2.1 Historical development of dental composite

The first material developed for use as a direct esthetic restorative was silicate cement. It was developed in the late 1800s and the cement was prepared from an alumina-silica glass and a phosphoric acid liquid. Silicate however, deteriorated rapidly, because it was highly soluble in oral fluids as stated by O'Brien (2002).

Self-curing acrylic resins were then developed in 1941 by German chemists. They used tertiary amines with benzoyl peroxide to initiate methacrylate polymerization reactions. Their discoveries led to the development of acrylic filling materials (eg, Sevriton) in 1948, where polymethyl methacrylate is mixed with methyl methacrylate. The major problems with these materials were high levels of polymerization shrinkage (about 20 to 25%), poor color stability, limited stiffness, high thermal expansion, and no adhesion to tooth structure (Albers, 2002). Albers (2002) believed that the polymerization shrinkage itself could result in leakage and bacterial penetration, prompting high incidence of dental caries.

In the 1950s, adhesive dentistry began with acid-etch technique. The early attempts to reduce polymerization shrinkage and improve resin physical properties involved incorporation of fillers, which worked to improve acrylic denture-base materials. Acrylic filling materials containing alumino silicate glass fillers were then formulated. In 1959, ESPE (Seefeld, Germany) introduced Cadurit, the first glass-reinforced methyl methacrylate composite restorative manufactured for dentistry. Improved properties were obtained with these materials when silicate glass particles were precoated with polymer or primed with silane (Jones, 1995; Albers, 2002).

These early acrylic composite materials however, showed very high polymerization contraction and were difficult to handle. It was not until the early 1960s when Bowen developed Bis-GMA resin (Jones, 1995; Albers, 2002), that dental composites made its entrance as direct tooth colored restorative materials. In 1963, Addent™ (3M Dental Products, St. Paul, Minnesota) was the first composite restorative to use Bis-GMA resin. The Bis-GMA component greatly reduced polymerization shrinkage and color stability, since the resin was more hydrophobic. In 1969, the first two-paste Bis-GMA system, Adaptic (Johnson & Johnson) was introduced (Albers, 2002). There were many advantages for using Bis-GMA, which includes less shrinkage, higher modulus and reduced toxicity due to its lower volatility and diffusivity into tissues. Therefore, Bis-GMA is still used as the dimethacrylate monomer to create dental composite materials today (Sideridou et al., 2002; Ogliari et al., 2008).

In the 1970s, urethane dimethacrylate-based chemistry was introduced. Urethanes are a series of monomers that incorporate a urethane group into the backbone of a dimethacrylate monomer molecule (Rueggeberg, 2002). On other hand, Thompson et al. (1979) developed spiro-orthocarbonates (SOC), which are unsaturated monomers that expand on polymerization and will co-polymerize with conventional Bis-GMA based resins. In 1977, light-activated initiators, methyl-p-toluene, was incorporated. This eliminated the porosity, which was inherent in the paste mixing system and gave the dentist more control over the placement and setting of the material (Jones, 1995). By 1980, acid-etch retained composites and adhesive dentistry, were being used routinely for (a) repairing broken teeth incisally, (b) sealing fissures of vulnerable molars against decay and (c) treating caries in the interproximal areas of front teeth (Jones, 1995).

In the 1990s, in an attempt to eliminate polymerization of methacryalte-based monomer materials, scientists have investigated the use of monomers that do not decrease in volume on polymerization. Polymerization with expansion in volume can be achieved with SOC monomers through a double ring-opening process wherein two bonds are cleaved for each new bond formed. The resulting expansion can be applied to counter the polymerization shrinkage associated with the conventional methacrylate monomers used in dental composites and thereby provide formulations with drastically reduced degrees of shrinkage (Stansbury, 1992). Stansbury (1992) synthesized 2,3-Bis(methylene) spiro orthocarbonate monomers and reported that these novel monomers appear to offer significant potential for future development of free-radical ring-opening polymerization. However, Shalaby & Salz (2007) summarized serious disadvantages in the application of methylene-substituted SOC-monomers for free radically cured composites, as in the following:

- Crystalline SOCs showed only a limited solubility in methacrylate based compositions, making the incorporation of a high SOC content in a composite formulation is almost impossible.

- SOCs are less reactive than methacrylates, which significantly prolonged the necessary irradiation time.

- The low degree of ring-opening at room temperature results in a significant reduction of the shrinkage potential.

- The sensitivity of the SOCs to water, acidic compounds, and fillers decrease the storage stability of the uncured composites pastes.

- The polymers formed by the free-radical ring-opening polymerization of the SOCs show only a low UV-light stability and therefore the cured composites tend to be vulnerable to discoloration.

Present day developments in filler technology and initiation systems have considerably improved composite physical properties and expanded their clinical applications (Braga and Ferracane, 2004). The advantages of composite materials are good aesthetics and the use of adhesive systems that can bond the composite to enamel. Dental composite is considered to be a good material for replacement of amalgam (Wilson et al., 2002). Dental composites are advocated as a possible solution to amalgam problems because they are mercury-free, thermally non-conductive; match the shade of natural teeth, and bond to tooth structure readily with the use of adhesive systems (Deliperi and Bardwell, 2002).

In 1998, Mair started his study of clinical performance of three posterior resin and two amalgams. He found that all materials undergo degradation and wear, but none of the restorations reviewed at 10 years appeared to require replacement, indicating that posterior composite materials can be a good alternative to amalgam (Mair, 1998). In 1999, 86 million composite restorations were placed in the United States, as opposed to 71 million amalgam restorations. This was due to the improvements in composite materials and clinical techniques, and public demand for more esthetic, tooth-colored restorations (Hyson, 2006). Sunnegadh-Gronberg et al. (2009) concluded that the use of amalgam was negligible and substituted with dental composite is the material of choice for both first and replaced restorations in Northen Sweden. Class II cavities were the most frequent placed and replaced restorations. Replaced dental composite restorations showed a median longevity of 6 years, with Class II being the shortest (5years) and Class III restorations being the longest (7 years).

Current dental composites comprise of a blend of hard, inorganic particles bound together by a soft, resin matrix, and generally encompass three main components (Peutzfeldt, 1997; Vasudeva, 2009):

(1) The resin matrix comprised of:

(i) a resin system composed of 2 or more monomers

(ii) an initiator system for free radical polymerization and stabilizers to maximize the storage stability of the uncured resin composite and the chemical stability of the cured resin composite.

(2) The inorganic filler consisting of particulates such as glass, quartz, and/or fused silica etc.

(3) The coupling agent, usually an organo-silane that chemically bonds the reinforcing filler to the resin matrix.

The properties of dental composites depend on several factors, related to the resin matrix, the filler particles, and the coupling between filler and matrix (Asmussen and Peutzfeldt 1998). For example, the new Z250 composite showed higher Young's modulus, and lower water sorption and solubility than the previous Z100 composite. These differences in composite properties were most probably due to the filler content of Z250 and the different monomer structure of the organic matrix resin (Sideridou et al., 2003).

The selection of appropriate monomers for the formulation of a dental composite strongly influences the reactivity, viscosity, and polymerization shrinkage of the composite paste, as well as the mechanical properties, water uptake, and swelling by water uptake of the cured composite (Shalaby and Salz, 2007). It is therefore necessary to have some understanding of the chemical monomers structure in order to appreciate the properties, limitations, and the progress that is being made and planned in this area.

2.2 General aspects of methacrylate-based monomer of current dental composites

2.2.1 Chemical structure and polymerization reaction

Monomers used in dentistry are generally liquids which are converted to solids during the process of polymerization. The process by which monomers are joined together and converted into high molecular weight polymers is termed as polymerization (Craig and Powers, 2002; Peutzfeldt, 1997). Macromonomer is the alternative name for macromer, which is macromolecular monomer (Alger, 1997). A polymer is defined as a macromolecule formed by the linkage of monomers (O'Brien, 2002). A macromer, in its broad sense, has reactive functions at the ends and/or on the chain, which can constitute a building block of the final polymers of certain values via suitable chain-extending reaction (Cho, 1980). Macromer is defined as a prepolymer containing one or more polymerizable groups, usually a carbon-carbon double bond, for example of vinyl acrylic. The term macromolecule is often used synonymously with the term polymer. Thus, the subject of polymer science could also be referred to as macromolecular science. The term polymer, however, implies that the molecules have many repeated units such as polymethyl methacrylate (PMMA), whereas the term macromolecule does not. It is therefore favored over the term polymer by many biochemists, since biological macromolecules (biopolymer) frequently consist of a complex arrangement of many different repeat units (Alger, 1997).

A common feature of acrylate and methacrylate monomers are that they all contain a “vinyl” methacrylate group (functional group), which is an unsaturated carbon-to-carbon double bond (C=C) (Rueggeberg, 2002). The molecular chemical structure of methacrylate-based monomers, composing the resin of dental composite, have functional methacrylate groups at the ends of the molecule, which are joined or carried by a spacer. The mono-functional monomers have only one methacrylate group per molecule, which is involved in the polymerization reaction. Polymers derived from these monomers form linear chains, with less than desirable properties, to function as restorative materials, for example, the PMMA. However, the monomers with more than one functional group per molecule are used as difunctional monomers and have 2 groups. The advantage of these monomers is that while one methacrylate group enters into a linear chain, the other group is free to join a different chain, thus greatly increasing the molecular weight of the resulting polymer. This is termed as a cross-linked polymer, such as Bis-GMA and UDMA (Albers, 2002; Rueggeberg, 2002). Besides this, when there is an increase in the number of functional groups in the monomer, the density of cross-links increased too (Tanaka et al., 2001).

The spacer of the monomer does not have a function as such, except for keeping both functional and polymerizable groups well separated, but it has an important influence on the properties of the monomer and the resulting polymer (Nishiyama et al., 2004). The spacer is usually an alkyl chain, but can also contain several other groups, like esters, amides, or aromatic groups. The polarity of the spacer will partly determine the solubility of the monomer in water, and in other solvents. The hydrophilicity of the spacer group may also cause water uptake, which leads to higher hydrolysis, thus the monomers will be susceptible to swelling and discoloration even as cured resin. The size of the spacer group determines the viscosity of the monomers (Landuyt et al., 2007). For example, the structural formula of Bis-GMA has 2 methacrylate groups; they are polymerizable in the terminals, and form thermosetting polymers by free radical systems, bis-phenol A nucleus, and hydroxyl groups in the spacer. This induces hydrogen bond resulting in high viscosity (1200 poise) and enhances the water absorption (Braden, 1978).

Almost all resins of current dental composites are methacrylate-based monomers, which polymerized via free radical-addition reaction of their double bonds, using initiator systems. A new resin based on molecules called oxirane-based resin was recently developed as Silorane dental composite. The name silorane was derived from the combination of siloxanes and oxiranes (epoxies). These molecules polymerize by cationic photo-initiation and produce dental composites with comparable properties with slightly reduced shrinkage compared to materials that are based on methacryalte monomers. However, the long term clinical data of Silorane dental composite still is unavailable, while, the dental composite based on methacrylate monomers have 50 years of clinically-well-accepted proven success (Terry et al., 2009). When comparing two commercially available, dimethacrylate based restoratives (Z250 and Z100) against oxirane-based composite, a study done by Palin et al. (2003) concluded that the decreased conversion rates within the first hour following irradiation of experimental oxirane-based composite may compromise the flexural strength properties which may be inadequate under masticatory loading. All polymerization reactions can be described in terms of Initiation Propagation, and Termination (O’Brien, 2002), as illustrated in

Figure 2.1. In chemically-activated systems, free radicals are generally produced through the reaction of an organic peroxide initiator and an amine accelerator. In light-activated systems, the scission of camphorquinone results in the production of two molecules with one unshared electron each. Whatever the means of production, the free radicals attack the double bonds of available monomer molecules, resulting in the shift of the unshared electron to the end of the monomer and the formation of activated monomer molecules. The activated monomers then attack the double bonds of additional available monomers, resulting in the rapid addition of monomer molecules to the free radicals. This propagation stage continues as the chain grows in length. Finally, termination of the growing free radical may occur by several mechanisms and can result in the formation of branches and cross-links (O’Brien, 2002).

