance imaging equipments [1]. The versatility of polymers, polymeric fibres and polymer composites is creating a growing worldwide demand for these materials in a wide variety of applications. Fibre-reinforced composites have demonstrated a high resistance to wear, and may therefore be advantageous for dental applications, where high wear resistance is essential to functionality [2]. Dental practices involve the use of clips, plates and pins of metal that are commonly referred to as splints and restorations. The functions of a splint include post-orthodontic retention and stabilisation, tooth replacement and periodontal splinting [2].

Periodontal disease, a condition of weakened teeth due to bacterial growth, requires these splints and restorations during treatment to resist the load-bearing forces of occlusion and mastication [3]. The combination of chemical adhesive and aesthetic characteristics of composite resin with the high-performance fibres used as the splinting materials was found to have superior properties compared to conventional splinting materials [1]. A large number of developments in fibrous composite implants and devices for orthopaedic and dental applications have taken place [3, 4]. Apart from biocompatibility, aesthetic property is also required for fibrous composites in dental applications [2].

The excellent handling properties of the fibres and matrix systems, their ability to adapt to any shape and the availability of light curable matrix systems have imparted ease of chair-side handling to fibrous composites [4]. Their superior mechanical properties coupled with their ease of construction have increased their usage in dental applications [1]. Long slender fibrous materials were investigated clinically to reinforce multiple tooth appliances such as dentures, retainers and splints [2].

Different fibre and matrix combinations as well as various constituent material compositions were studied to achieve the required performance for splinting [5]. Especially in moist environments, the interface between fibre and matrix has a significant effect on the performance of fibrous composites [6].

Nowadays, changing demographic trends in dental practice have revealed an increase in the number of older adults seeking care. Improvements in periodontal therapy have allowed them to keep their natural teeth intact for longer periods of time [7]. These facts have been clinically investigated, and treatment to reduce the mobility of periodontally involved teeth by means of splinting has been accepted [5]. In this review, an overview of splinting materials is presented and the suitability of fibre-reinforced composites used for splinting has been analysed.

## Splinting

Splinting is the process of stabilising weakened tissues using reinforcement composites and resins [4]. Splinting is applied as a support for bone fractures or cracks and weak mobile teeth. In the case of periodontal treatment, splinting is carried out for either permanent or temporary immobilisation and the stabilisation of affected teeth. A broad classification of the denture base materials is shown in Figure 1 [8].

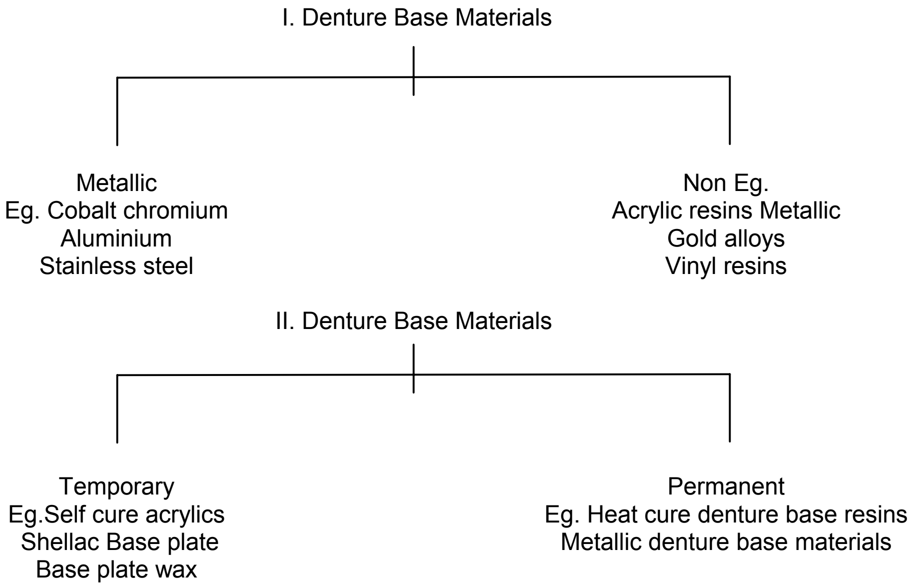


**Figure 1.** Classification of denture base materials [8]

**<u>Temporary crowns and bridges</u>**

The fabrication of a crown or fixed bridge is generally a laboratory procedure, and several weeks may elapse between the preparation of the teeth and the cementation of the permanent restoration. Therefore a temporary restoration must be made in order to provide protection to the pulp from thermal and chemical irritation caused by food and liquids, for positional stability, mastication and aesthetics.

The requirements of temporary crowns and bridges are as follows [8]:

- should be non-irritating to soft tissues and pulp;
- should have adequate strength to withstand forces of mastication;
- should have good texture, contour, colour, and translucency;
- should display low thermal conductivity;
- should display low dimensional change and low exothermic reaction;
- should be easy to manipulate

The available crowns are in a form that can be luted directly to prepared teeth after adjustment, or which may be relined with a plastic material prior to cementation. The preformed crowns are made from various materials such as polycarbonate, cellulose acetate, aluminium, tin-silver, and nickel-chromium.

**Polycarbonates**

This is high impact-resistance polymer. It has the most natural appearance of all the preformed crowns. It is available only in a single shade. They are supplied as incisor, canine, and premolar shapes.

**Cellulose acetate crowns**

Cellulose acetate is a thin transparent material available in all tooth shapes and a range of sizes. The tooth-coloured chemically-activated resin is mixed and filled in a preformed cellulose acetate shell. After the acrylic resin sets, the cellulose acetate is peeled off and discarded, and the crown is trimmed and cemented.

**Temporary restorative materials**

Temporary restorations can also be custom-made from resin. Custom-made restorations have an advantage over the preformed variety in that the original tooth morphology is more easily reproduced, as are the relationships with adjacent and opposing teeth.

Temporary restorative materials fill the cavity formed by the external and tissue surface forms while in a fluid state, and then they solidify, producing a rigid restoration.

The materials used are:

1. polymethyl methacrylate resins;
2. polymethyl (isobutyl) methacrylate resins;
3. epimine resins;
4. microfilled composite resins;

A comparative study of restorative materials is shown in Table 1 [8].

