

The Latest Developments Related to Composite Resins

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Abstract

In the field of restorative dentistry, the use of composites has become widespread with increasing aesthetic demand. Nowadays the composites are divided into various classes depending on the type and size of the filler particles. Apart from this, many new composites have been produced in order to protect the healthy tooth structure, to reduce microleakage and secondary caries formation, to reduce marginal pigmentation and postoperative sensitivity together with developments in technology. The aim of this review is to improve the clinical performance and to evaluate new composite resins that will provide more selection criteria for dentists.

Keywords: Composite resin, particle size, microleakage, marginal coloration

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Introduction

Composite resins first started to be used in conservative dentistry in the 1940s to minimise the disadvantages created by acrylic resin which was replacing silicate cements. In 1955, Buonocore used orthophosphoric acid to strengthen the adhesion of acrylic resins to the enamel surface. In 1962, Bowen developed bisphenol A glycidylmethacrylate (BISGMA) to improve the physical characteristics of acrylic resins. Despite more than 50 years of the Bowen formulation, no significant developments have been recorded in mechanical properties (1).

After the 1970s, composite materials emerged which were polymerised with electromagnetic radiation. An ultraviolet light source at 365 nm wavelength was first used to provide the light energy. However, due to poor polymerisation and iatrogenic side-effects, this was replaced by light seen at 425-491 nm wavelength (2). From then on, the development of composites has continued.

The aim of this review was to evaluate new composite resin systems that have demonstrated significant developments in clinical performance and to form a basis which will provide more selection criteria to meet the criteria of dental practitioners.