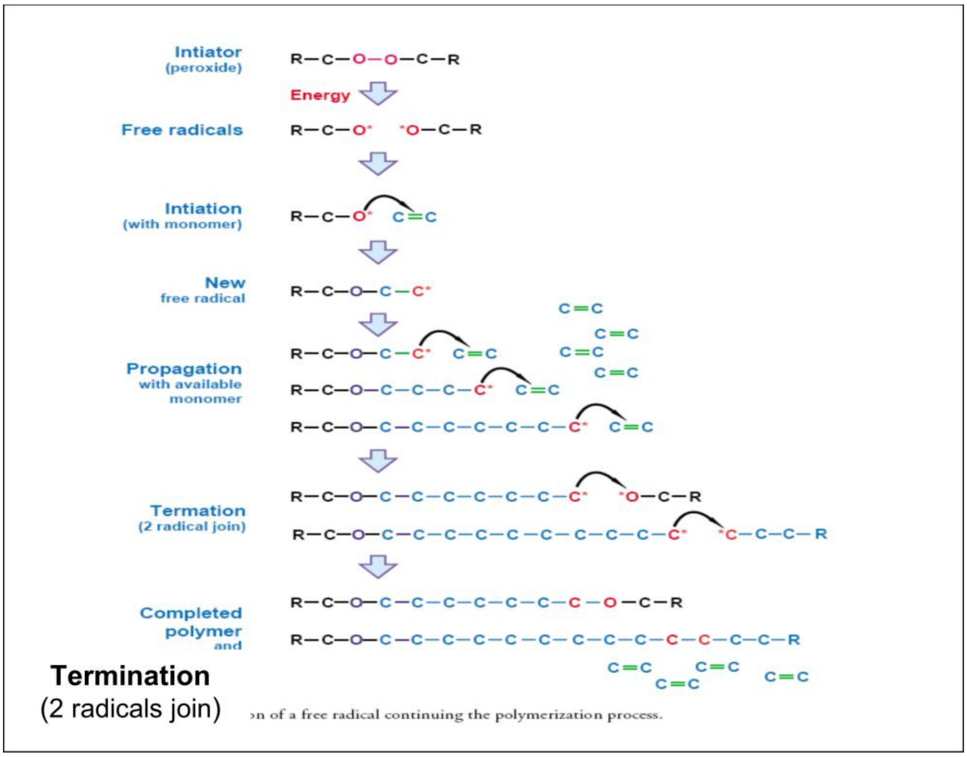


Figure 2.1 Free radical polymerization (O’Brien, 2002)

2.2.2 Monomers

2.2.2.1 Bis-GMA-based monomer

The 2, 2-bis [4-(2-hydroxy-3 methacryloyloxypropyl) phenyl]-propane or bisphenol A glycidyl methacrylate (Bis-GMA) is a high molecular weight monomer (Mw = 512 g/mol), which had been present in the vast majority of current dental composites. Bis-GMA is obtained through the addition reaction of glycidyl methacrylate and bisphenol A, or alternatively through the reaction of methacrylic acid and the diglycidyl ether of bisphenol A (Bowen, 1962; Floyd and Dickens, 2006), as is shown in Figure 2.2. In fact, the Bis-GMA is an oligomer formed from 2 monomers. The term monomer is commonly used to indicate its liquid status, despite the composition.

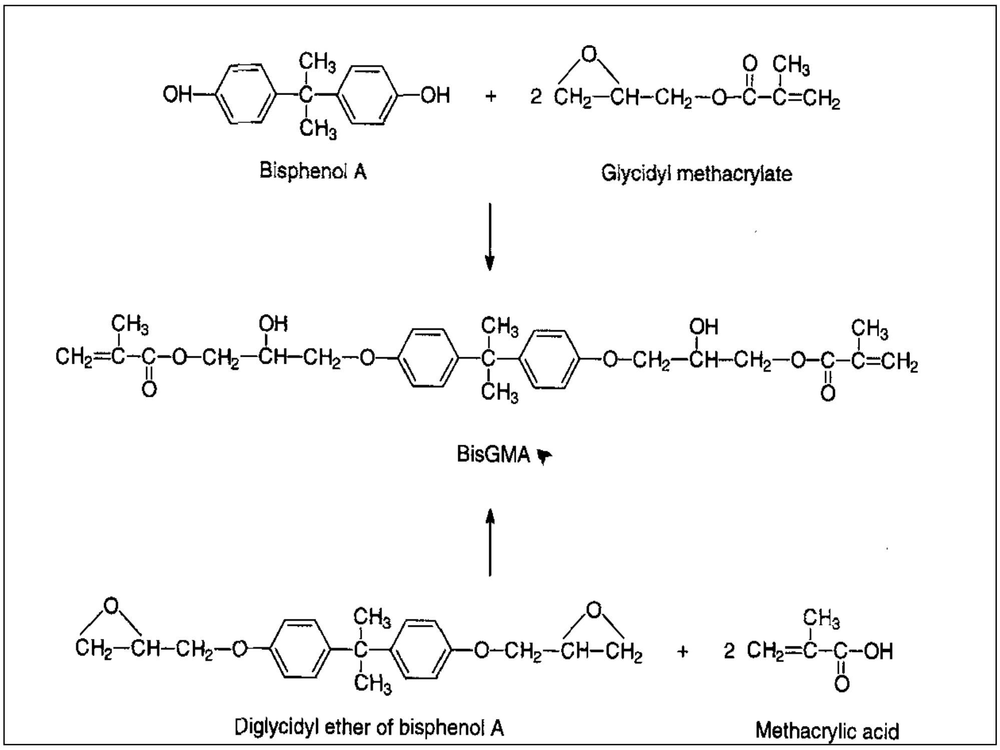
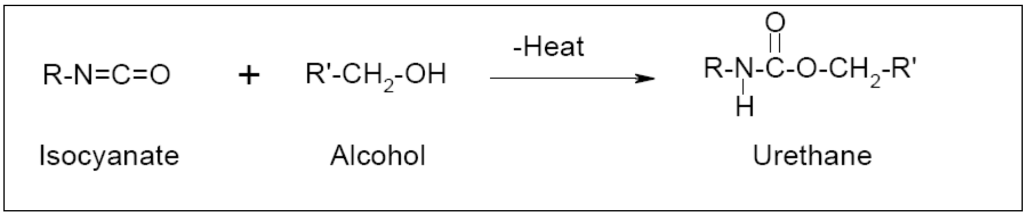


Figure 2.2 Synthesis of Bis-GMA (Peutzfeldt, 1997)

Bis-GMA appeared to have much less shrinkage compared to methyl methacrylate (MMA) because the methacrylate groups containing double bonds are a relatively small part of large molecules, if the vinyl groups are not more than two (Braden, 1978). The presence of phenolic groups and strong intermolecular interactions of hydroxyl groups in the Bis-GMA structure contributes to high rigidity, and lower polymerization shrinkage (Sideridou et al., 2003; Matasa et al., 2004). At the same time, these groups, however, are responsible for the disadvantage, and subsequently stimulate the development of Bis-GMA modification or substitute. The Bis-GMA disadvantages are; very high viscosity, low degree of conversion with water sorption susceptibility and proneness to brittle fracture and wear (Moszner and Salz, 2001; Siderdou et al., 2002; Sideridou et al., 2003; Floyd and Dickens, 2006).

2.2.2.2 UDMA-based monomer

Urethanes are chemically complex polymeric materials, usually formed by the reactions of liquid isocyanate components with liquid polyol, such as alcohol or polyethylene glycol (polyol) components (Figure 2.3). Urethanes have widespread applications in automotive parts, coatings, adhesives and other infrastructure uses (Gary, 2005). The use of isocyanate in the synthesis of urethane are potentially toxic, therefore it is pertinent that all isocyanate groups be reacted completely in the synthesis of urethane.



$$R{-}N{=}C{=}O + R'{-}CH_2{-}OH \xrightarrow{-Heat} R{-}\underset{H}{N}{-}\overset{O}{\overset{\|}{C}}{-}O{-}CH_2{-}R'$$

Figure 2.3 Chemical reaction of urethane (Gary, 2005)

They exhibit excellent mechanical and physical properties, high wear resistance, and good tissue compatibility. For this reason, they are widely used in medical applications

(Koprululu et al., 2008). Polyurethanes based on renewable resources can be prepared by reacting the polyol made from plant (vegetable) oil and an isocyanate. Vegetable oils are primarily water insoluble, hydrophobic substances that are made up of one mole of glycerin and three moles of fatty acids, called triglycerides. Fatty acids vary in carbon chain length and the number of unsaturated bonds (Gary, 2005). Polyurethanes are also synthesized by the reaction of diisocyanates with hydroxyl-containing oils or with partial glycerides prepared from oil/fatty acid and glycerol (Koprululu et al., 2008). The structure of triglyceride molecules (type of fatty acids in the triglycerides of the same oil) differs from molecule to molecule. This causes a variation in the chain length between cross-links in polyurethanes obtained from oil based polyols (Gary, 2005). Gan (2004) patented palm oil-based polyol and produced polyurethane foam for industry. The properties of the foam were comparable to polyurethane produced from petrochemical-based polyol (Gan, 2004).

Urethane macromers, containing a polymerizable double bond at the ends are also synthesized and used for many different applications such as coatings, printing inks and medical applications (Koprululu et al., 2008). Lu et al. (2003) synthesized urethane methacrylate macromer (UMM) by reacting 2-hydroxyethyl methacrylate (HEMA) with an isocyanate group terminated polythiourethane oligomer obtained from polyaddition of 2, 2’-dimercaptoethyl sulfide (MES) with 2, 4-tolylene diisocyanate (TDI). Previous studies indicated that transparent polymeric membranes can be prepared from oil- or fatty acid-based polyurethanes for wound dressing applications (Koprululu et al., 2008 quoted from Gultekin et al., 2006). Koprululu et al. (2008) synthesized oil-based urethane macromers and triglyceride oil-based urethane macromers (TGU) containing vinyl double bonds by reacting partial glyceride mixture (PGM) and methyl vinyl isocyanate (MVI).

In dentistry, urethane dimethacrylate (UDMA) is another monomer that is commonly used for resin matrix for dental composites. The UDMA is commonly abbreviated from urethane dimethacrylate monomers that have been used commercially. Polydorou et al. (2009b) reported that UDMA is one of the monomers that are most often tested with regard to elution and cytotoxicity of resin-based materials. Although each chemical name represents the chemical type, chemical structure, and molecular weight of a molecule, it does not seem to be the same with UDMA. In their study, the different forms of UDMA are presented. These include those used by dental manufacturers to produce composite materials and the different types of urethane dimethacrylate used in studies concerning the elution of monomers from composite materials. High-performance liquid chromatography (HPLC) is usually used to detect the eluted monomers, but it does not appear to be adequate in determining the different forms of UDMA. The combination of HPLC with mass spectrometry is shown to be able to specifically identify the compounds eluted in addition to those compounds used as standards in the various studies. The fact that the same name is given to different molecules causes confusion about the results of studies testing the elusion of monomers from composite materials and their possible toxicity.