**Table 1.** Comparative study of restorative materials [8]

| S.No | Restorative Materials | Advantages | Disadvantages |
|---|---|---|---|
| 1. | Polymethyl methacrylate resins | Acceptable mechanical properties, colour stabiliy is better than that of poly ethyl methacrylate resins | High polymerisation shrinkage, high heat liberation during setting and high irritation to gingival tissues |
| 2. | Polymethyl (isobutyl) methacrylate resins | Less polymerisation shrinkage and heat liberation, Flow better during adaptation and less irritation to soft tissues | Less tensile strength and poor colour stability |
| 3. | Epimine resins | Less polymerisation shrinkage, Less exothermic heat and good flow properties | Tissue irritation, Poor impact strength, poor resistance to abrasion and expensive |

## Removable partial dentures

An important step in maintaining a healthy smile is to replace missing teeth. When teeth are missing, the remaining ones can change position, drifting into the surrounding space. Teeth that are out of position can damage tissues in the mouth. In addition, it may be difficult to clean thoroughly between crooked teeth. The result is a risk of tooth decay and periodontal (gum) disease, which can lead to the loss of additional teeth.

A removable partial denture fills in the space created by missing teeth. A denture helps to properly chew food, a difficult task when missing teeth. In addition, a denture may improve speech and prevent a sagging face by providing support for lips and cheeks.

Removable partial dentures usually consist of replacement teeth attached to pink or gum-colour plastic bases, which are connected by metal framework. Removable partial dentures attach to the natural teeth with metal clasps or devices called precision attachments. Precision attachments are generally more aesthetic than metal clasps, and they are nearly invisible. Crowns on the natural teeth may improve the fit of a removable partial denture, and are usually affixed with attachments. Dentures with precision attachments generally cost more than those with metal clasps.

## Need for splinting

Splinting has been recommended to reduce tooth mobility and for patient comfort [2]. Once the biological controls are in place and the disease is stabilised, the splint's mechanical influence will then aid the weakened condition of the periodontal ligament system [3]. Splinting is also used to distribute and redirect functional and para-functional forces to the teeth, and to bring the teeth and tissues within the tolerance level [5]. Among the various stabilisation techniques followed for stabilisation or immobilisation of teeth, splinting of periodontally involved teeth has been proved successful by long-term clinical evaluation [2].

A range of methods for dental composites such as a partial denture, a conventional fixed bridge, a resin-bonded bridge or an implant has advantages and disadvantages such as overall complexity, cost and difficulties with oral hygiene [9,10]. The various methods of splinting are removable-to-fixed appliance therapy, and range from conservative non-invasive procedures to intensive, time-consuming irreversible methods that involve multifaceted materials [5].

The applications of a splint are [5]:

- splinting loose anterior teeth caused by periodontitis or trauma;
- fibre-implantation of extracted or totally luxated anterior teeth to act as a long-term temporary bridge;
- reinforcing temporary crowns and bridges fabricated in the mouth or the laboratory;
- reinforcing acrylic denture repairs.

## Splinting procedure

The splinting material is used for strengthening the dental resin. It should be handled carefully since there are chances that the reactive surface layer may be contaminated by finger oils, acids or talcum powder from rubber or vinyl gloves [4].

The flow chart shown in Figure 2 explains the splinting procedure for periodontally affected teeth [11].

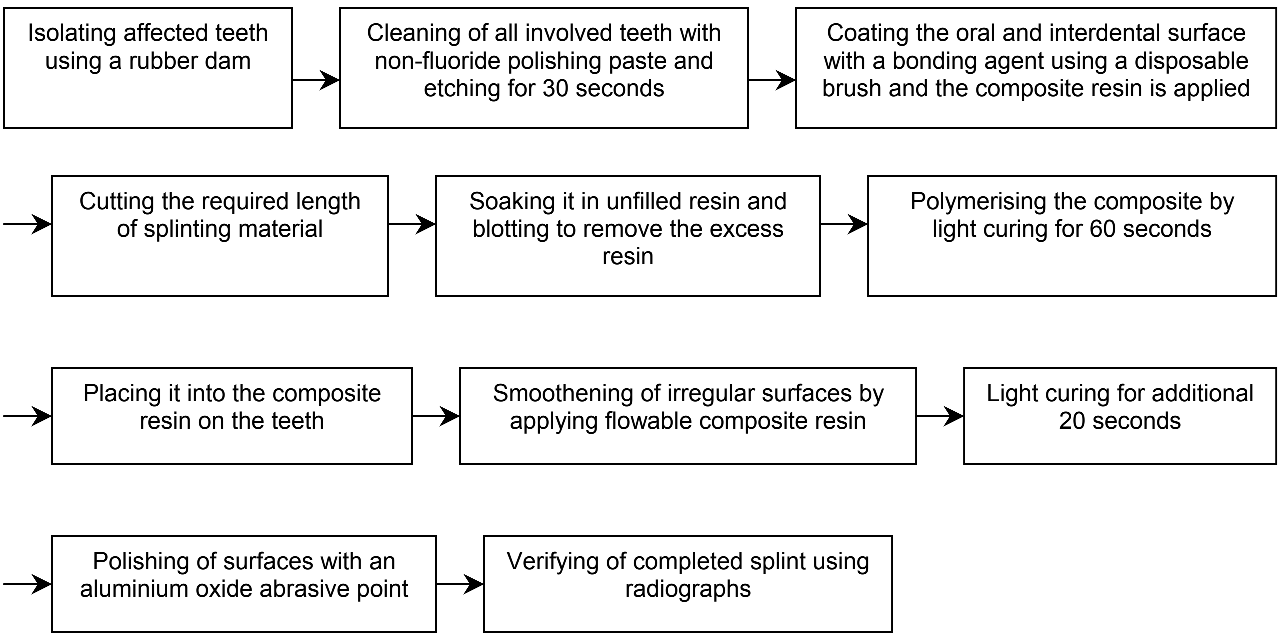


**Figure 2.** Splinting procedure [11]

## Splinting materials

### Conventional methods

In the past, wires, pins, mesh grids, etc were used in direct stabilisation and splinting of teeth using an adhesive technique [2]. The resin-bonded bridge, usually with a metal substructure, is the least invasive method to conserve as much tooth structure as possible [12]. The spectrum of available methods include fixed, removable, combination, intra-coronal and extra-coronal devices, bonding with acrylic resins, wires, bands, plastics, composites, pipes, plates, screws, amalgam, cemented, bonded or removable castings as well as commercial kits of prefabricated material [5].