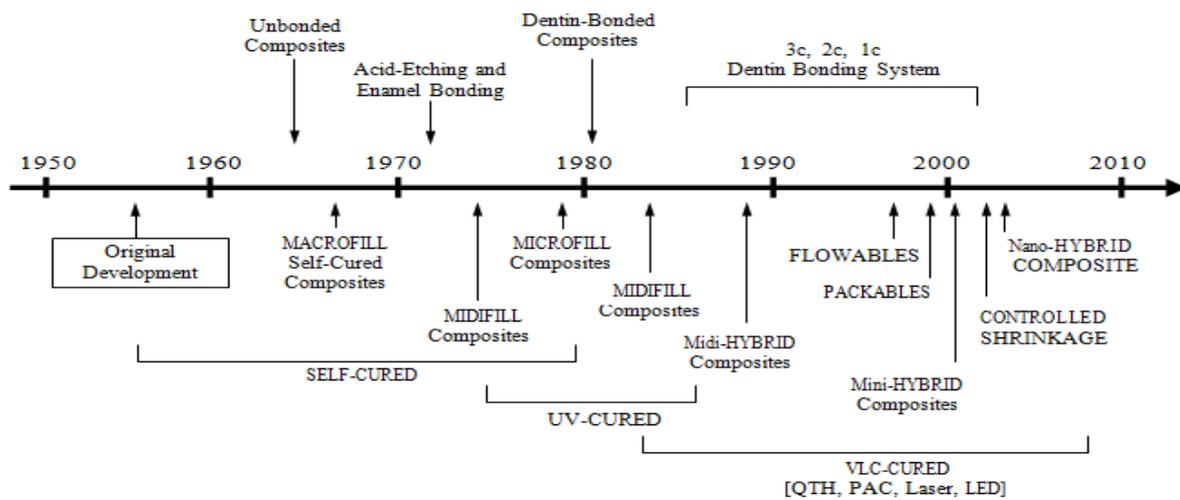


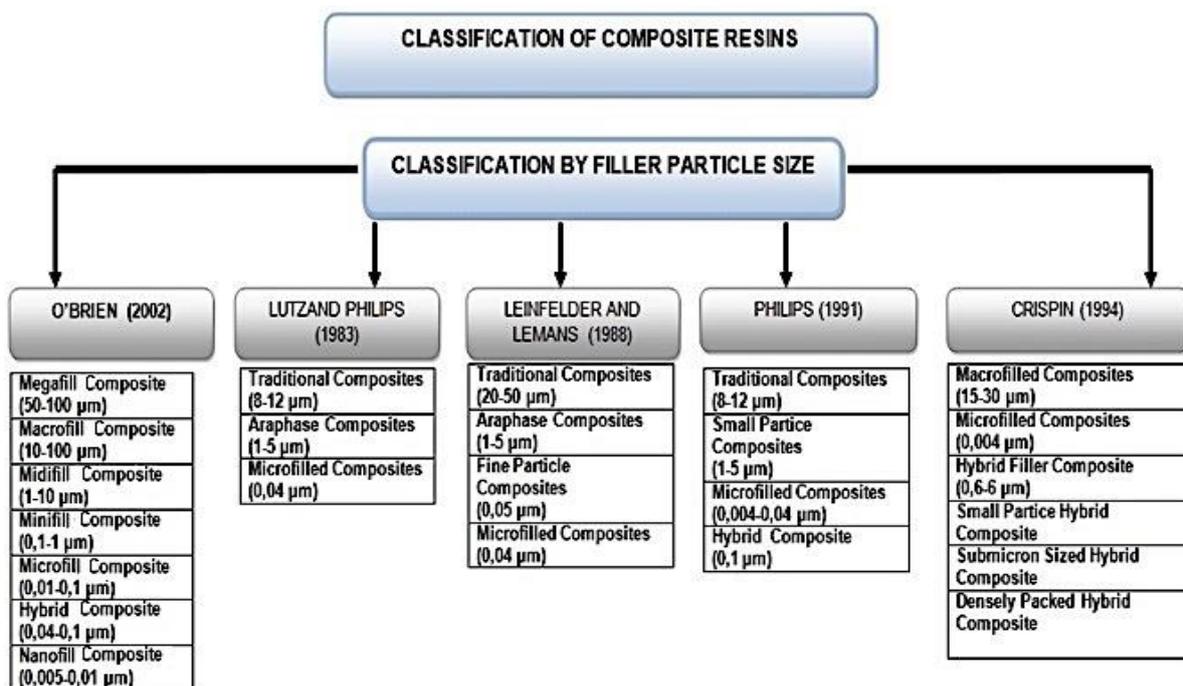
Figure 1: The history of composite resins (3)

THE CLASSIFICATION OF COMPOSITE RESINS

Various classifications have been made related to the rapid developments in composite resins (Table 1). Current classifications of composite resins are

made according to the size of the inorganic filling particles, the weight or percentage volume of the particles, the form in which they are added to the polymer matrix, viscosity or polymerisation methods (3).

Table 1: Various classifications made according to particle size



A classification with proven current validity is the Lutz and Philips classification which is based on the inorganic filling size and amount (Table 2).

Table 2: Classification according to the inorganic filling particle size and percentage

Composite resin type	Particle size	Particle percentage
Megafill	50-100 μm	-
Macrofill	10-100 μm	70-80%
Midifill	1-10 μm	70-80%
Minifill	0.1-1 μm	75-85%
Microfill	0.01-0.1 μm	35-60%
Hybrid	0.04-1 μm	75-80%
Nanofill	0.005-0.01 μm	-

a. Megafill Composites

These composites have particle size varying from 50-100 μm and are known as "insert". The use of glass particles is recommended on occlusal worn surfaces or in very worn areas (4).

b. Macrofill Composites

The most important disadvantages of these composites with particle size varying from 10 to 100 μm are the difficulties of finishing and polishing procedures, the discolouration of the restoration in a short time and plaque accumulation. As they are also not resistant to chewing forces, they are not recommended for use in posterior teeth (5).

c. Midifill Composites

Midifill composites are known as traditional composites with filling particle size of 1-10 μm and were developed to minimise the disadvantages of Macrofill composites. As they create problems such as surface roughness and discolouration like the Macrofill composites, their use is limited currently (4).

d. Minifill Composites

Minifill composites with a filling particle size of 0.1-1 μm are better than macrofill and midifill composites in respect of aesthetics and surface smoothness but have the disadvantage of low resistance to chewing forces (5).

e. Microfill Composites

These composites have particle size of 0.01-0.1 μm and can be polished due to the aesthetic form and surface smoothness and contain colloidal silica particles. As this type of composite has low resistance to chewing forces, they are generally not recommended for class III cavities, class V lesions or in laminate veneers (5).

f. Hybrid Composites

These composites with a filling particle percentage of 75%-80% are formed of a mixture of filling particles of different sizes and are a type of resin combining the properties of microparticle and macroparticle resins. They have been developed to combine the positive physical and mechanical properties of traditional composites with the smooth surface property that can be polished of microfill composites (5).

g. Nanofill Composites

These composites which are visible at smaller light wavelength values have inorganic filling particle size of 0.005-0.01 μm (2-20 nm) (6). While nanocomposites are used for aesthetic purposes in anterior teeth, they function as stress absorbers in posterior teeth. They also have advantages such as high resistance to wear and good surface quality. They are often used in anterior region restorations due to their superior optic and aesthetic properties (7).