The first type of urethane dimethacrylate used was synthesized from hydroxyalkyl methacrylates and disocyanates. These monomers have molecular weight nearly equal to that of Bis-GMA, but are less viscous. The most commonly used monomer of this type is the 1,6-bis (methacrylyloxy–2-ethoxy– carbonylamino)-2,4,4-trimethythexan (UEDMA = UDMA), a reaction product of 2-hydroxyethyl methacrylate and 2,4,4-trimethyl- hexamethylenediisocyanate (Figure 2.4). This monomer has been used alone (e.g., Isocap, Vivadent; Isopast, Vivadent) or in combination with other monomers such as Big-GMA and TEGDMA (e.g., Heliomolar, Vivadent; Estic Microfill Composite, Kulzer; Estilux Microfill Kulzer; Durafill Light-curing Composite, Kulzer) (Peutzfeldt, 1997; Floyd and Dickens, 2006; Khatri et al., 2003; Vasudeva, 2009). The advantage of the UDMA monomer is that it has 100 times lower viscosity (11 Millipascal Second at 23°C) compared to that of the Bis-GMA (1000 Millipascal Second at 23°C), because the imino groups of UDMA form weaker hydrogen bonds compared to hydroxyl groups in Bis-GMA (Sideridou et al., 2002; Peutzfeldt, 1997). Also, the functionality offered by urethane groups adds toughness and flexibility to the monomer backbone chain, providing the possibility for enhanced conversion and durability (Peutzfeldt, 1997; Rueggeberg, 2002).

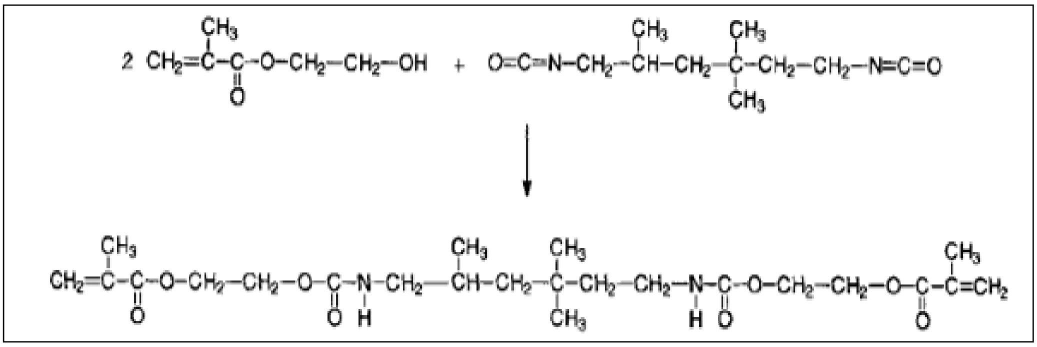


Figure 2.4 Synthesis of urethane dimethacrylate (Peutzfeldt, 1997)

Another urethane dimethacrylate (Figure 2.5), which contains diphenyl groups, was used in Fotofil (Johnson & Johnson ICI), and was the very first visible light-activated proprietary resin composite (Vasudeva, 2009).

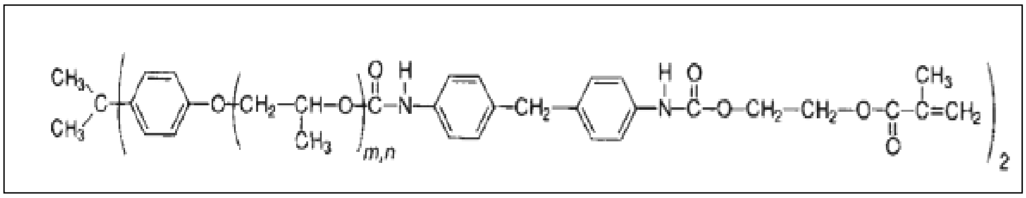


Figure 2.5 Schematic representation of the UDMA used in Fotofil composite (Peutzfeldt, 1997)

Urethane dimethacrylate oligomer was synthesized through the reaction of secondary hydroxyl groups of BisGMA with isocyanates to create less hydrophilic monomer (Figure 2.6). Nuva-Fil (L.D. Caulk), Ful-Fil and Prisma-Fil (L.D. Caulk) were based on oligomers synthesized from BisGMA and hexamethylene diisocyanate (Peutzfeldt, 1997; Vasudeva, 2009).

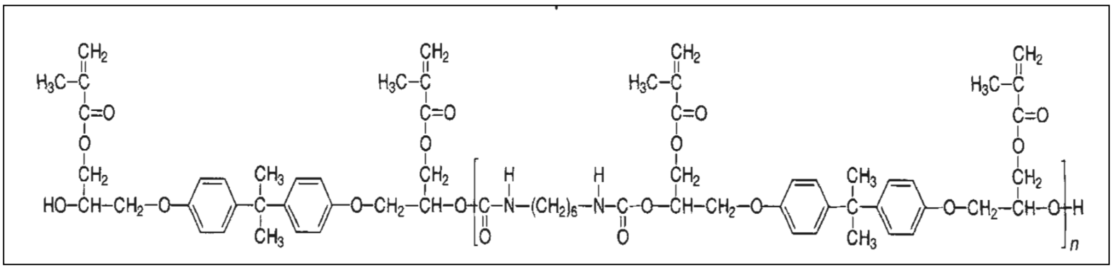


Figure 2.6 Schematic representation of the UDMA oligome used in Ful-Fil composite (Peutzfeldt, 1997)

UDMA has also been used for denture base materials (Eclipse, Dentsply, USA). Ali et al. (2008) concluded that the surface hardness, flexural strength, and flexural modulus of light- and heat-cured UDMA (Eclipse) were significantly higher than the values obtained for heat-only cured (Meliodent, Bayer Co. Germany) and auto-cured (Probase Cold, Ivoclar Vivadent Inc, USA) PMMA denture base systems.

There is a new composite resin system (Kalore, GC America) that is based on a technology recently developed by Dupont, which utilizes a DX-511 molecule in its matrix. The Dupont molecule, DX-511, is a new monomer family based on urethane dimethacrylate chemistry that is compatible with the current composite and bonding systems. This monomer has a long rigid molecular core and flexible arms in the structure (Figure 2.7). The long rigid core prevents monomer deformation and reduces polymerization shrinkage. On the other hand, if the molecular core is flexible, the monomer may fold and will occupy less space, causing a loss in dimension. The molecular weight of this monomer is 895, which is twice that of Bis-GMA or UDMA. Generally, short chain monomers with lower molecular weight have greater polymerization shrinkage and inferior physical characteristics as compared to long chain monomers. High molecular weight monomer reduces polymerization shrinkage because it contains only a small number of double bonded C=C, which is a factor in polymerization shrinkage. However, if the monomer chain becomes too long, then reactivity decreases. To overcome this challenge, flexible arms were created on the new Dupont monomer, thus increasing the potential for reactivity. The manufacturer has reported volumetric shrinkage values of 1.72%, claiming it to be the lowest of any composite resin system (Terry et al., 2009; Kalore GC America, Technical overview, 2009).

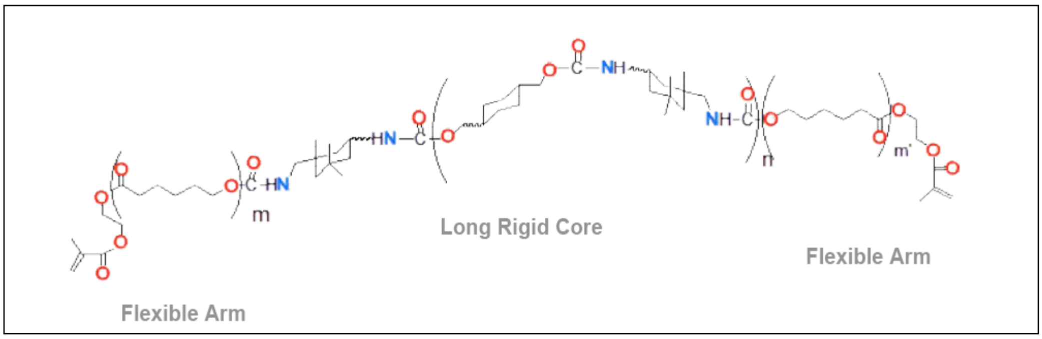


Figure 2.7 Schematic representation of the UDMA used in Kalore composite

2.2.2.3 Co-monomers

The highly viscous Bis-GMA monomer caused the incorporation of reinforcing fillers to the resin matrix to be limited and lower degree of conversion (Sideridou et al., 2002). If a very small mono-functional monomer such as methyl methacrylate was used to lower the viscosity, these more volatile components could shorten the shelf life of the composite, as well as increase polymerization shrinkage, hence, monomers that are less volatile are typically used to control viscosity. A reactive diluent, such as triethylene glycol dimetharylate (TEGDMA) is often added to improve the viscosity, reactivity and final conversion of the matrix phase. Unfortunately, the polymerization of reactive diluents, which are relatively low molecular weight monomers, results in higher shrinkage as well as lower mechanical properties owing to the monomers structure (Atai et al., 2005). The TEGDMA molecules are a small sized and flexible aliphatic with 2 vinyl groups (Figure 2.8), compared to Bis-GMA. The TEGDMA is called a co-monomer because it is used as a diluent of the viscous resins to control the viscosity of the composite material (Albers, 2002; Anusavice, 2003).

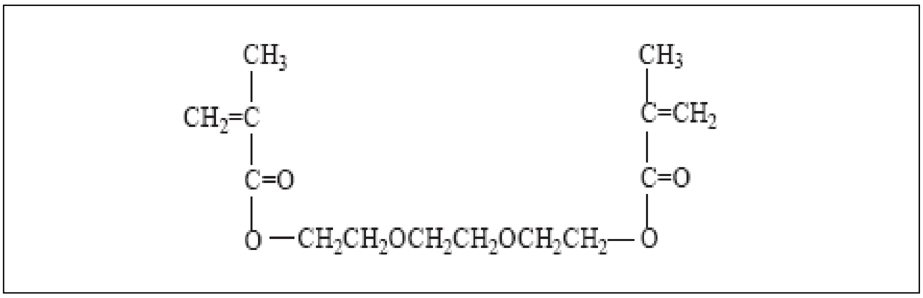


Figure 2.8 Chemical structure of TEGDMA

When the hydroxyl groups of Bis-GMA have been replaced with an ethoxy species (-CH2-CH2-O-), the resulting structure is referred to as a “ethoxylated Bis-GMA” (Figure 2.9). This ethoxylated bisphenol A dimethacrylates (EBPADMA or Bis-EMA) is a more hydrophobic analog of Bis-GMA and is present in many current restorative materials (Rueggeberg, 2002). Generally, the rationale of using a Bis-GMA analogue (Bis-EMA) as a diluent instead of TEGDMA is due to its lower water sorption and polymerization shrinkage relative to TEGDMA (Pereira, et al., 2002).

A study done by Sideridou et al. (2002) showed that Bis-EMA is lower in viscosity than that of the UDMA, due to the presence of hydrogen bonds between the –NH- and >C=O groups in UDMA. However, they also found that the degree of conversion of Bis-EMA is lower than UDMA and TEGDMA.

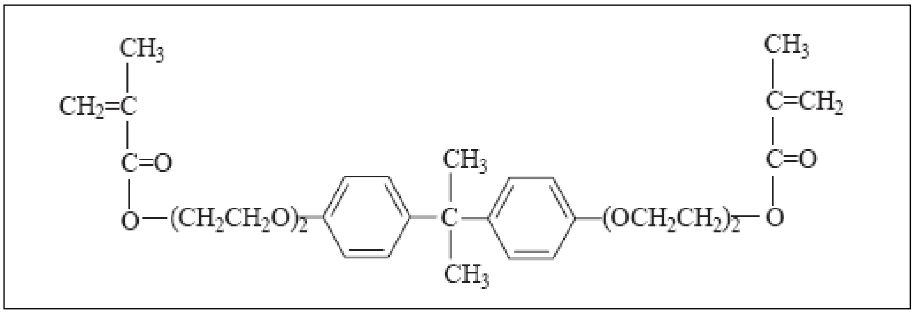


Figure 2.9 Chemical structure of Bis-EMA

Manufacturers have added hydrophilic monomers to hydrophobic dimethacrylates in an attempt to promote effective bonding between hydrated dentine and resin composites (Malacarne, et al., 2006). The addition of 2-hydroxyethyl methacrylate (HEMA) (Figure 2.10) or acidic monomers to composites is of particular interest for the development of self-adhesive composites (Moszner and Salz, 2001). The simplest methacrylate of the hydroxyl group-containing surface active monomers, HEMA, was introduced into ternary formulations as a potential adhesion-promoting diluent co-monomer (Mendes et al., 2005).