Restoration using a metal substructure requires significant laboratory work, and the cost of the metal is high [13]. Debonding at the interface of metal- or enamel-composite cement can also be a problem. This is because they could only mechanically lock around the resin restorative, and were not chemically integrated [3]. The interface created between the composite resin or acrylic resin and wire, pins or grid mesh and the potential of creating shear planes and stress concentrations would lead to breakage and the premature failure of the splinting material [2].

The clinical failures seen were generally due to the lack of bulk of composite resin or acrylic resin when used with these splinting materials, which further weakened the already weak affected tissues [3]. When any restorative resin is placed as a thin veneer (cover) over a mesh for splinting teeth, it exhibits poor load bearing properties [9]. The failure of the splint can result in the progression of periodontal disease. However, a mesh-type splint with over-bulked composite resin would result in significant plaque retention and tissue inflammation [14].

## Reactions of bone and soft tissues to implant materials [15]

***Ceramics:*** These have the general composition of quartz, feldspar and kaolin. Most ceramic materials have very low toxic effects on tissues, either because they are in an oxidised state or are corrosion resistant. Their disadvantages are that they are brittle and lack impact and shear strength.

***Pure metals and alloys:*** These are the oldest type of oral implant materials. All metal implants share the quality of strength. A variety of implant materials have been used, including stainless steel, chromium-cobalt-molybdenum and titanium & its alloys. Stainless steel has mostly been used because it is inexpensive, easily available and strong. It can be cast or wrought and can be fabricated into various forms. However, stainless steel is susceptible to corrosion in a saline environment such as tissue fluid. With corrosion, it undergoes metal fatigue, which immediately leads to implant failure. The corrosion products cause adverse inflammatory reactions.

***Cobalt-chromium-molybdenum alloys:*** These are castable and have been used in dentistry for about 40 years. The elements released from the implants accumulate locally and in systematic organs such as the lung, liver and kidney.

***Titanium:*** It is difficult to cast. When it is wrought into endosteal blades, metallic impurities are introduced into the surface that may adversely affect bone response. Though the corrosion rate is lower than other metals, titanium and titanium alloy implants can release titanium into the body.

***Reactions to other materials:*** Polymer cements have been used for fixation in dentistry and orthopaedics. The most common of these is polymethyl methacrylate (PMMA) cement. The biological response to PMMA cements is not favourable, because the monomer is quite toxic to the bone tissue and the heat generated during the setting can kill tissue.

## Requirements of a splint

A simpler approach of splinting is to construct direct, resin-bonded, fibre-reinforced composites using the dental resins to obtain a firm bond to the enamel of teeth [3]. The advantage of this approach is the savings of laboratory time, materials and cost. An evaluation of various reinforcement fibres used for splinting teeth for their effect on properties and performance of a splint in the clinical trials have shown that all fibres improved the flexural strength and flexural modulus of composite resin [1, 16].

The performance of the splint fabricated using the fibre-reinforced materials were also clinically successful after one year [2,17].

The material should be thin and flexible so that there is no difficulties in cleaning of teeth and it could be pressed into the interstices between teeth [18]. Hence "the challenge to the clinicians is to place a thin but strong composite resin-based splint" [4]. It should be bondable, biocompatible, aesthetic and easily manipulated [19].

## Fibre-reinforced composites

A composite may be defined as a bi-phase or a multi-phase material that is made by combining two or more materials differing in composition or form, which remain bonded together but which nevertheless retain their identity and properties [2]. Fibre-reinforced composites possess a fibrous phase as their reinforcement with a soft matrix for holding the fibres together [20]. The matrix contributes to the cohesion of the product by keeping the fibres in the desired location and orientation [21]. Furthermore, it protects them from abrasion and from environmental damage due to elevated temperature and humidity [22].

### Adhesion between fibre and matrix[14]

If the adhesion between the two phases is non-existent or very poor, the stress transfer is poor and the full advantage of the reinforcement is not obtained [23]. The presence of the fibre influences the surrounding matrix. The matrix extending to about 0.1μm around the fibre of 10μm diameter will have different characteristics than a matrix which is far from the fibre [20]. It is in this interfacial region that stress transfer takes place, which is performed by the matrix in which the fibres are embedded [24].

### Matrix materials

It is essential that a composite product based on a specific reinforcing fibre should be used for design and manufacture; the choice of the matrix should be made considering both the phases as parts of a total system and the end use of composite [22]. Matrices based on polymers, which can be thermosetting or thermoplastic, are extensively used [20]. The interface between the fibre and matrix has a significant effect on the performance of fibrous composites, especially in moisture. This effect acquires significant importance since the dental composites are to be used in the mouth where a moist environment prevails [2].

The selection of matrix polymers is important since some polymers show toxic or inflammatory reaction with human tissues. Generally, thermoset polymers are not completely polymerised, and some monomers still exist in the material after polymerisation [1]. For dental applications, polycarbonate, polyurethane and acryl base polymers such as polymethyl methacrylate (PMMA) and bisphenol-A glycidyl methacrylate (bis-GMA) were reinforced by fibres [5].

## Dental resins

Synthetic resins are non-metallic compounds synthetically produced which are moulded into various forms and then hardened for commercial use (e.g. clothing, electronic equipment, building materials and household appliances) [25]. These materials are composed of polymers or complex molecules of high molecular weight.

The types of resins used in dentistry are:

1. acrylic resins,
2. vinyl resins,
3. polystyrene,
4. epoxy resins,
5. polycarbonates,
6. polyurethane, and
7. cyanoacrylates

Due to their heterogenous structure and complex nature, it is difficult to classify them. Based on their thermal behaviour, they are classified as follows [26]:

1. ***Thermo plastic:*** this refers to resins that are softened and moulded under heat and pressure without any chemical change occurring. They are cooled after moulding. They are fusible and are usually soluble in organic solvents, e.g. polymethyl methacrylate, polyvinyl acrylics and poly styrene

2. ***Thermo set:*** this refers to resins in which a chemical reaction takes place during moulding. The final product is chemically different from the original substance. Reheating like the thermoplastic resins cannot soften them. They are generally infusible and insoluble. Generally, thermoset polymers are not polymerised completely, and some monomers still exist in the material after polymerisation [1], e.g. cross-linked poly (methyl methacrylate), silicones, etc.