In addition to the positive properties of these composites which means they can be used in anterior and posterior restorations, they are also aesthetic, can be polished well, are compatible with dental thermal expansion, have low water absorption, show wear similar to the tooth structure, have good resistance and have high radio-opacity from the enamel.

Hybrid composites are separated into 3 groups as traditional, microhybrid and nanohybrid composites. Microhybrid composites are formed as a result of the combination of submicron size particles

(0.4 μm) and smaller particles (0.1 μm →1 μm) which provide an increase in manipulation and polishing properties (8).

Nanohybrid composites are the result of the combination of nanometre dimension particles (0.005 μm →0.01 μm) and traditional type filling particles and are universal composite resins that can be used in anterior and posterior restorations combining the positive properties of microfill and hybrid composites (9).

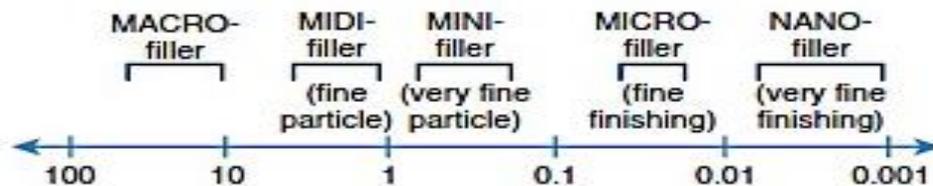


Figure 2: Composite resins according to filling types shown in a logarithmic scale (3).

Nanofillers strengthen the long-term stability and polishability properties of microfill composites. The mechanical stability obtained from hybrid

composites is due to the large filling particles. Surface filling particles are removed with abrasion (5).

Table 3: Comparison of properties of composites (10)

	Macrofill	Midifill	Microfill	Hybrid	Flowable	Packable	Nanofill
Material	Adaptic	Concise	Heliomolar	HerculiteXRV	Æliteflo	SureFil	Filtek Supreme
Manufacturer	J&J	3M	Kulzer	Kerr	Bisco	Dentsply	3M ESPE
Filler level (weight%)	78	81	70	79	60	77	—
Filler level (volume%)	64	68	48	66	42	65	—
Depth of cure (mm)	—	—	—	6.1	5.6	5.5	—
Flexural modulus(GPa)	—	—	5.8	10.2	5.4	10.3	7.2
3-pt. Flexure strength (MPa)	100	111	85	135	—	100	150
Compressive strength (MPa)	236	262	210	285	203	256	225
Diametral tensile strength (MPa)	—	—	36	45	34	34	35
Fracture toughness (MPa·m^{1/2})	[Poor]	[Poor]	0.8	1.2	1.1	1.2	1.3
Diamond pyramid hardness (kg/mm²)	—	—	70	68	—	96	85
In vitro wear ($\mu\text{m}/100\text{K}$ cycles)	—	—	12	9	28	2	7

THE CURRENT VIEW OF COMPOSITE RESINS

With the introduction to dentistry of resin-based composite materials, a great development was created in restorative dentistry. There are many advantages of adhesive restorations such as the protection of healthy tooth structure, reduced microleakage and prevention of postoperative sensitivity, marginal discolouration and the formation of secondary decay. The light cured composite resins used today are composed of an organic matrix, inorganic filler particles and an intermediate linker connecting the two components. In addition to these 3 components, activators which increase polymerisation of the composites to the structure and colour molecules which form colour compatibility with the dental hard tissues have been added (11).