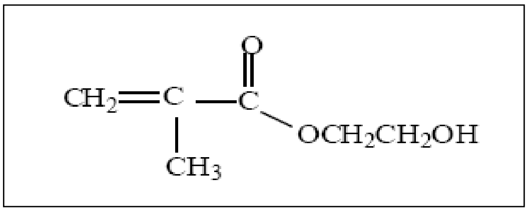


Figure 2.10 Chemical structure of HEMA

2.2.3 Degree of conversion and cross-linking density

During the polymerization of methacrylate-based monomers, the viscous liquid gradually transforms into a rigid material by radical polymerization involving the double bonds (C=C) of methacrylate groups. The extent of transformation of double to simple bonds (monomers in polymer) is known as degree of conversion (Dewaele, et al., 2006). Network formation occurs during polymer chain propagation and includes a mixture of linear, cross-linked, entangled, and interpenetrating chain segments, which determines the materials properties. Cross-linking density is associated with increased mechanical properties and stability (Daronch et al., 2005). In addition, further conversion of monomer to polymer, limits the number of unreacted monomers that may serve as plasticizers in the polymer matrix as is shown in Figure 2.11 (Ferracane, 1995).

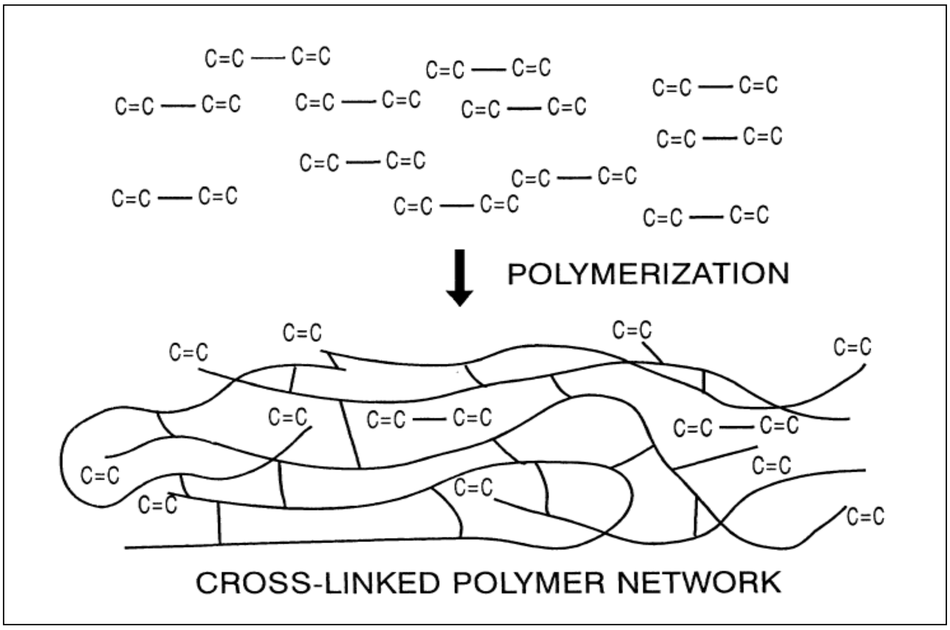


Figure 2.11 Schematic representing the polymerization and cross-linking polymer network containg unreacted monomers and pendant methacrylate group (C=C) (Ferracane 1995)

The polymerization of dimethacrylates usually leads to glassy resins where only a part of the available double bonds are reacted. The unreacted double bonds may either be present in free monomer or as pendant groups in the network. Only very flexible monomers with reactive methacrylate groups which are relatively far apart can be completely reacted at ambient temperature (Sideridou et al., 2002).

It has been reported by Stansbury & Dickens (2001) that the determination of conversion is a critical component in the interpretation of test results of both commercial and experimental dental materials (Stansbury and Dickens, 2001), since the mechanical strength, modulus, hardness and leachable components, are linked clearly to polymer conversion. Fourier-transform infrared (FT-IR) spectroscopy is the most widely used for degree of conversion determination by the calculation of C=C of uncured monomer and cured polymer (Sideridou et al., 2002; Imazato et al., 2001; Young et al., 2004; Atai et al., 2004). It is based on the absorption of radiation in the infrared frequency range as a result of the molecular vibrations of the functional groups contained in the polymeric chain. The calculation of degree of conversion is based on the fact that the conversion of aliphatic C=C to C-C, however the aromatic C=C could not be converted. Therefore, the absorbance of the unreacted aromatic C=C will act as an internal standard.

Barszczewska-Rybarek et al. (2000) developed an equation that relates the cross-linking density to degree of conversion, so that it can be used as a direct method for determination of the cross-linking density for polymers prepared by dimethacrylate monomer polymerization. Silva et al. (2008) estimated the cross-linking density indirectly by Knoop diamond indentation depth of two dental composites, with the same polymeric matrix and different types of filler particles.

2.2.4 Structure-properties relationship

A better understanding of the structure-property relationship can be used to improve the resin matrix system and this can be done by modification of the existing monomers or developing a new resin for dental composite (Tiba and Culberson, 1999). The influence of chemical structure on the properties resin has been investigated (Dulik et al., 1981). Kawaguchi et al. (1984) and Kalachandra et al. (1997) showed that the change introduced in the dimethacrylate structure could alter the physical and mechanical properties of the resulting polymer. It has been reported that the properties of resin are affected by its molecular structure.

The Bis-GMA molecule, having a stiff bisphenol A core and two pendant hydroxyl groups which are able to form strong hydrogen bonds, is the largest and has the lowest concentration of double bonds. The UDMA molecule, with its flexible aliphatic core and two urethane links, is also able to form hydrogen bonds, is smaller in size and therefore has a higher concentration of double bonds. TEGDMA has the smallest size and the highest concentration of double bonds. So, the latter monomer should exhibit the highest crosslink density and be able to form the tightest networks (Sideridou et al., 2002; Barszczewska-Rybarek, 2009).

Kim & Jang (1996) concluded that the flexible TEGDMA caused higher degree of conversion than rigid Bis-GMA. Sideridou et al. (2002) studied the room-temperature photo-polymerization of the most widely used dimethacrylate in dentistry using FT-IR. The degree of conversion was found to be in the following:

Bis-GMA<Bis-EMA<UDMA<TEGDMA:

In the case of UDMA, the degree of conversion is higher than expected; this is most probably due to the chain transfer reactions caused by the –NH- groups, which increase the mobility of radical sites in the network. These chain-transfer reactions may also be responsible for the high polymerization reactivity of UDMA. In the polymerization of UDMA the initiation rate is higher than that for all the other monomers and the formed network is more dense and rigid than is predicted by its structure, considering the cross-linking sites are only those at the two vinyl groups (Sideridou et al., 2002).

Barszczewska-Rybarek (2009) investigated the flexural strength of Bis-GMA, UDMA, and TEGDMA homopolymer, and it was in the following order:

TEGDMA < Bis-GMA < UDMA.

It might be seen that the flexural strength Bis-GMA/TEGDMA increased when the UDMA was introduced. However, the flexural modulus of Bis-GMA was higher than UDMA and lower than TEGDMA (Barszczewska-Rybarek, 2009).

Sideridou et al. (2003) reported that Young's modulus of the homopolymers follows the following order: poly-TEGDMA <poly-Bis-EMA < poly-UDMA < poly-Bis-GMA. It is noteworthy that poly- TEGDMA with the highest cross-linking density is the most flexible polymer, due to its flexible aliphatic monomer units. Poly-UDMA also consists of aliphatic monomer units, but it is a relatively rigid polymer, due to the existence of hydrogen bonds between them. This significant effect of hydrogen bonds on the rigidity of the polymer network is also evidently when comparing Young's modulus of poly-Bis-GMA and poly-Bis-EMA. The monomer units of these polymers have similar chemical structure, but the former (Bis-GMA) has an additional two hydroxyl groups, which can form strong hydrogen bonds and increase the rigidity of the polymer network (Sideridou et al., 2003).

Water sorption is also highly dependent upon the chemistry of the monomers. An examination of the structure of the most popular monomers such as Bis-GMA, UDMA, Bis-EMA and TEGDMA reveals that they are heteroatom polymers, having carbon and oxygen or nitrogen in their backbones. In addition, their structure shows the presence of hydrolytically susceptible groups, such as ester, urethane, and ether linkages, as well as hydroxyl groups. While these monomers and their resultant polymers are not considered to be extremely hydrophilic, they absorb water to a potentially damaging extent (Ferracane, 2006). All polar dental monomers such as Bis-GMA, TEGDMA and UDMA have hydrophilic functional groups, e.g., hydroxyl, ethylene oxide, and urethane groups, respectively, that can serve as sites for water absorption (Antonucci et al., 2005).

Water enters the polymer network through porosity and intermolecular spaces. The extent and rate of water uptake is dependent upon the density of the polymer network and the potential for hydrogen bonding and polar interactions (Ferracane, 2006). Water molecules that are firmly bound to polar sites along the polymer networks exhibit high plasticizing effects, thus causing the reduction of the polymer’s mechanical properties by altering the mobility of their chain segments (Malacarne et al., 2006). Taking into account the possible effects of the chemical and physical structure of the polymer network on moisture absorption, the higher water sorption of poly-Bis-GMA is most probably due to the higher hydrophilic character of its monomer units. Hydroxyl groups form stronger hydrogen bonds with the water molecules than urethane groups of poly-UDMA or ether groups of poly-Bis-EMA. Therefore, the Poly-UDMA and especially poly-Bis-EMA showed lower water sorption than poly-Bis-GMA (Sideridou et al., 2003). The monomer TEGDMA does not contain any hydroxyl groups but still has some affnity to water because of the water compatible ether linkage structure within the molecule. TEGDMA has an aliphatic chain composed of ether linkages, which are hydrophilic, and Bis-GMA has an aromatic chain with polar hydroxyl groups. On the other hand, although Bis-EMA is an aromatic dimethacrylate like Bis-GMA, the former has ether linkages in its molecular structure, but the hydroxyl groups, which form strong hydrogen bonds with water molecules, are not present (Moraes et al., 2008).

Sideridou et al. (2003) found that water sorption of poly- TEGDMA is much higher than that of poly-Bis-GMA, in spite of the hydrophilic character of the monomer units of polymers being the same. The much higher water absorption of poly-TEGDMA than that of poly-Bis-GMA is not due to the different chemical structure of the polymer networks, but most probably due to their different physical structure. On the other hand, TEGDMA creates a much denser network than Bis-GMA, so it initially seems strange that it absorbs a much higher water amount. However these networks are not homogeneous (Sideridou et al., 2003). The poly-TEGDMA network is more heterogeneous than poly-Bis-GMA and this higher heterogeneity seems to favor the higher water sorption of the former. In a more heterogeneous network, the space created between the polymer clusters (microporous) is larger and can accommodate a larger quantity of water (Sideridou et al., 2003). The higher water sorption of poly-TEGDMA than that of poly-Bis-GMA may also be due, to some extent, to the higher flexibility of the network of the former than the latter, which permits the higher swelling of polymer chains by water (Sideridou et al., 2003).

Generally, polymer networks prepared by free radical polymerization of dimethacrylates show a spatial heterogeneity, and some parts are densely cross-linked while some parts are loosely cross-linked. Elliot et al. (2001) studied the structural heterogeneity of polydimethacrylate-based networks which showed that the more densely cross-linked the network, the more heterogeneous is its structure.