**Ideal requirements of dental resins** [8]

Generally dental resins are utilised in various applications such as the preparation of dentures, artificial teeth, teeth restoration, cements, orthodontic space maintainers and elastics, crown and bridge facings, maxillofacial prosthesis, inlay patterns, implants, dies, temporary crowns, endodontic filling material, athletic mouth protectors, and impression trays.

Dental resins should exhibit the following qualities:

- tasteless, odourless, non-toxic and non-irritant to oral tissues;
- aesthetically satisfactory, i.e., should be transparent or translucent and easily pigmented. The colour should be permanent;
- dimensionally stable, should not expand, contract or warp during processing and subsequent use by the patient;
- should have adequate strength, resilience and abrasion resistance;
- should be insoluble and impermeable to oral fluids;
- should have a low specific gravity (light in weight);
- its softening temperature should be well above the temperature of any hot foods or liquids likely to be taken in the mouth;
- should be easy to fabricate and repair;
- should have good thermal conductivity;
- should be radio-opaque (so that a denture or a fragment of a broken dentures can be detected by X-rays if accidentally inhaled or swallowed, and also to examine the extensions of the resin restoration in a tooth).
- If used as a filling material:
    a) it should bond chemically with the tooth;
    b) the coefficient of thermal expansion should match that of the tooth structure.

No resin has yet been found that will meet all the above requirements.

## Basic nature of polymeric resins

The structure of polymers may be linear, branched or cross-linked. The polymerisation reactions are of three types, namely addition, condensation and copolymerisation. All resins employed extensively in dental practices are mostly produced by addition polymerisation [25]. There is no change in chemical composition, and no by-products are formed during the formation of macromolecules. The four stages in polymerisation process are initiation or induction, propagation, termination and chain transfer.

The dental resin polymerisation processes are usually activated by one of three induction systems [26]:

*a)* ***Heat activation***

Most denture base resins are polymerised by this method. For example, the free radicals liberated by heating benzoyl peroxide will initiate the polymerisation of methyl methacrylate monomer.

b) ***Chemical activation***

This system consists at least two reactants, and undergoes chemical reaction by liberating free radicals when they are mixed. For example, the use of benzoyl peroxide and an aromatic amine (dimethyl-p-toluidine) in the self-cured dental resins.

c) ***Light activation***

In this system, photons of light energy activate the initiator to generate free radicals that in turn can initiate the polymerisation process. For example, camphroquinone and an amine will react to form free radicals when they are irradiated with visible light.

## Restorative resins

The direct filling resins are of two types, namely

1. unfilled resins-acrylic resins
2. composite resin

**Acrylic resins**

The acrylic resins are derivatives of ethylene and contain a vinyl group in their structural formula [28]. The acrylic resins are the derivatives of ethylene and contain a vinyl group in their structural formula.

The acrylic resins used in dentistry are the esters of:

1. acrylic acid, $CH_2CHCOOH$
2. methacrylic acid, $CH_2=C\ (CH_3)\ COOH$

Acrylic resins, available in the form of methyl methacrylate (liquid) and polymethyl methacrylate (powder) cover about 95% of the dental resins used today [8].

There are at least two acrylic resin series that are of dental interest. Although the poly acids are hard and transparent, their polarity, related to the carboxyl group, causes them to absorb water. The water tends to separate the chains and to cause a general softening and loss of strength. However, the esters of these polyacids are of considerable dental interest.

They are supplied as powder and liquid. The powder contains polymethyl methacrylate as beads or grindings, benzoyl peroxide (0.3 to 3%) as initiator and colour pigments. The liquid contains methyl methacrylate monomer, ethylene dimethacrylate (5%) as a cross-linking agent and hydroquinone (0.006%) as an inhibitor.

There are three systems of activation and initiation:

a) the amine peroxide system,
b) the mercaptan-peroxide system, and
c) the sulphinate curing system.

The various manipulation methods are [28]:

- the pressure or bulk technique,
- the non-pressure or bead technique,
- the flow technique, and
- cavity lining agents.

**Methyl methacrylate**

Polymethyl methacrylate is the hardest resin of the series with the highest softening temperature. Ethyl methacrylate possesses a lower softening point and surface hardness, and n-propyl methacrylate has an even lower softening point and hardness. Polymethyl methacrylate by itself is not used in dentistry to a great extent in moulding procedures. Rather, the liquid monomer methyl methacrylate is mixed with the polymer, which is in powdered form [8]. The monomer partially dissolves the polymer to form a plastic dough. This dough is packed into the mould, and the monomer is polymerised by one of the methods discussed previously. Consequently, the monomer methyl methacrylate is of considerable importance in dentistry.

The important properties of methyl methacrylate monomer are [29]:

- clear, transparent, volatile liquid at room temperature
- melting point - 48ºc
- boiling point – 100.8ºc
- density – 0.945 gm/ml at 20ºC
- heat of polymerisation – 12.9 Kcal/mol
- volume shrinkage during polymerisation – 21%
- exhibits a high vapour pressure
- excellent organic solvent

Although the polymerisation of methyl methacrylate can be initiated by ultraviolet light, visible light, or heat, it is commonly polymerised in dentistry by the use of a chemical initiator. The conditions for the polymerisation of methyl methacrylate are not critical, provided that the reaction is not carried out too rapidly. The degree of polymerisation varies with the conditions of polymerisation, such as the temperature, method of activation, type of initiator, initiator concentration, purity of chemicals, and similar factors. Because they polymerise readily under the conditions of use, the methacrylate monomers are particularly useful in dentistry [8]. Many other resin systems do not polymerise at room temperature in the presence of air.

## Polymethyl methacrylate

Polymethyl methacrylate is manufactured industrially by free radical polymerisation for preparing clear sheets, rods, etc., and by solution polymerisation for surface coating. The molecular weights of final polymers range from 90,000 to about 1,000,000 [27]. Polymethyl methacrylate meant for injection moulding and extrusion is prepared by suspension polymerisation with a molecular weight of 60,000.

Polymethyl methacrylate is a transparent resin of remarkable clarity; it transmits light in the ultraviolet range to a wavelength of 250nm. It is a hard resin with a Knoop hardness number of 18 to 20 [8]. Its modulus of elasticity is approximately 2.4 GPa.