The most important disadvantages of composite resins can be said to be microleakage and postoperative sensitivity which cause low resistance to tensile stress and abrasion and discolouration. The latest developments in restorative composites have focussed on reducing polymerisation shrinkage, increasing the aesthetic appearance and polishability and resistance to wear and breakage and providing colour compatibility. With this aim, various makes of composites have been introduced to the market with several positive properties in respect of clinical performance. As the application of composite is a procedure that requires technical sensitivity, the correct application technique demands as much attention as the selection of the correct material.

COMPOMERS

Compomers were introduced to the market in 1990 as polyacid-modified composite resins, and were derived from a combination of composites and glass ionomer cements as a material which can be attached to dental hard tissues, provides fluoride expression and is biocompatible. The aim of this new material was to attempt to maintain the benefits by minimising the disadvantages of composites and glass ionomers. Due to the superior properties, primarily hardening with light, the use is simple and they have gained popularity in a short time. In respect of physical properties, compomers are worse than composite resins but have superior properties compared to glass ionomers and RMGIs (12).

Compomers have limited indications for clinical use and in accordance with the manufacturer's recommendations are used in all milk tooth cavity types, and in adults, in cervical erosion

and abrasion lesions with or without decay, in anterior proximal restorations, in the second class laminate and sandwich technique, in restorations with small weight-bearing, in the temporary repair of broken teeth and as core material if there is <50% crown dentin present. They should not be used when there are contraindications of direct or indirect capping of the pulp required, when isolation cannot be provided, in the core structure of all ceramic crowns or when the patient has an allergy to dimethacrylate resins (13).

The content of compomers is formed of methacrylate and polycarboxylate groups with resins which can be polymerised, glass filling particles such as fluoroaluminosilicate, strontium fluorosilicate or barium fluorosilicate glass, photo-triggers (camphoroquinone/amine system) and balancers (13).

Dyract (Dentsply), Compoglass (Vivadent), F 2000 (3M) and Hytac Aplitip (Espe) are examples of compomers.

FLOWABLE COMPOSITES

Flowable composites are hybrid composites obtained by increasing particle size and reducing the filling amount, which have been used in dentistry since 1995. Generally the reduction in the viscosity of flowable composites is obtained by reducing the amount of filling content or by increasing the ratio of diluent monomers such as triethylene glycol dimethacrylate (TEGDMA) in the composite structure (14). As a result when the ratio of dimethacrylates increases, although the total shrinkage is known to increase, there is a significant increase in polymerisation shrinkage (15). This polymerisation shrinkage is a large proportion of the organic matrix in composites and thus a gap forms and the amount of wear increases (16, 17).

This resin-type composite can be used as a stress breakage technique substance in restorations, in Class V cavities, in enamel defects, the repair of crown edge fractures, in cervical lesions without decay, in the coverage of pits and fissures, in cavity edges with undercut and in air abrasion cavities (18). Use is also indicated in Class II restorations in difficult to reach areas. However, despite these advantages, flowable composites are not recommended for use in class IV cavities and there are disadvantages such as the flow being difficult to control and low resistance to pressure (6).

In comparison with microfill and hybrid composites, these composites which have thermal expansion coefficients and elasticity modules that are close to those of dental tissue have greater amounts of wear, heat expansion coefficients and surface smoothness. In comparison with traditional

composites, they have better resistance as they contain more resin (6, 18).

In a previous study in 2013, the microleakage values were examined in Class V restorations applied with 3 different flowable composites and 1 self-adhesive flowable composite. Greater microleakage was seen in the cervical edges compared to the occlusal edges, but in respect of cavity coverage, all four composite materials were found to be successful. With the development of new generation self-adhesive flowable composites, the formation of a gap between the tooth and the restoration has been reduced by removing the thickness of adhesive in the interface and thereby microleakage has been reduced to a minimum (19).

PACKABLE COMPOSITES

These composites have been introduced to the market as an alternative to amalgam in posterior restorations and are composite resins with high viscosity known as packable composites in the sense that they can be tightly packed as filling.

These composites have a higher filling particle content and greater viscosity than hybrid composites and are as good as hybrids in respect of physical properties. These packable composites have a greater particle distribution than traditional composites. When the mechanical and physical properties are evaluated, they are similar to the natural tooth structure. These properties provide tighter interproximal contact and the possibility to be more easily condensed in Class II restorations (20). These composite types which can be marketed under the same concept exhibit significant differences because of the variations in filling types and viscosities (21).