Since the polymer network contains porosity and free volume between chains, especially in the region near cross-links, it is theoretically possible for water to be absorbed. In addition, water uptake is accompanied by a loss of unreacted components (Ferracane, 2006), which can be used to explain the concept of solubility in polymers.

The water sorption of polymer is combined with volume change. Sideridou et al. (2008) found that the volume increase due to water absorption is in the following order: poly-TEGDMA>poly-Bis-GMA>poly-UDMA>poly-Bis-EMA, with the resins of Bis-EMA showing the lowest values. Hydroxyl groups form stronger hydrogen bonds with the water molecules than urethane groups of poly-UDMA or ether groups of poly-Bis-EMA (Sideridou et al., 2003).

2.2.5 Trails to develop new methacryalte-based monomers for dental composite

Many modifications of Bis-GMA have been done to overcome its hydrophilic nature (hydroxyl group). Fluorination generally improved the hydrophobicity of composites. Sankarapandian et al. (1997) developed several novel dimethacrylates in the laboratory based on structural modifications of Bis-GMA in the core and the side chain units. They found that systems having fluorine containing core groups exhibit low water sorption, low reduction in Tg, and higher surface hardness values than the control Bis-GMA. However, the phosphine oxide core group causes more water sorption and hence lower surface hardness in the wet samples.

Another structural modification of Bis-GMA is by acrylation, Ahn et al. (1999) prepared multifunctional methacrylates derived from Bis-GMA, by reacting hydroxyl groups of 2,2-bis[4-(2′-hydroxy-3′-methacryloyloxypropoxy)phenyl]propane (Bis-GMA) with methacryloyl chloride to produce two multimethacrylates having three methacrylate groups (BPA-3M) and four methacrylate groups (BPA-4M, BPA-3M and BPA-4M) with much lower viscosities than the starting Bis-GMA. This is because they have only one or no hydroxyl groups. High conversions >50% resulted from photo-polymerization of BPA-3M, whereas Bis-GMA showed lower conversions under the same condition, implying better mechanical properties for the composite resins made from BPA-3M. BPA-4M showed much lower conversions in the photo-polymerization condition. Water sorption of the light-cured composite of BPA-3M containing 50 wt % of inorganic fillers was found to be 0.15%, which is only one-tenth of the commercial Bis-GMA composite.

Interesting bismethacrylates with lower shrinkage than Bis-GMA have been produced by reacting various branching molecules at the hydroxy groups of the Bis-GMA (Holter et al., 1997). However, initial results suggest that these polymers have low elastic modulus. While this low modulus and lower shrinkage would likely result in lower contraction stress than in Bis-GMA-based polymers, the low modulus (50% of Bis-GMA-based resins) may limit their usefulness as dental restorative resins.

A new developed trifunctional methacrylate monomer, Tris [2-hydroxy-3-methacryloyoxypropoxy) phenyl] methane (TTEMA), which exhibited a very low photopolymerization shrinkage of 2.09%, and 3:2 TTEMA/TEGDMA unfilled resin revealed 10% lower shrinkage than the conventional Bis-GMA system containing the same amount of TEGDMA. However, the flexural strength of light-activated composite resin formulated with TTEMA is comparable to that of a Bis-GMA composite resin under the same conditions (Chung et al., 2002).

Carioscia et al. (2005) prereacted thiol-ene monomers to create reactive thiol or vinyl (ene)-functionalized oligomers, and investigated the use of these materials as novel dental restorative material. They found that the polymerization shrinkage and stress of oligomeric thiol-ene systems were significantly lower, however, the flexural strength and modulus of the monomeric and oligomeric thiol-ene resins were not significantly different compared with Bis-GMA/TEGDMA at a ratio of 70/30.

On the other hand, branched macromonomers and hyperbranched polyester methacrylates demonstrated low monomer viscosity and low polymerization shrinkage, as well as high flexibility of the formed polymer networks and formed composites with poor mechanical properties. These monomers are promising use of low-shrinking composites because of their relatively low viscosity and efficient incorporation into the formed polymer network. However, for a successful application in dentistry, those monomers that will produce polymer networks with improved mechanical properties have to be synthesized (Shalaby and Salz, 2007).

For a multifunctional monomer designs, Chung et al. (2002) developed a new trifunctional methacrylate monomer, Tris [2-hydroxy-3methacryloyoxypropoxy)phenyl] methane (TTEMA),which exhibited a very low photopolymerization shrinkage of 2.09%, and 3:2 TTEMA/TEGDMA unfilled resin revealed 10% lower shrinkage than conventional Bis-GMA system containing the same amount of TEGDMA. However, the flexural strength of light-activated composite resin formulated with TTEMA is comparable to that of a Bis-GMA composite resin under the same conditions (Chung et al., 2002).

Fong et al. (2005) explored the possibility of using polyhedral oligomeric silsesquioxane methacrylate monomer (POSS-MA) to partially (or completely) replace the commonly used dental base monomer 2, 20-bis-[4-(methacryloxypropoxy)- phenyl]-propane (Bis-GMA) to prepare novel dental restorative composites. Their result indicated that the maximum flexural strength of the composites occurred when 10% (mass fraction) of Bis-GMA was replaced by POSS-MA, while the highest modulus occurred when the mass fraction of POSS-MA was 2%.

Labella et al. (1998) used alternative monomethacrylate co-monomers in place of conventional dimethacrylate co-monomers as viscosity modifiers. The alternative monofunctional co-monomers were tetrahydrofurfuryl methacrylate, hydroxypropyl methacrylate and isobornyl methacrylate. The Bis-GMA-based resins exhibited lower shrinkage when mixed using the monomethacrylates rather than with conventional glycol dimethacrylates.

Dulik et al. (1981) studied the triethylene glycol spacer group of TEGDMA. The study showed that when TEGDMA was substituted with poly (ethylene glycol), lower shrinkage would be obtained at the expense of rapidly decreased glass transition temperature and mechanical properties of the resulting polymer.

Pereira et al. (2002) found that the use of Bis-GMA mixed with hydrophobic low viscosity CH_3Bis-GMA comonomer, as a substitute for the commonly used TEGDMA, resulted in significant improvement of properties such as polymerization shrinkage, water sorption and extent of polymerization, thereby reducing the unreacted double bond concentration

For urethane-based chemistry, many monomers have been developed aiming to be an alternative or modified Bis-GMA. Sterrett et al. (1987) synthesized and evaluated the fracture toughness of a series of urethane toughened methacrylate resins (UTM). The polyol used in formulation of UTM resins serves as both an oligomer backbone and a urethane soft segment. The structure of, and functionality of the polyol, have a direct effect on the toughness and mechanical properties of the resultant resin. Their study dicated that UTM resins based on polyfunctional polyols tend to possess improved toughness. Surprisingly, the formation with the highest molecular weight did not lead to the highest fracture toughness. The improved toughness in these materials may be due to the combined effect of a tough, elastomer like urethane, and its three-dimensional network structure, which deform and relax in three dimensions to the same extent as the polyol structure. In contrast, the structure of resin contains linear two-dimensions, capable of relaxation in only two dimensions (Sterrett et al., 1987).

Matsukawa (1994) produced polyurethane dimethacrylate and explained its toughness by the favorable combination of the rigidity of the aromatic ring and the flexibility of the long chain. However, the idea of combining hard and soft segments in one dimethacrylate was implemented already in the Fotofil and Occlusin urethanes dental composite (Peutzfeldt, 1997).

Chowdhury et al. (1997) used polyfunctional urethane, experimental tri-functional urethane monomer EXP3, in binary monomer mixtures, and found that the mechanical strength of these resin matrices values was increased. The increased strength obtained for these resin matrices is assumed to be due to urethane linkages increasing the degree of cross-linking and having a positive effect on mechanical properties.

Krishnan et al. (1999) synthesized urethane tetramethacrylates (UTMA) by reacting 2, 3-epoxypropylmethacylate with acrylic acid in the presence of a base catalyst, which reacted then with a hexamethylene diisocyanate under an inert atmosphere at 40 °C. The

UTMA was characterized after being reinforced with silanated radiopaque glass fillers and other additives to produce composite pastes, which hardened upon visible light curing within 10-20 seconds. The compressive strength and micro hardness of urethane adduct-based composite was found to increase with increasing urethane content in the resin mixture and was highly superior to conventional Bis-GMA-based composites. The diametral tensile strength and transverse strength were however comparable. Water sorption and solubility values increased with time and urethane content in the composite samples.

Khatri et al. (2003) modified Bis-GMA monomer by reacting it with stoichiometric amounts of various alkyl isocyanates (ethyl, n-propyl, n-butyl, n-hexyl and n-octyl isocyanates) and used FTIR spectroscopy by monitoring the disappearance of the isocyanate absorption band. They reported that the low viscosities of urethane modified Bis-GMA monomers compared to unmodified Bis-GMA were attributed to the increase in backbone mobility resulted from the presence of the alkyl pendant substituent’s from the side chains and the weaker intermolecular hydrogen bonding of the urethane groups compared to the stronger hydrogen bonding interactions of the hydroxyl groups of Bis-GMA. Polymerization shrinkage of the urethane modified Bis-GMAs would always be lower than Bis-GMA if compared at constant conversion values, e.g. if both are extrapolated to 100% conversion, because of their greater molecular masses. Measurements of water uptake showed that all the urethane modified Bis-GMA polymers were significantly less hydrophilic than the Bis-GMA polymer. The cross-linking urethane-modified Bis-GMAs reached equilibrium faster compared to Bis-GMA. They suggested that as the length of the hydrocarbon side chain was increased, the modified Bis-GMAs polymers became increasingly hydrophobic. This is consistent with the replacement of the hydrophilic hydroxyl groups of Bis-GMA with increasingly hydrophobic substituent.

Antonucci et al. (2006) concluded that introducing a new high molecular mass oligomeric urethane dimethacrylate co-monomer (PEG-U) into UDMA based matrices improves degree of conversion while not adversely affecting the polymerization shrinkage, stress development and mechanical strength of their amorphous calcium phosphate (ACP) composites. Less polymerization stress of PEG-U formulations and the expected improved biocompatibility of such materials may lead to better clinical performance.

Atai et al. (2007) synthesized an isophorone-based urethane dimethacrylate (IP-UDMA) monomer through the reaction of polyethylene glycol 400 and isophorone diisocyanate. This was followed by reacting it with HEMA to terminate it with methacrylate end groups. They obtained a lower shrinkage-strain and higher degree of conversion in comparison with the commercially available resin-monomer, Bis-GMA, suggesting that it is a feasible alternative for dental restorative materials and other applications where minimizing polymerization shrinkage is important.

Chen et al. (2008) developed a urethane acrylate-modified epoxy acrylate, which is a mixture of HEMA, TDI, and epoxy acrylate. They found that when compared with bisphenol-A/glycidyl dimethacrylate (Bis-GMA)-based dental restorative materials, the polymer composites obtained in this study exhibited greatly reduced degrees of shrinkage and better mechanical and physical properties. It was concluded that the urethane-modified epoxy acrylate monomers have great potential as dental restorative matrices.

2.3 Resin matrix and its influence on the dental composite performance

2.3.1 Resin system composition and viscosity

The monomer system can be viewed as the backbone of the resin system of dental composites. Presently no monomer has shown optimal properties such as high degree of conversion and strength with low viscosity, water uptake and polymerization shrinkage. The resin system of current commercial dental composite matrix resins are usually composed from the admixture of 2 or 3 or more of methacryalte monomers to form binary or ternary or complex resin systems respectively. High molecular weight dimethacrylate monomers are often used as the matrix phase of dental restorative composites because of their higher strength and lower polymerization shrinkage (van Noort, 2002). As, reported earlier, Bis-GMA has been one of the more commonly used monomer in composite restorative materials. However, due to the very high viscosity of the monomer, the incorporation of reinforcing fillers limits the matrix, causing the final conversion of homopolymerized Bis-GMA to be low (Sideridou et al., 2002). A reactive diluent, such as triethylene glycol dimetharylete (TEGDMA) is often added to improve the viscosity, reaction conversion and final conversion of the matrix phase (Atai et al 2005). In particular, triethylene gly-col dimethacrylate (TEGDMA) has been widely used for this purpose, added in mass fraction commonly ranging from 20 to 50% (Barszczewska-Rybarek 2009). Lovell et al. (2003) reported that 25 % of TEGDMA and 75% of Bis-GMA are similar to the commercial dental resin formulations.