The resin is extremely stable. It does not discolour in ultraviolet light, and it exhibits remarkable aging properties. It is chemically stable to heat and softens at 125°C, and it can be moulded as a thermoplastic material. Between the temperature and 200°C, depolymerisation takes place. At approximately 450°C, 90% of the polymer depolymerises to the monomer. Polymethyl methacrylate of high molecular weight degrades to a lower polymer at the same time that it converts to the monomer.

The performance properties of polymethyl methacrylate are as follows:

- density – 1.19 gm/cm$^3$
- compressive strength – 75 MPa
- tensile strength – 52 MPa
- volume shrinkage during polymerisation – 8%
- virtually insoluble in water and all oral fluids

Like all acrylic resins, polymethyl methacrylate exhibits a tendency to absorb water by a process of sorption. Its non-crystalline structure possesses a high internal energy; thus, molecular diffusion can occur into the resin, because less activation energy is required. Furthermore, the polar carboxyl group, even though esterified, can to a limited extent form a hydrogen bridge with water.

Because both absorption and adsorption are involved, the term sorption is usually used to describe the total phenomenon. Typical dental methacrylate resins show an increase of approximately 0.5 wt%

after 1 week in water. Higher values have been reported for a series of methyl methacrylate polymers. The sorption of water is nearly independent of temperature from 0°C to 60°C, but is markedly affected by the molecular weight of the polymer. The greater the molecular weight, the smaller is the weight increase. Sorption is reversible if the resin is dried. Because polymethyl methacrylate is a linear polymer, it should be soluble in a number of organic solvents, such as chloroform and acetone.

They are widely used in dentistry for fabrication. Although it is a thermoplastic resin, in dentistry it is not usually moulded by thermoplastic means. Rather, the monomer methyl methacrylate in liquid form is mixed with the polymer in powder form [30]. The monomer plasticises the polymer to a dough-like consistency, which can be easily moulded.

Based on the methods of activation, these are classified as [8]:

1. heat-activated resins,
2. chemically-activated or self-curing or cold-cure or auto-polymer resins, and
3. light-activated resins.

A comparative study on the properties of heat-activated and chemically-activated resins are shown in Table 2 [26].

**Table 2.** Comparison of heat activated and chemically activated resins [28]

| S.No | Property | Heat activated resins | Chemically activated resins |
|---|---|---|---|
| 1 | Available form | Powder or liquid, gel-sheets or cakes | Powder and liquid |
| 2 | Polymerising medium | Heat and pressure | Initiator is activated by amine accelerator |
| 3 | Formation techniques | Compression moulding, Injection moulding | Sprinkle on, adapting, fluid resin, compression moulding injection moulding |
| 4 | Advantages | Good appearance, high glass transition temperature, ease of fabrication, low capital costs, good surface finish | Better tissue fit, fewer open bites, less chances of fracture, reduced material costs, simplified laboratory procedure |
| 5 | Disadvantages | Radiolucency, free monomer content causing sensitisation, short fatigue life, low impact strength | Air inclusion (bubbles), shifting of teeth during processing, closed bites, occlusional imbalance due to shifting of teeth, incomplete flow of denture base material, poor bonding. |

***Light-activated resins*** are supplied as premixed sheets in opaque tight packages. Polymerisation is carried out in a light chamber with blue light of wavelength 400-500nm from high-intensity quartz halogen bulbs.

## Recent advances in resins

Modified polymethyl methacrylate materials include four types; hydrophilic polyacrylates, and high-impact strength resins, rapid heat polymerised acrylic and light-activated denture base material.

## Allergic reactions

The monomer content (methyl methacrylate) of 0.5% in a well-processed denture is found as an irritant. It can be recognised by a patch test [8].

## Composite resins

A composite resin system is composed of a mixture of two or more macromolecules, which are essentially insoluble in each other and differ in form. For example, fibreglass has a resin matrix, which is reinforced by glass fibres. The resulting composite is harder and stiffer than the resin matrix material, but less brittle than glass. In dentistry, composite resin is a restorative material (usually in paste form) consisting of an organic binder containing at least 60% inorganic fillers by weight incorporated into a system that would include polymerisation [8]. The filler particles are coated with a coupling agent to bond them to the resin matrix.

The composite resins are mainly used for the restoration of anterior teeth. They may also be used for posterior teeth when aesthetics is the prime consideration, or when silver amalgam is contraindicated. Resins are also employed for other purposes, such as pit and fissure sealants, as coatings for eroded areas, as veneers for crowns and bridges, for core build-up, for repair of fractured porcelain restorations, and cementation of orthodontic brackets.

Chemically activated composite resins are available as:

a) a two-paste system (base and catalyst paste), or
b) powder-liquid systems: powder (inorganic phase plus the initiator) and liquid (Bis-GMA diluted with monomers).

Light-activated composite resins are available as:

- a single-paste system supplied in light-tight (dark) syringes.

The essentials of a composite are the resin matrix/binder, filler and coupling agent. They also contain hydroquinone (inhibitor), U.V absorbers, opacifiers and colour pigments.

## Resin matrix

Aromatic or aliphatic diacrylates are the monomers mostly used in composite resins. Of these, BIS-GMA is most commonly used [25]. The full name for BIS-GMA is 2,2-bis [4(2-hydroxy-3-methacryloyloxy-propyloxy)-phenyl] propane. It is fluid in nature, and thus can penetrate into the pits & fissures as well as the etched areas produced on the teeth enamel. Three parts of the viscous BIS-GMA are mixed with one part of diluent such as methyl methacrylate to obtain a low-viscosity sealant [25]. The sealants, photo-initiated by blue light, are activated by the inclusion of a diketone and an aliphatic amine. Premature contamination with moisture during insertion and the early application of biting forces can disrupt the setting and affect its strength.

It has some limitations:

- high viscosity, which required the use of diluent monomers;
- difficulty in synthesising a pure composition;
- strong air inhibition to polymerisation;
- high water sorption because of diluents used;
- polymerisation shrinkage and thermal dimensional changes still exist;
- not adhering to the tooth structure.

## Polymerisation mechanisms

As these are dimethacrylate monomers, they polymerise by the addition mechanism that is initiated by free radicals. The free radical can be generated by chemical activation or external energy (heat, light).