These composites have advantages such as interproximal contact can be more easily formed in Class II cavities, restorations can be hardened as a single mass, decay can be treated, it can be placed more easily in the cavity by applying pressure and deep polymerisation is possible because of the high densities. Disadvantages can be said to be that aesthetics and polishing are not very good as there is a limited colour choice, and air bubbles may remain if not condensed (22).

In addition to developments in use related to the high filling ratio of these materials, they are also expected to exhibit better mechanical and physical properties.

NANOPARTICLE COMPOSITE RESINS

Composites including filling particles of nano dimensions which have been developed with

nanofilling technology have come onto the market in recent years with the aim of improving the physical properties and performance of composite resins. In addition to the superior aesthetic properties acquired by the material with nanoparticles, a smooth surface after polishing is also provided. These composites have the advantages of high resistance to wear, low polymerisation shrinkage, can be polished well and the application and layering is easy (23).

The inorganic part of nanoparticle composite resins contains two different fillers of silica nanofillers and zirconia/silica nano-blocks. It has been suggested that by adding nanomers to the organic matrix structures, the particle content has reached 72%-87%. Previous research results support this hypothesis (24).

ORMOCERS

Ormocers, which were developed by the Fraunhofer Silicate Research Institute and produced from organic modified ceramic, started to be used in dentistry in 1998. This composite group is produced with a change to the resin matrix (25). Different to conventional composites, they are formed from inorganic-organic copolymers with silanized filling particles. In ormocers, which are formed of three basic components, while the organic polymer structure is responsible for resistance, the optical behaviours and the cross-link capability, the inorganic structure is responsible for thermal expansion and chemical stability and polysiloxanes do not affect the elasticity and interface properties (26).

The solution and gelation process in ormocers is followed by water and alcohol polycondensation, and the polymerisation of titer oligo methacrylate alcoxycsilane induced with multi-functional urethane. As a result of hydrolysis and polycondensation reactions, the alcoxycsil groups of silane form an inorganic Si-O-Si network and the methacrylate groups undergo organic polymerisation using traditional phototriggers (27, 28). In ormocers with filling particle size varying from 1µm – 1.5µm, the large size of monomer molecules can increase resistance to wear by reducing polymerisation shrinkage and leakage (6). In addition to these properties, the resistance to wear of ormocers, which have biocompatibility and highly effective prevention of decay, is higher than that of traditional composites and in respect of shear bond force they are equal to traditional composites which include Bis-GMA matrix. The values of impermeability and polymerisation shrinkage (1.97%) are similar to those of packable composites. Due to the nanoparticle content which increases the

polishability of the restoration and microsurface hardness, the roughness values following polishing are similar to those of nanofill composites. Another advantage of these composites is that properties such as the heat expansion coefficient are similar to those of the natural tooth (29).

The disadvantages of ormocer-based composites include the high toxicity shown which can be related to the high amount of Bis-GMA expressed. In a previous *in vitro* study, Admira, Tetric Ceram and Z250 were compared and it was seen that there was higher exposure to 3T3 fibroblast toxicity with the polymerising discs of Admira. When the use was examined in clinical applications, it included the same construction stages as direct composite resin. The low number of previous studies in general is not sufficient to evaluate clinical performance.

ION RELEASING COMPOSITES

Ion releasing composites, also known as smart composites, were first produced in 1998, and release calcium, fluoride and hydroxyl ions depending on the pH change on the restoration surfaces. Ariston is an example of these kinds of composites.

The aim of producing these composites was to inhibit the growth of bacteria. Consequently, with an increase in the ions expressed, it was aimed to prevent the effect of bacteria, the buffering capacity and the formation of secondary decay which develops at the edges of the restoration (6).

In respect of fluoride expression, a lower rate of expression is seen compared to glass ionomers, compomers or resin-modified composites (30).

The most important property of this material is that it can release ions at the right time, which will ensure the start of remineralisation. However, in addition to this positive property, as there are several negative characteristics such as low bonding and resistance to wear, poor physical properties and pulpal sensitivity, it has been withdrawn from the market.