By increasing the low molecular weight monomers TEGDMA to the Bis-GMA resin, the polymerization results in higher shrinkage as well as lower mechanical properties (Atai et al., 2005; Floyd and Dickens, 2006). Imatzo et al. (1999) found that an increase in the proportion of TEGDMA to Bis-GMA resulted in the increase of its hydrophilic nature and subsequently provoked greater water uptake. The relatively high hydrophilicity and penetrability to tissues of TEGDMA raises biocompatibility issues, and recent studies have suggested that TEGDMA should be replaced by larger, more hydrophobic and biocompatible monomers (Geurtsen and Leyhausen, 2001). Imazato et al. (1999) findings indicated that Bis-GMA/TEGDMA resins showed the greatest water uptake at the ratio of 1/1 compared to 3/1, and the water sorption characteristic was not influenced by the degree of conversion but mainly by the hydrophobicity of the material. Therefore, it was considered that although the cross-linking nature reduces the water uptake of polymer compared to a single strand configuration, an increase in the conversion of dimethacrylate resins, whose degree of curing is generally large, does not contribute significantly to reducing the water uptake.

Tanaka et al. (1991) evaluated the residual monomers from Bis-GMA/TEGDMA of set visible-light-cured composite resins when immersed in water and found that lower molecular weight TEGDMA molecules eluted faster and were more in number when compared to other components. While the Bis-GMA polymer per se is too bulky to leach, Bis-GMA/TEGDMA-based composites release twice as much TEGDMA than these made of UDMA/ TEGDMA (Muller et al., 1997). The HPLC analysis of eluted components revealed that TEGDMA was the main monomer released, where the maximal monomer concentration in the eluate was observed after 7 days (Örtengren et al., 2001).

The molecular structure and the degree of conversion of the functional group determine the features of the organic matrix of composite materials (Ilie et al., 2005). Ferracane and Greener (1984) concluded that the degree of cure for the resins varied between 55 and 72% and the more diluted resins had a more complete cure, probably due to the reduced viscosity and improved mobility of reactive species during curing. Chung and Greener (1990) reported that the degree of conversion of composites ranged from 43.5–73.8%. Where Sinterfil and Ful-fil computes are Bis-GMA and UEDMA combined base resins and P-30, Bis-fil I, and Estilux Posterior are Bis-GMA based resins. However, no significant difference was noted between combined UDMA and Bis-GMA-base resins and Bis-GMA-based resins in the degree of conversion.

However, the structures of the Bis-GMA and UDMA monomers, and consequently, the resin viscosities of the co-monomer mixtures (with TEGDMA) strongly influenced both the rate and the extent of conversion of the photo-polymerization process (Floyd et al., 2006). They found that the optimum conversion in the Bis-GMA and UDMA resin systems were obtained when TEGDMA concentrations were high. With decreasing TEGDMA and increasing Bis-GMA content the conversion decreased dramatically owing to the increased viscosity of the resin mixture. It would be helpful, in the development of improved dental resin materials, to be able to assess rapidly and conveniently the extent of polymerization of any dental monomer system which can be hardened under controlled conditions that are clinically relevant (Antonucci and Toth, 1983). In order to increase the conversion and allow for the incorporation of high filler levels, composite formulations must include one or more monomers with lower viscosity, such as TEGDMA, UDMA, Bis-EMA (Pfeifer et al., 2009).

The viscosity is a measure of the resistance of molecules to flow and a high viscosity value is indicative of the presence of intermolecular interactions. These interactions can cause a decreased mobility of monomer molecules during polymerization and also decreased flexibility of the corresponding polymeric network (Sideridou et al., 2002).

The viscosity of the matrix-forming monomers has a controlling effect on the amount of filler that can be mixed into a composite, and thus on the properties of the resultant materials. Silikas & Watts (1999) found that the viscosity of UDMA formulations using TEGDMA, HEMA and HPMA as diluents exhibited Newtonian behaviour and decreased as the percentage of the diluent monomer increased in their resin formulations. There is also a correlation between the polymerization shrinkage, filler load and the viscosity of the dental resin composite. Therefore, a favourable mixture of high molecular monomers and reactive diluents, in combination with different filler are used in dental composites (Moszner and Salz, 2001).

Taylor et al. (1998) investigated the relationships between filler type, filler content, matrix resin composition and viscosity and the flow characteristics of composite past formulations. Bis-GMA and Bis-GMA analogus and TEGDMA was used in the formulation of the resins of experimental composite. They found that the composite consistencies (plasticities) was increased when the filler decreased and the maximum filler content is predominantly an effect of the nature of the filler, where less micro filler than hybrid filler is needed to produce a similar plasticity. At a constant plasticity, lower viscosity matrices can accept more filler. Ellakwa et al. (2007) observed an inverse relationship between the polymerization shrinkage and complex viscosity. It was found that the substitution of UDMA for TEGDMA can reduced the shrinkage level but increased the viscosity.

Amirouche-Korich et al. (2009) indicated that the shrinkage strain and degree of conversion were significantly decreased when BisGMA concentration increases in resin matrix of experimental composites based on BisGMA/TEGDMA: (75/25, 50/50, and 25/75). The degree of conversion and shrinkage increase significantly with the increasing of TEGDMA concentration in the organic matrix. A linear correlation between the shrinkage-strain and degree of conversion of the investigated composites had been obtained. They then confirmed that direct relationships linked these two properties.

Musanije & Ferracane (2004) evaluated the effects of nanofiller surface treatment and resin viscosity on the early and long-term properties of experimental hybrid composites. Three resin formulations (low, medium and high viscosity) were prepared by varying the ratio of TEGDMA:UDMA:Bis-GMA (47:33:16 wt%; 30:33:33 wt%; 12:33:51 wt%). They found that non-bonded nanofillers had no significant effect on the long-term properties of hybrid composites. Moreover, they concluded that the medium-viscosity composites containing an equal mixture of Bis-GMA/TEGDMA/UDMA provided optimum mechanical properties compared to low-viscosity with high TEGDMA and high-viscosity with high Bis-GMA. While resin viscosity only had marginal effects on the mechanical properties, its adjustment still needed consideration so as to achieve a balance between degree of conversion and the mechanical properties such as flexural modulus, fracture toughness and Knoop hardness (Musanije and Ferracane, 2004).

Asmussen & Peutzfeldt (1998) found that the increase in tensile and flexural strength observed by the substitution of Bis-GMA or TEGDMA by UEDMA was reported to be possibly associated with the ability of the urethane linkage to form hydrogen bonds in the copolymer which would restrict the sliding of polymer segments relative to each other. It was also observed that there was a moderate increase in the modulus of elasticity when Bis-GMA was substituted with low levels of TEGDMA, followed by a relatively steep decline in stiffness as the content of TEGDMA increased. The reduction in the modulus of elasticity was explained to be due to the substitution of the stiffer Bis-GMA by TEGDMA. The natural flexibility of TEGDMA molecules is related to the ether linkages of the molecule allowing free rotation about the bonds (Asmussen and Peutzfeldt, 1998).

Emami & Söderholm (2009) found that the Young's modulus also increased as the concentration of the Bis-GMA increased in the monomers' mixtures. For higher concentrations of Bis-GMA, the strong impact of stiffness and hydrogen bond formation ability can explain why the modulus increases despite a decrease in conversion. The low modulus value at higher concentration of TEGDMA may also be due to the block and/or random polymerization units of Bis-GMA/TEGDMA form. In such polymers, some of the TEGDMA may not be able to cross-link, because the longer Bis-GMA molecules keep the growing chains too far apart to allow cross-linkage with the shorter TEGDMA molecules. However, as such a copolymer forms, the Bis-GMA molecules will be separated from TEGDMA molecules. This separation will decrease the contribution from hydrogen bond formation between Bis-GMA molecules. Under such a situation, the stiffness of the polymer should decrease and reach a minimum level (Emami and Söderholm, 2009).

With the use of urethane monomer as an additive to Bis-GMA/TEGDMA resin system it was possible to cure more rapidly with lower activation energy (Priyawan et al., 1995). Chowdhury et al. (1997) demonstrated that incorporating an additional urethane monomer into the system improved properties such as diametral tensile strength and hardness, when they compared ternary visible-light-cured system with Bis-GMA/TEGDMA/urethane resin to Bis-GMA/TEGDMA resin system as the control.

Deepa & Krishnan (2000) concluded that urethane blended with Bis-GMA resin were found to considerably enhanced the properties of dental composites. They also found that the higher fractions of Bis-GMA in resin matrix result in higher sorption and solubility values resulting in weaker composites.

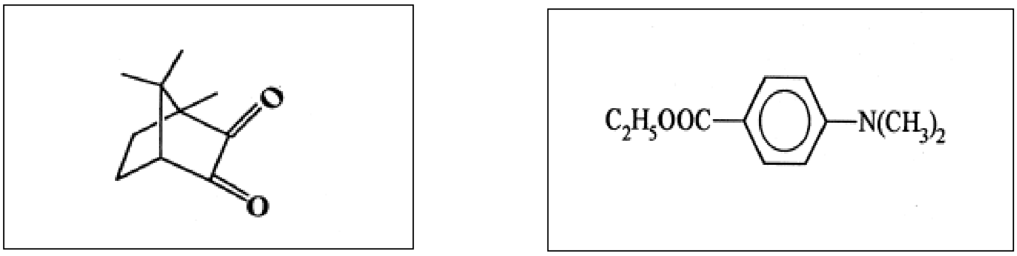
2.3.2 Initiator and stabilizer

The dental resin composite can be light-or chemically-activated. The degree of conversion of the chemically-cured composite is significantly lower compared to the light curing. The light cured material releases less monomer and therefore might be less dangerous with respect to toxicological effects (Polydorou et al., 2009a). Benzoyl peroxide and tertiary amines serve as the source of free radicals for chemically-activated resin composites. Tertiary amines such as N, N-dimethyl- p-toluidine and N, N-dihydroxyethyl-p-toluidine are used, the latter more commonly than the former because the former tends to cause discoloration.

For light-activated resin composites, the light-initiator consists of a two-component system: the initiator which can absorb light directly such as Camphoroquinone (CQ) (Figure 2.12a) and a co-initiator that does not absorb light but interacts with the activated photoinitiator to generate free radicals and initiates polymerization such as N, N-dimethylaminoethyl methacrylate (DMAEMA) or ethyl 4-(dimethylamino) benzoate (4EDMAB) (Figure 2.12 b). CQ is a typical visible light-activated free radical photoinitiator which exhibits an absorbance range between 400 and 500nm and requires a reducing agent as an electron donor for efficient polymerization (Albers, 2002; Ogunyinka et al., 2007). The concentration of CQ should be as little as possible because of its inherently yellowish-brown color and cytotoxicity issue (Landuyt et al., 2007). Krishnan & Yamuna (1998) found that any concentration above 0.25% of CQ does not significantly improve the diametral and compressive strength of dental composites.

Light-polymerization is induced by irradiation with halogen or LED lamps, emitting light in the wavelength range of 380-500 nm (Moszner and Salz, 2001). The optimum emission spectrum of a polymerisation source lies between 440 and 480 nm (Hervás-García et al., 2006). Smaller filler particles (0.01 to 1 µm) are most likely to cause scattering and will reduce the penetration of light because these particle sizes are similar to the wavelengths emitted from composite curing lights (Caughman et al., 1995).