Based on the mode of activation of polymerisation, the two types of composites are:

- chemically activated resins, and
- light-activated resins:
    a) UV light-activated resins
    b) visible light-activated resins

Table 3 shows the properties of light-activated and chemically-activated resins [8]. Visible light-activated resins are now widely used; they are supplied as a paste containing the photo initiator (camphroquinone) and the amine accelerator (diethyl-amino-ethyl-methacrylate). When they are exposed to light of the correct wavelength, the photo initiator is activated and interacts with the amine to form free radicals. Camphroquinone has an absorption range between 400 and 800 nm. This is in the blue region of the visible light spectrum. The light source is usually a tungsten halogen bulb. The white light generated passes through a filter that removes the infrared and visible spectrum for wavelengths greater than 500 nm. The degree of conversion depends upon several factors, namely the transmission of light through the material, the amounts of photo initiator and inhibitor present and the time of exposure.

**Table 3.** Study on light activated and chemical activated resins [8]

| S.No | Light activated resins | Chemical activated resins |
|---|---|---|
| 1 | Requires light of correct wavelength for its activation | Activated by peroxide-amine system |
| 2 | Cures only where sufficient intensity of light is received | Cures through its bulk |
| 3 | Working time under control of operator | Working time is limited |
| 4 | Shrinkage is towards light source | Shrinkage is towards centre of bulk |
| 5 | Supplied as single component in light-fast syringes | Supplied as two-component system |
| 6 | Less chance of air entrapment during manipulation; more homogenous mix | Air may become incorporated during mixing resulting in a reduction of properties |

### **Classification of composite resin restorative materials**

Based on the average particle size, composite resin restorative materials are categorised as:
- conventional – 8 to 12 μm
- small particle – 1 to 5 μm
- micro-filled – 0.04 to 0.4 μm
- hybrid – 1.0 μm

Ground quartz is mostly used as the filler in conventional composite resins [26]. The polishing is difficult and tends to discolour. Micro-filled composite resins were developed to overcome the problems of the surface roughness of conventional composites. Small particle composites have good surface roughness, and yet retain or improve the physical and mechanical properties of conventional composites. The hybrid composites are the newest category; they have better surface smoothness but still maintain the properties of small particle composites.

### **Acid etch technique**

This is one way of improving the bond and marginal seal between the resin and enamel. It creates micro-porosities by discrete etching of the enamel. Etching increases the surface area and surface energy, allowing the resin to wet the tooth surface better and penetrate into the micro-porosities [8]. The most commonly-used etchant is 37% phosphoric acid.

### **Bond agents**

The composite resins are more viscous, and they do not flow easily into the micro-porosities of etched enamel. Bonding agents were used to increase the wettability of the etched enamel [25]. They are unfilled resins similar to that of the resin matrix of composite resin, diluted by other monomers to lower the viscosity. They improve the mechanical bonding by optimum resin tag formation.

## Fibres used

The reinforcing fibres are available as filaments, yarns, cords, rovings, tows, woven tapes, woven & knitted two-dimensional and three-dimensional fabrics and single & multi-layer non-woven fabrics [20]. Various fibres used for reinforcing include glass, polyamides, polyethylene, carbon, ceramic, metallic, etc. The performance properties of a fibre-reinforced composite are decided by the matrix strength, the type of fibre used, and reinforcement methods depending on the requirements of applications for that composite [21]. Fibre reinforcement materials have superior properties, and have virtually replaced the conventional stabilising materials such as metallic crowns and bridges used in dentistry [31]. Their advantages include flexibility, thinness, and bondability to resins, stretchability, biocompatibility, resistance to loading in axial directions, etc [19]. Among the different fibres that have been tried as splinting materials, a number of investigations were carried out on glass, polyaramids and high-performance polyethylene fibres. Their performance was clinically evaluated in the oral environment for their advantages and disadvantages.

## Glass fibres

The spinning of glass into fine filaments is an ancient technology used for decorative purposes [20]. Glass fibres are used in a number of applications like insulation, filtration, reinforcements and optical fibres, and as blends in various high-performance applications. For reinforcements, the strength of any material was determined by the presence of flaws of critical dimension. Increasing the surface-to-volume ratio of glass would lead to increased strength, as the number of flaws is reduced [32]. Inorganic glasses for fibres are all based on silica, with additives to obtain significant properties.

Over 99% of continuous glass fibres are spun from E (electric)-glass formulation. Compositions (in weight %) of typical E-glass for fibres mainly include the oxides of silica, aluminium, calcium, boron, magnesium and traces of sodium, potassium and iron [32]. The fibres were manufactured mainly by the melt-spinning process, by rapid attenuation of the molten glass extruding through nozzles specially made of rhodium-palladium alloy. Immediately after cooling with water, the fibres are coated with an aqueous size to obtain the handle ability and compatibility with the matrix.

The introduction of surface flaws during manufacture and storage can significantly reduce the fibre strength. Hence the 'size finish' is applied to the fibres at the bushing immediately after spinning to provide maximum protection. The population of flaws and their size therefore determines the failure of the composite, so a fine filament, which will have a lower density of critical flaws, will be stronger than the bulk solid [20]. Obviously fine filaments of glass fibres or woven glass are suitable for dentistry. The mechanical properties of glass fibres are shown in Table 4 [32].

**Table 4.** Mechanical properties of glass fibres [32]

| S.No | Properties | E-Glass | S-Glass | Bulk Glass |
|---|---|---|---|---|
| 1 | E(Gpa) | 72 | 87 | 60 |
| 2 | $\sigma_u$(Gpa) | 1.5-3.0 | 3.5 | 0.05-0.07 |
| 3 | $\rho$(g/cm3) | 2.55 | 2.5 | 2.6 |
| 4 | $E/\rho$(Mm) | 2.8-4.8 | 3.5 | 2.3 |
| 5 | $\sigma_u/\rho$(Km) | 58-117 | 140 | 1.9-2.7 |
| 6 | $\varepsilon_u$(%) | 1.8-3.2 | 4.0 | 0.08-0.12 |
| 7 | $d_f$($\mu$m) | 10-20 | 12 | - |

$E$ = Young's modulus, $\sigma_u$ = tensile strength, $\rho$ = density, $E/\rho$ = specific modulus, $\sigma_u/\rho$ = specific strength, $\varepsilon_u$ = failure strain, $d_f$ = fibre diameter.

Corrosion of the glass is clearly pH-dependent. Glass fibres were used widely in dental applications mainly due to their inertness and ability to bond with dental resins [33]. The use of fibre bundles for splinting led to difficulties of thickness and tongue movement[2]. In woven form, they have the advantages of flexibility and adaptability [11,34]. The main limitation of using glass fibres as a splint is their irritability when exposed to soft tissues and the oral environment [3].