SILORANES

Silorane-based composite resins were developed to increase the clinical performance of composites and have been produced showing cationic ring opening formed as a result of the sioxane and oxyrane chemical structures reaction. The function of the oxyrane structure in this reaction is to reduce polymerisation shrinkage and the siloxane function is the formation of a hydrophobic

structure. According to the manufacturers, the combination of these two chemical structures creates a biocompatible, hydrophobic system with less shrinkage (31, 32).

In addition to reducing polymerisation shrinkage, these resins have several advantages such as reducing marginal discolouration to a minimum, not being mutagenic, increasing resistance to weakening and providing resistance to liquids. Previous studies have found the shrinkage rate of silorane-based composites to be <1% (33, 34).

ANTIBACTERIAL COMPOSITES

Composites obtain antibacterial properties in two ways. In the first method, they are formed with the addition into the resin matrix of chlorhexidine which shows an effect by expression from the filling material.

In the second method, they are produced with the expression of antibacterial agents remaining fixed in the resin matrix. For this purpose the monomer, 12-methacryloyloxydodecyl-pyridinium bromide (MDPB) was developed which does not allow bacteria production or the accumulation of bacterial plaque on the material (35).

COMPOSITES STRENGTHENED WITH FIBRE

Composites strengthened with fibres are materials containing fibre within the resin matrix which have a wide area of use. They can be used as infrastructure material in prostheses as they have high resistance to bending (36). As a veneer composite, it is added over seromer, which is a fragmentary composite.

As these composites, which have been newly added to the prosthesis treatment options, increase resistance and hardness under seromer, a bond is formed between the upper and lower structure which is resistant, aesthetic and durable (37). Over time, these materials have been developed to a degree that they can be used in both direct and indirect restorations.

GIOMERS

Giomers are hybrid restorative materials formed from the combination of glass ionomers containing active filling particles and composite resins. In the structure of giomer restorative materials are glass ionomer particles which have formed from a previous reaction to provide production of glass ionomer. By fluoride aluminium

previously entering into a reaction with silicate glass polyacid, giomers which form the glass ionomer matrix are then included in the resin producing silica filler (38).

Giomers have advantages such as good aesthetic properties, being resistant, ease of polishing and being able to express and store fluoride (39). Giomers are bonded to the tooth surface through a bonding system like the composite resins. As giomers do not require acid and washing stages, they save time and application is simple so they can therefore be used safely on paediatric patients. When evaluated in respect of resistance and bonding strength, they are better than glass ionomers. However, previous studies have reported that bonding resistance values are negatively affected in the presence of moisture (40, 41).

Areas of use of giomers in dentistry are Class II, III, IV and V cavities, milk and permanent tooth restorations, root surface decay and restorations of cervical lesions.

The majority of giomers are used as restorative material in areas where the dentin bonding agent does not have great fissure coverage and strength with conditions of composite indications. When examined generally, giomers, the glass ionomers of which have gone through a previous reaction, are used more often together with an adhesive system because of the greater water absorbancy following giomer polymerisation (F-PRG) (12). When previous studies are examined, Mungara et al evaluated the fluoride expression of giomers and nano-ionomers and it was reported that giomers did not express as much fluoride as nano-ionomers (42).

In a study by Jyothi et al of a 1-year clinical follow-up of cervical lesions without decay, Beautiful II giomer restorative material was seen to have superior surface finishing compared to RMGIC (Fuji II LC) material (43).

In a study by Jingaward et al that examined the fluoride expression of Fuji II, Ketac N100 and Beautiful II materials on days 1, 7 and 15 the material with the lowest fluoride expression was determined to be Beautiful II. The material with the highest expression on days 1 and 7 was Fuji II and on day 15, Ketac N100 (44).

In another clinical study, which compared Beautiful II giomer restorative material with traditional resin-based material, no statistically significant difference was recorded. In a different study by Itota et al, it was reported that Reactmer expressed more fluoride than a compomer and composite. In contrast to that study, Yap et al reported that there was no initial fluoride expression from the material, but it occurred later and at the end of 28 days, expression from a compomer was lower (45).

INDIRECT RESIN COMPOSITES

Indirect inlay and onlay systems have been introduced because of significant clinical problems experienced by clinicians with direct posterior composite resins. Restorations made not directly on a tooth but on a model for good adaptation, show regular contours and proximal contact. Hybrid composite resins, the majority of which generally show good development in clinical performance and indirect resin restorative systems, which contain a high rate of glass fillers, have revealed significantly developed properties, such as superior aesthetic properties, high resistance to wear, good marginal adaptation and low polymerisation shrinkage. To increase the mechanical properties of indirect resin composites, the application of additional heat and pressure should be made after the first polymerisation (6).