For maximum curing, the exposure time of 40 seconds with at 400 mW/cm^2 intensity, is recommended for a 2mm-thick layer of resin. However, this exposure time can be reduced when the intensity is increased (Anusavice, 2003). Rueggeberg et al. (1994) concluded that exposure time and light intensity positively affects the degree of conversion, while sample thickness negatively influences the cure polymerization.



(a) (b)

Figure 2.12 Chemical structure of light-initiator system

(a) CQ and
(b) 4EDMAB

Stabilizers have been used to maximize the storage stability of the uncured resin composite and the chemical stability of the cured resin composite. As dimethacrylate monomers can be polymerized spontaneously under normal storage conditions, inhibitors are added, such as hydroquinone (HQ), hydroquinone monomethyl ether or hydroquinone monoethyl ether, and butylated hydroxytoluene. Small amounts of inhibitors, such as hydroquinone, may be added to the monomer to increase its shelf life. The inhibitor molecules react with the free radicals generated by photo-activation, and polymerization proceeds at a reduced rate until the inhibitor is completely consumed (O’Brien, 2002; Braga and Ferracane, 2004). Thus, when the polymerization reaction is set off by either light or admixture of two components, a much higher amount of radicals will be formed, outweighing the amount of inhibitor (Landuyt et al., 2007).

2.3.3 Filler and its influence on the dental composite performance

Filler particles vary from material to material; it could be colloidal silica, barium silicate, strontium/borosilicate glass, quartz, zinc silicate, or lithium aluminum silicate. The most common filler material used throughout the 1970s was quartz because of its chemical inertness and high refractive index and hardness. Its disadvantages included lack of radiopacity, high coefficient of thermal expansion, and abrasiveness (Albers, 2002). Owing to the clinical need for radiopacity, radiopaque heavy-metal glass fillers have replaced quartz in most new macrofilled composites. The most common elements added to increase radiopacity are barium, strontium, zinc, zirconium, and ytterbium (Albers, 2002). Barium silicate has medium hardness and is very radiopaque, which is important for diagnostic purpose, especially when composites are used in posterior teeth (Ferracane, 2001). Barium fillers have a number of advantages: (1) good radiopacity; (2) fine particle size (average 0.4 to 0.6 µm; the size of enamel crystals, which makes them more polishable and wear-resistant); (3) good index of refraction relative to resins; (4) lower cost; and (5) ready availability in pre-ground fillers (Albers, 2002).

Zirconium is harder than heavy-metal glass but not as hard as quartz. The zirconium fillers used in Z250 (3M ESPE, St. Paul, MN) are made through a priority precipitation process. Zirconium fillers can also be coated with silica to improve attachment to the matrix (eg, Palfique Estelite, J. Morita, Tustin, CA) (Albers, 2002). The fillers in Z100 is zirconia/silica particles with a particle size range from 3.5–0.01 mm and an average particle size of 0.6 mm. The filler in Filtek Z250 remains essentially similar as in Z100, but there have been significant processing changes to maximize fillers consistency. The particle size distribution for Filtek Z250 is also from 3.5 to 0.01 mm, with an average particle size of 0.6 mm, but contains a larger number of finer particles than is found in the Z100 composite (Sideridou et al., 2003).

The filler particles are added to the organic phase to improve the physical and mechanical properties of the organic matrix, so incorporating as high a percentage as possible of filler is a fundamental aim (Anusavice 2003; Hervás-García et al., 2006). Li et al. (1985) indicated that increased filler loading resulted in increased hardness, compressive strength and stiffness, and decreased water sorption. The composite filler content has an inverse linear relationship with co-efficient of thermal expansion shrinkage (Söderholm, 1984; Razak and Harrison, 1997).

Razak (1995) found in his study that there was an inverse relationship between the filler content and water sorption and solubility values of experimental composite inlay materials. A positive correlation was found between storage time in water and the water sorption and solubility process. The hygroscopic expansion, however, observed in this part of the study was not sufficient to compensate fully for the polymerization shrinkage process (Razak 1995).

Composites generally are classified based on filler content (weight or volume percent), filler particle size, and method of filler addition. Accordingly, composites are classified by particle size as megafill, macrofill (10 to 100 µm), midifill (1 to 10 µm), minifill (0.1 to 1 µm), microfill (0.01 to 0.1 µm), and nanofill (0.005 to 0.01 µm) (Roberson et al, 2002). Filler size, filler content and distribution were determined to highly influence the physical and mechanical properties of composite resins (Li et al., 1985).

Traditional composites contained glass filler particles with a mean particles size of 10-20 µm. The disadvantages of these composites were that their finished surfaces were very poor with a dull appearance which was due to the filler particles protruding from the surface as the resin was preferentially removed around them (van Noort, 2002). Quartz and heavy-metal glass are commonly used fillers in conventional macrofilled composites (Albers, 2002).

In an effort to overcome the problems of surface roughness associated with traditional composites, a class of materials was developed that used colloidal silica particles as the inorganic filler. The individual particles are approximately 0.04 μm, while the final inorganic filler content may be only about 50 wt% (or 30 to 40 vol%). Most microfilled composites are unsuitable for use at stress-bearing surfaces because the bond between the composite particles and the curable matrix is weak, facilitating chipping of the restorations (Anusavice, 2003). Submicron silica is the predominant filler in microfilled composites (Albers, 2002). These microfill composites can be polished to a very smooth and shiny surface, because of their small particle size, and have excellent esthetic qualities (Ferracane, 2001). Clinically, microfilled composites can be used as restorations in the anterior areas, where esthetics is a main concern. Although they lack in strength when compared with other types of composite resins, their small particle size allows for an excellent final finish. Consequently, they have been quite successful in the restoration of class III and V cavity preparations and as a direct restorative resin for facial veneers. Existing examples of microfilled composites are Renamel® Microfill (Cosmedent, Inc, Chicago, IL) and Durafill® VS (Heraeus Kulzer, Inc, Armonk, NY) (Radz and Leinfelder, 2008).

Small particles-filled composites were developed in an attempt to retain the surface polishability of microfilled composites and improve their physical and mechanical properties comparable if not better than traditional composites. The average filler size of these material ranges from 1 to 5 μm and contains more inorganic fillers (80 wt% or 60-65 vol %) than traditional composites. These materials have been indicated for applications in large stress bearing areas (Anusavice, 2003).

The hybrid composite was developed in an effort to obtain even better surface polishability than that provided by small particles composites. As the name implies, there are two or more kinds of filler particles in the hybrid composite. Most modern hybrid fillers consist of colloidal silica and ground particles of glasses containing heavy metals, of approximately 75 to 80 wt%, in which the glasses have an average particles size of about 0.6 to 1.0 µm. In a typical size distribution, 75% of the ground particles are smaller than 1.0 µm. Colloidal silica represents 10 to 20 wt% of total filler content. The hybrid composites are also used widely for stress-bearing restorations (Anusavice, 2003). Commercially available existing examples of hybrid composites include: TPH Spectrum® (Dentsply Caulk, Milford, DE), Z100™ Restorative (3M ESPE, St. Paul, MN), Herculite® XRV™ (Kerr Corporation, Orange, CA), and others. Although still available, this category of composite resins is fading out of existence (Radz and Leinfelder, 2008), and this could due to the introduction of nanotechnology.

The lower filler content of microfilled composites results in elastic moduli of one quarter to one half that of the more highly filled fine-particle composites, (O'Brien, 2002). More than ten years ago, microhybrid and/or nanohybrid composite resins began to appear in the market. It was developed to improve the hybrid composites and create a more universal material. Most composite resins in this category exhibit an average particle size of 0.5 µm. Currently, these materials are the most popular commercially available composite resins. Existing examples include: Premise™ (Kerr Corporation), Esthet-X® Improved (Dentsply Caulk, USA), 4 Seasons® (Ivoclar Vivadent, Inc, Amherst, NY), Tetric EvoCeram® (Ivoclar Vivadent, Inc), Vitlessence® (Ultradent Products Inc, South Jordan, USA), Gradia Direct (GC America, Inc, Alsip, USA), and Artiste® (Pentron Clinical Technologies, LLC, Wallingford, CT, USA), and others (Radz and Leinfelder, 2008).

Because of the positive correlations between the volume fraction of filler and the diametral tensile strength, and between the volume fraction of filler and the Knoop hardness numbers, it was concluded that the filler concentration plays a prominent role in determining the properties of contemporary posterior composite resins (Chung and Greener, 1990). The percent of filler load by weight is a larger number than percent filler by volume, which is the clinically significant factor. For example, a typical composite filled 75% by weight is usually filled only 50 to 60% by volume (Albers, 2002). A summary of some properties of different types and filler load of dental composites is shown in Table 2.1.

Table 2.1 Physical properties of composite

Properties	Traditional	Micro filled	Small particles	Hybrid
Filler vol% Or wt%	60-65 70-80	20-55 35-60	65-77 80-90	60-65 75-80
Compressive Strength MPa	250-300	250-350	350-400	300-350
Tensile Strength MPa	50-65	30-50	75-90	70-90
Elastic modulus GPa	8-15	3-6	15-20	7-12
Water sorption mg/cm²	0.5-0.7	1.4-1.7	0.5-0.6	0.5-0.7
Knoop hardness	55	5-30	50-60	50-60
Curing Shrinkage	-	2-3	2-3	2-3

Adapted from Anusavice (2003).

Kim et al. (2002) classified the contemporary composites, which they divided in their study, into 4 categories according to filler morphology: prepolymerized, irregular-shaped, both prepolymerized and irregular-shaped, and round particles. Filler loading was influenced by filler morphology. Composites containing prepolymerized filler particles had the lowest filler content (25% to 51% of filler volume), whereas composites containing round particles had the highest filler content (59% to 60% of filler volume). The mechanical properties of composites were related to their filler content. Composites with the highest filler by volume exhibited the highest flexural strength 120 to 129 MPa, flexural modulus 12 to 15 GPa, and hardness 101 to 117 VHN. Fracture toughness was also affected by filler volume, but maximum toughness was found at a threshold level of approximately 55% filler volume. Within the limitations of their study, the commercial composites tested could be classified by their filler morphology. Both filler morphology and filler loading influenced flexural strength, flexural modulus, hardness, and fracture toughness.

Miyasaka (1996) found that the strength for the hybrid of irregular and spherical fillers tended to increase as the size of component fillers decreased. The strength for the hybrid of the same fillers in shape also increased as the size of fillers decreased.

Generally, the smaller the average particle size, the easier it will be to polish the resin. Nanotechnology has led to the development of a new composite resin characterized by containing nanoparticles measuring approximately 25 nm and nanoaggregates of approximately 75 nm, which are made up of zirconium/silica or nanosilica particles (Hervás-García et al., 2006). The drawback is that since the particles are so small, they do not reflect light, so they are combined with larger-sized particles, with an average diameter within visible light wave lengths (i.e. around or below 1µm, to improve their optical performance and act as a substrate (Hervás-García et al., 2006).

Turssi et al. (2005) concluded that the different shapes and combinations of size of filler particles significantly affected the wear behavior and degree of conversion of the experimental composites. The improvement of the wear resistance with the smaller particles is due to the mean distance between neighboring particles being smaller than that with the coarser filler particles. The lowest degree of conversion was achieved in composites with monomodal particle size closest to the critical wavelength of the activating light (470 nm), and was essentially independent of particle shape as the light scattering is most dependent upon the particle size.

Composites with altered viscosity and handling characteristics have been produced for use in specific application. Flowable composites are typically, diluted minifill composites which are made more fluid by reducing the overall filler content to less than 45 vol%. In contrast, packable composites have a very thick and heavy consistency and are designed for posterior teeth. These composites have similar filler volume as normal midifill and minifill composites, but the heavy consistency is produced by using modified fillers or by altering the distribution of particle sizes to include smaller fillers (Ferracane, 2001).