The reduction in strength is a stress corrosion mechanism in the presence of water [35, 36]. The static fatigue of the glass fibres determines the minimum life of a structural composite under load [32]. Thus, the rate of moisture diffusion can determine the protective effectiveness of a well-bonded matrix.

## Polyaramid

Aramid is a manufactured fibre in which the fibre-forming substance is a long-chain synthetic polyamide in which at least 85% of the amide (-CO-NH-) linkages are attached directly to two aromatic rings [20]. Aramids are prepared by the reaction between an amine group and a carboxylic acid halide group. High-modulus polyaramids have improved tenacity compared to the standard aramids [13]. A comparison of the mechanical properties of para-aramid and other high-performance fibres is shown in Table 5 [32].

**Table 5.** Properties of commercial reinforcement fibres [32]

| S.No | Fibres | Tensile Strength (MPa) | Modulus (Gpa) |
|---|---|---|---|
| 1 | E-Glass | 1.5-3.0 | 72 |
| 2 | S-Glass | 3.5 | 87 |
| 3 | Bulk Glass | 0.05-0.07 | 60 |
| 4 | Polyethylene | 3.6 | 116 |
| 5 | Aramid | 3.3 | 120 |
| 6 | Polyamide | 0.9 | 6 |
| 7 | Polyester | 1.1 | 14 |
| 8 | Polypropylene | 0.6 | 6 |

The most frequently used methods of preparation are interfacial polymerisation and low-temperature polycondensation [32]. Commercialised polyaramids were popularly known under the trade names Nomex® and Kevlar®. Copolyamides are produced by the incorporation of comonomers, usually diamines with wider distances between the two amino groups, such as Technora. The spinning solution corresponds to a nematic liquid crystalline phase. It is spun by dry-jet wet spinning, resulting in a radial crystal orientation of para-aramid fibre [20].

The mechanical properties of aramid fibres have led to their significant commercial utilisation in various applications such as sports, high-speed and air transportation, ropes and cables, communication, protective textiles, etc. On a weight basis, they are stronger than steel wire and stiffer than glass. Aramid fibre-reinforced composites have the advantages of good strength-to-weight and stiffness-to-weight ratios [32]. In dental applications, Polyaramids have replaced fibreglass due to the increased strength factor [2]. They are available as curled and straight-line designs that have been used in high-performance applications. The straight-line design is used for splinting teeth. These are 5 times stronger than the equivalent weight of steel in the same volume [5]. Other advantages are their resistance to acids, flexibility and inertness.

The major drawback of polyaramid fibres is their tendency to shred due to the nature of multi-stranded material, and are thus difficult to handle [3]. The amber colour of the fibre makes it show through the acrylic or composite resins, thus affecting the aesthetic property.

## High-performance polyethylene

High-performance polyethylene fibres are produced from polyethylene with a very high molecular weight by a gel-spinning process [32]. They are based on simple and flexible polyethylene molecules, and have the advantages of low density, good mechanical properties and high performance on a weight basis. Dyneema®, Spectra®, Toyobo and Honeywell are some commercially produced polyethylene fibres. Gel-spun polyethylene fibres are produced with high chain extension, high orientation and high crystallinity, which are difficult to attain in other solid-state processes [32]. Based on density, they are classified as low-density, medium-density and high-density polyethylene fibres.

The tenacity of high-performance fibres can be expressed in terms of free breaking length (the theoretical length at which a rope breaks under its own weight in km), which is shown in Table 6 [32]. Elongation at break is low, but owing to the high tenacity, the energy to break is high. The good flexural fatigue resistance is related to the low compressive yield stress. Because of the low friction coefficient and good abrasion resistance, internal abrasion is usually negligible. Polyethylene is not hygroscopic and the fibres have a very low porosity, and therefore the water absorption is negligible [5].

The thinner strands of high-performance polyethylene fibres were lock-stitched, cross-linked and leno-woven to form ribbons under the trade name of Ribbond THM Reinforcement ribbon [2]. This structure is used for splinting teeth, which allows for an open, lace-like pattern that can be formed to follow the contours required for restorative dentistry. It is reputedly ten times stronger than steel, being embedded in the composite or acrylic resin [16]. The natural colour of the reinforcing material helps to maintain aesthetic qualities. Furthermore, polyethylene is biologically inert and not sensitive to attack by micro-organisms [32].

**Table 6.** Free breaking length of high performance fibres [32]

| Fibre | Dyneema | Aramid | Carbon fibre | Glass | Polyester | Steel |
|---|---|---|---|---|---|---|
| Free breaking length (Km) | 400 | 235 | 195 | 135 | 85 | 25 |

Compared to the conventional methods of unbondable, rigid metal and the previous methods of bundles of loose fibres, the ribbon configuration imparts a multidirectional reinforcement when incorporated in the dental resin [32]. It is electrochemically treated to make its surface chemically reactive to the composite or acrylic resins, thus forming a truly integral reinforcing member of the splint [5]. However, this kind of surface treatment does not increase the strength of the composite, compared with that obtained with untreated fibres [12]. The material does not unravel, and is dimensionally constant when embedded within composite materials [23]. Due to the tight weave, the ribbon maintains a structural integrity that imparts a multi-directional reinforcement to restorative polymer resins that acts as a crack stopper [4].

The polyethylene fibres selected were tenacious ultra-high strength, ultra-high modulus, ultra-high molecular weight, extended chain, highly oriented, biocompatible, and extremely pliable with no memory [4]. They are chemically incorporated into the polymers to create high strength compositions that can withstand the demanding testing requirements in the laboratory comparable to aerospace and other high-technology applications [4]. The strength and modulus value of polyethylene is higher than the other high performance fibres as shown in Table 7. These high-performance fibres were found to be an ideal reinforcement material for polymers, and it was logical to incorporate their use in dentistry. The same material is used for construction of stress-bearing laminate composite structures such as boats and submarines, as well as high impact-absorbing bullet-proof vests [32]. In block form, it is used in artificial hip and knee joint sockets [1].