Tomati and Mormann used the first generation of indirect resin composites for posterior inlays and onlays in the 1980s. The majority of the first generation indirect resin composites had a similar composition to direct resin composites formed of an organic matrix, inorganic fillers and a bonding agent. The construction stages are more difficult and time-consuming compared to direct resin composites. Indirect resin composites which have been seen to be unsuccessful in research have led to the development of second-generation indirect composites. In contrast to the first generation, these composites have microhybrid fillers of 0.04 μm -0.1 μm diameter (30).

The first indirect composite resins sold were Isosit N (Ivoclar), then Coltene Brilliant Dentin System (Coltene), Targis (Ivoclar, Vivadent), Concept Inlay/Onlay System (Ivoclar Vivadent), and Herculiten XRV Lab System (Kerr) systems entered the market (46).

In addition to these systems, there are also laboratory-supported indirect composite resins such as Artglass (Heraeus-Kulzer), Solidex (Shofu), belleGlass HP (Kerr), Gradia (GC America), Symphony (3M ESPE), Targis (Ivoclar, Vivadent), Estenia (Kuraray), Cristobai (Dentsply), and True Vitality (Den-Mat) (31, 47).

BULK FILL COMPOSITES

The area of use in dentistry for resin-based composites is a broad spectrum, from small areas of decay to direct restorations of heavily damaged teeth (48). The reasons for selecting these composites is that the majority have the potential to mimic the aesthetic nuances of dental tissues (49). There are advantages such as ease of use, good aesthetics and they can be repaired. However, there

are also disadvantages such as the high rate of wear, polymerisation shrinkage and postoperative sensitivity, and over time they can cause secondary decay and marginal discolouration (50, 51).

Traditional resin-based composites are hardened with light in the form of 2 mm layers. To shorten the application time and provide ease of use of resin-based composites, bulk-fill composites have been produced which can be placed at a thickness of 4 mm and in the form of a single block (52). There are several properties required of these composites; these can be said to be ease of application, little polymerisation shrinkage, a fluid texture for good adaptation and for polymerisation to be effective up to 4 mm (53).

Bulk fill composites are examined in 2 categories, as low viscosity flowable composites and high viscosity restorative materials:

- i) The low viscosity flowable bulk fill composites such as (SDR (Dentsply), Venus BulkFill (Hereaus Kulzer), Filtek BulkFill (3M/ESPE), X-tra Base (Voco) are placed as a preparation of the lower part dentin layer and then after the placement of a second layer as an enamel layer, polymerisation is applied.
- ii) As the high viscosity restorative materials, SonicFill (Kerr), X-tra Fill (Voco), Filtek BulkFill (3M ESPE), Tetric Evo Ceram BulkFill (Ivoclar Vivadent) and QuiXfil (Dentsply) do not have good adaptation to cavity walls, a low-viscosity resin is placed as a first layer and polymerisation is then applied with light.

SELF-ADHESIVE COMPOSITE RESINS

In self-adhesive composite resins, the size of the gap between the tooth and the restoration is reduced to minimum by reducing the thickness of the adhesive hybrid layer. Thus, it is attempted to eliminate the formation of microleakage (54). In recent years, Vertise Flow (Kerr) has been introduced which is self-adhesive to dental tissues and contains glycerol phosphate dimethacrylate (GPDM) as a special monomer.

These resins differ from traditional flowable composites in that they do not require any preparatory procedure. However, for self-adhesive resins to be able to make a strong bond to dentin tissue, the cavity surface must be actively made thoroughly oval.

As attachment to enamel tissue is weaker than to dentin tissue, to obtain a strong bond in shallow Class V cavities, they must be used together with an adhesive system (55). They can also be used for the attachment of braces in orthodontics

and with the benefits of this system, acid damage on enamel is removed.

Conclusion

Together with the use of nanotechnology, knowledge of materials and developments in biomaterials, it is thought that high quality dental composites will be produced in the future. Accordingly, there is a need for further clinical research to achieve these goals.

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