**Table 7.** Comparison of mechanical properties of polyethylene with other fibres [32]

| S.No | Fibre | Strength | | Modulus | |
|---|---|---|---|---|---|
| | | GPa | N/tex | GPa | N/tex |
| 1 | Polyethylene | 3.6 | 3.7 | 116 | 120 |
| 2 | Aramid | 3.3 | 2.3 | 120 | 83 |
| 3 | Polyamide | 0.9 | 0.8 | 6 | 5 |
| 4 | Polyester | 1.1 | 0.8 | 14 | 10 |
| 5 | Polypropylene | 0.6 | 0.6 | 6 | 6 |

Polyethylene is chemically inert and remains chemically unaffected by almost all solvents, strong acids and bases [32]. Its load absorbency feature retards the sudden transfer of input stresses to the bond to the teeth and contributes to the bonding success [3]. The stress transfer is effective throughout the entire fibre network, giving rise to successful crack stopping and superior durability [4]. The polyethylene ribbons are flexible, but have a strong fracture resistance without generating stress [37].

These fibres give very good adaptation to the composite, because the fibre is not pre-impregnated, so a low-viscosity resin can be applied to the fibres and then cured [16]. The fibres are concentrated in the contact area, and oriented in the direction of the tensile force and lie within their original width [4]. The plasma treatment ensures a high level of interfacial adhesion between dental resins and the woven ribbon rather than being merely imbedded in the resin [3]. The adaptation to the varied surface topography of the teeth is attributed to the low memory.

## Tests for splinting materials

Adequate mechanical properties of the hard denture material are considered essential for a splint to withstand the loads of mastication and tongue movements [31]. As the denture polymer is immersed in water, soluble constituents such as unreacted monomers, plasticisers and initiators leach out [13]. The micro-voids thereby created are filled with water by inward diffusion, resulting in reduced strength of the material [35]. Also, the stresses built-up during polymerisation tend to relax due to the penetration of water molecules [38]. This facilitates the flow of long-chain polymers, and thus compromises the mechanical strength of the material [39]. Highly cross-linked, thicker materials generally exhibit lower water sorption compared to non-cross-linked, thinner reline denture base specimens [6].

The complex loading conditions in the mouth are difficult to simulate in laboratory testing models [35]. Specific objective clinical parameters that need to be evaluated are the loss of structural and marginal integrity. Flexural strength determines the resistance of a material to catastrophic failure, and the proportional limit reflects the resistance to plastic deformation, which will render it dimensionally inaccurate and thus clinically unstable [12,23]. Table 8 shows the flexural strength and flexural modulus values for various commercially available splinting materials [39].

**Table 8.** Mechanical properties of commercial splinting materials [39]

| S.No | Splinting Materials | Fibre mass (Kg) | Flexural Strength (psi) | Flexural Modulus (psi) |
|---|---|---|---|---|
| 1 | Fibre flex (full strand) | 0.019 | 49000 | 1.70E+06 |
| 2 | Orthodontic wire | 0.045 | 44000 | 2.10E+06 |
| 3 | Fibre flex (half strand) | 0.012 | 42000 | 1.75 E+06 |
| 4 | Ribbond tape | 0.01 | 38000 | 1.30 E+06 |
| 5 | Connect tape | 0.011 | 35000 | 1.40 E+06 |
| 6 | Fibre splint ML (4mm) | 0.031 | 31000 | 1.25 E+06 |
| 7 | DVA (full strand) | 0.02 | 26000 | 1.55 E+06 |
| 8 | Glass span tape | 0.01 | 25000 | 1.49 E+06 |

The experimental protocol for investigating the mechanical properties of denture base and denture reline materials frequently includes a standardised water immersion period in order to simulate the clinical condition. Water immersion for 50 hours and 28 days has been the standard experimental protocol for denture base materials [6, 34,38].

The effect of water sorption on the fibre-reinforced composite can be evaluated by determining the flexural strength of the specimens after immersion [22]. This was conducted by using a 3-point loading test.

The flexural strength (F), in MPa, was calculated using the formula [6,38]:

$$\mathbf{F=3PL/2bd^2} \qquad (1)$$

where:

P – the maximum load (N),
L – the span distance (20 mm),
b – the width of the specimen (2 mm), and
d – the thickness of the specimen (2 mm).

The flexural modulus (E), in GPa, was calculated using the formula [6,38]:

$$\mathbf{E=FL^3/4bd^3D} \qquad (2)$$

where:

F – the load at a convenient point in the straight-line portion of the load/deflection graph (N), and
D – the deflection (mm) at load F.

The physical properties of fibre-reinforced splinting materials are dependent on the type of matrix, type of fibre, fibre distribution, fibre/matrix ratio, diameter and length of the fibres [20]. Denture base polymers have been reinforced with various types of fibres such as glass, carbon or graphite, ultra-high modulus polyethylene, continuous unidirectional fibre rovings; continuous fibre weaves and chopped strand mats. The variation in the type of fibre used and the reinforcement methods influences the flexural properties of the splinting materials. This can be seen from Tables 9 and 10, where flexural strength and flexural modulus values for glass and fibre-splint are shown [39]. The performance properties of the denture implants differ with respect to the type of materials selected and the particular clinical case [21].

**Table 9.** Mechanical properties of glass splint variations [39]

| S.No | Glass splint | Flexural Strength (psi) | Flexural Modulus (psi) |
|---|---|---|---|
| 1 | Glass span tape (no FR) | 28000 | 1.50 E+06 |
| 2 | Glass span (m tube) | 28000 | 1.49 E+06 |
| 3 | Glass span (tape) | 25000 | 1.49 E+06 |
| 4 | Glas span (S tube) | 22000 | 1.30E+06 |

**Table 10.** Mechanical properties of fibre-splint variations [39]

| S.No | Fibre-splint | Flexural Strength (psi) | Flexural Modulus (psi) |
|---|---|---|---|
| 1 | Fibre splint (6 layers) | 33000 | 1.30E+06 |
| 2 | Fibre splint (multi layer) | 31000 | 1.25E+06 |

## Conclusions

A fibre-reinforced material exhibiting good strength, low water absorption, good adhesion, biocompatibility and low cost was expected to be an effective splinting material. By combining the chemical adhesive and aesthetic characteristics of composite resin with the high-performance polyethylene fibres, splints that will resist the load-bearing forces of occlusion and mastication have been produced. These fracture-resistant restorations will be more durable than the most splinting materials used in the past. By incorporating prompt fibres in reinforcing dental resins, improved properties which aer still better than the commercially available polypropylene and glass fibre reinforced splinting materials can be developed.

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