Several packable composites, such as Solitaire (Heraeus-Kulzer, USA) and A.L.E.R.T. (Jeneric/Pentron), have recently been introduced to the market. The first generation of flowable composites was introduced in late 1996, just before condensable composites (Bayne et al., 1998). Packable composites are indicated for use at stress bearing areas of posterior teeth, with an application technique similar to amalgam. The increased viscosity of these materials permits greater “packability” and has demonstrated less slumping characteristics (Attar et al., 2004). However, flowable composites have been recommended as liners beneath packable composites due to their low viscosity, increased elasticity and wettability. These handling characteristics and a syringe delivery system make flowable resins an ideal choice for use as a liner in a “sandwich” technique where they are placed at the cementum margins of proximal box of Class II resin composite restorations (Neme et al., 2002).

Packable composites may be easier for clinicians to handle than conventional resin-based composites. Their physical properties however were not superior to those of the conventional small-particle hybrid resin-based composite. In addition, these materials may have the clinical drawback of increased wear and surface roughness that was seen with early, large-particle composite restorative materials (Cobb et al., 2000).

It has been suggested that one key mechanical property for clinical prediction of performance may be toughness. This property could correlate with both wear and fracture resistance. Because flowable composites are more resin-rich than traditional composites, one might expect their toughness values to be better than those of conventional materials. Flowable composites might also have higher fracture toughness values because of their lower elastic moduli. On the other hand, due to the low filler content, flowable composites develop high volumetric shrinkage, approaching 6% in some products (Bayne et al., 1998). Their greater toughness might mean that they absorb sufficient energy to help postpone interfacial failures caused by cyclic loading (Bayne et al., 1998). Barron et al. (1992) found that the relationship between monomer conversion and inorganic filler loading was inversely proportional.

Flowable composite is clinically indicated for pit and fissure restorations and liner in Class I, II and V restorations. Deliperi & Bardwell (2002) clinically implicated that the use of flowable composite as a liner for composite restoration to reduce enamel microcracks and substantially improve the adaptation of resin-based composite to deep dentin. Currently there are many clinical examples: Revolution™ Formula 2 (Kerr Corporation, USA), Esthet-X® Flow (Dentsply Caulk, USA), AEliteFlo™ (Bisco, Inc, Schaumburg, USA), Venus® Flow (Heraeus Kulzer, Inc, USA), Tetric EvoFlow® (Ivoclar Vivadent, Inc), LuxaFlow (Zenith/DMG Brand Division, Foremost Dental LLC, Englewood, USA), and Flow-It® ALC™ (Pentron Clinical Technologies, USA) (Radz and Leinfelder, 2008).

2.5 Coupling agent and its influence on performance of dental composite

Coupling agents are used to bond resin matrix and filler particles together and they are sometimes called adhesives. In conventional composites, the matrix material and filler particles are different and no chemical bond exists between them. Coupling agents reduce the gradual loss of filler particles from the composite surface (Albers, 2002). Commonly used coupling agents are epoxy, vinyl, and methyl silanes. The single most commonly used silane in dental composites is 3-(methacryloyloxypropyl) trimethoxysilane (MPTMS) (Albers, 2002). The usual coupling agent for dental composites is a molecule which has silanol (Si-OH) groups on one end and methacrylate groups (containing C=C) on the other end. These molecules are capable of forming covalent bonds to both the silicon-oxygen groups in the silica-based fillers and the methacrylate groups in the resin matrix (Figure 2.13) (Ferracane, 1995; Antonucci et al., 2005).

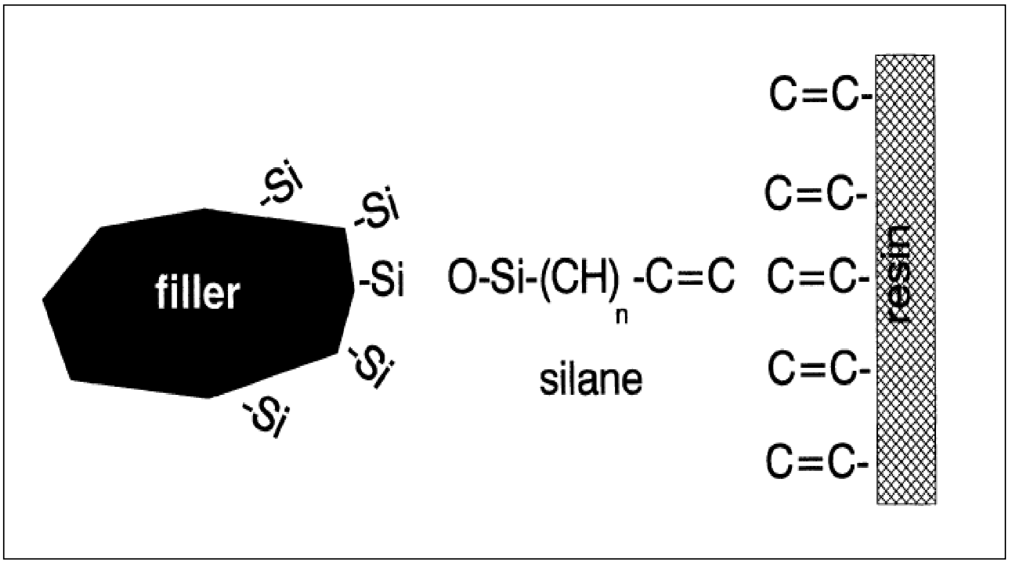


Figure 2.13 Simplified schematic representation of silane bonding the fillers and the resin (Ferracane, 1995)

The term conversion, for resin-based composites, generally refers to the percentage of C-C bonds of the matrix monomers reacted. Additional C=C on, for example, silane molecules can lead to errors in determining the conversion. The magnitude of such error is expected to be related to the amount and reactivity of the silane on the filler (Halvorson et al., 2003). Most manufacturers include the weight of these materials in the figures quoted as percent filler. The filler coupling agents have a thin film thickness. They generally add 1 to 6% to the weight of filler particles. Some microfills, such as those using Aerosil 200 (Ivoclar, Germany), do not have coupling agents.

By chemically bridging the matrix and filler phases, interfaces can effectively transfer stresses and also drive future cracks toward the stronger reinforcing filler phase. Silanation however, has never been optimized. Incomplete or non-uniform silane bonding to the filler particles prevents appropriate coupling, and local shrinkage may result in either separation or porosity along the filler interfaces. In addition to these porosity effects on fracture resistance, the same sites act as water absorption reservoirs (Bayne, 2005). Sideridou et al. (2007) showed that the effect of ageing in water or ethanol/water solution, after 30 days storage, on the mechanical properties of a light cured dimethacrylate resin depends on the chemical structure of the resin. In the case of resin composite, this effect depends on the filler-matrix bond strength.

2.6 Limitations of dental composite's properties

2.6.1 Polymerization shrinkage

The curing or hardening of dental composites occur by polymerization of its vinyl-based systems (methacrylate; C=C), making polymerization shrinkage an unavoidable phenomena (Ge et al., 2005). During the chain propagation process, the monomer units are more closely connected to one another in the polymer chain than they are in the starting monomer phase, which result in polymerization shrinkage production. In the liquid bulk monomer, the distance between the monomer units (molecules) is characterized by the van der Waals distance of about 0.340 nm. In the polymer the distance between the monomer units is about 0.154 nm, which corresponds with the distance of covalent carbon–carbon (C–C) bonds. This results in an increased density of polymer and subsequently volume shrinkage (Shalaby and Salz, 2007).

This shrinkage produces stresses, which tend to develop at the tooth\composite interfaces, weakening the bond and eventually producing a gap at the restoration margins. This can lead to staining, secondary caries, and other clinical problems (Anusavice, 2003; Ferracane, 2005). However, there is a lack of evidence that indicates polymerization shrinkage is the primary cause of secondary caries (Sarrett, 2005). Braga et al. (2005) concluded that volumetric shrinkage should not be the only parameter to be considered for predicting composite behavior regarding stress development. Materials with high inorganic fillers exhibited relatively low shrinkage and high elastic modulus, could give rise to increase stress. A significant relationship between higher filler volume and increased polymerization stress was found among the commercial materials (Condon and Ferracane, 2000). On the other hand polymerization shrinkage is implicated to cause fracture of cusps and to create another source of post-operative sensitivity. However, there is no scientific clinical evidence that the greater the shrinkage of a composite, the more likely the chance for post-operative pain caused by fractured cusps (Sarrett, 2005).

Polymerization shrinkage is directly related to the conversion of reactive double bonds. The concentration of double bonds in the monomer and the degree of conversion achieved would affect the final shrinkage results (Venhoven et al., 1993). Thus the ideal composite should exhibit an optimal degree of conversion and minimal polymerization shrinkage. These seemed to be antagonistic goals, as increased monomer conversion invariably leads to large polymerization shrinkage values. But both parameters are key ones for optimizing resin composite restoration (Dewaele et al., 2006). Polymerization shrinkage is related to the filler loading, amount of monomer, and type of monomer (Alvarez-Gayosso et al., 2004). However, even with the addition of inert filler limits, actual shrinkage in proportion to the volume fraction of the filler used (Ge et al., 2005), polymerization shrinkage ranges between 2 and 6% by volume (Labella et al., 1999).

Diluent monomers such as TEGDMA have been used with Bis-GMA to increase both its degree of conversion and filler loading. Venhoven et al. (1993) found that dental resins, based on Bis-GMA/TEGDMA (70:30 mass ratio) exhibit volumetric shrinkage of about 7.0% at typical conversions. However, the use of higher proportions of TEGDMA can increase the final conversion attained in dental resins. With this comes increased shrinkage, which is directly related to both initial reactive group concentration and conversion (Ge et al., 2005).

Patel et al. (1987) concluded that the percentage volume shrinkage depends principally on molar volume of the molecule, and hence the volume of the side group. In order to obtain lower shrinkage monomers, an obvious approach is to increase the molecular weight or molar volume of the monomers in order to decrease the concentration of the reactive double bonds.

The methods used to determine polymerization shrinkage range from simple static techniques to elaborate dynamic procedures such as dilatometry. Static shrinkage measurement methods include monomer/polymer densities obtained by measured dimensions and buoyant mass determinations known as the Archimedes principle (Stansbury and Ge, 2003). This technique is easy, cost effective and widely used (Labella et al., 1998; Chutinan et al., 2004; Uhl et al., 2005; Ruttermann et al., 2007). Mercury in the dilatometer has the opaque nature of mercury. Options for introduction of the curing light are limited and control of the irradiation intensity is complicated by the reflective surface of mercury. There are also obvious health concerns associated with the use of mercury (Stansbury and Ge, 2003).

2.6.2 Water sorption, solubility and volumetric change

Dental composite materials undergo a series of physical changes as a result of the polymerization reaction and subsequent interaction with the oral environment. Following polymerization, the inward movement of water molecules causes mobilization of ions within the resin matrix and an outward movement of unreacted monomers leaches out ions from fillers and activators. The subsequent interaction with the wet oral environment results is water absorption which causes two opposing phenomenon. 1) the diffusion of water leaches out the free unreacted monomers and ions from the resin matrix, which leads to loss of weight resulting in solubility. 2) the absorption of water results in a hygroscopic expansion which may be able to compensate for the effects of polymerization shrinkage, relieve stresses and thereby reduces marginal gaps to a certain extent (Martin et al., 2003).

Bowen et al. (1982) concluded that composite resins can be formulated to have hygroscopic expansions sufficient to compensate for polymerization shrinkage. On the contrary, Momoi & McCabe (1994) reported, sometimes expansion, which is in excess of polymerization shrinkage, may cause an outward force against cavity walls, causing cracking and fracture of enamel. Feilzer et al. (1990) studied the relaxation by hygroscopic expansion of the interfacial polymerization shear stress of bonded resin composites. They found the shear stresses in Bis-GMA/TEGDMA and urethane dimethacrylate-based resins were either fully relieved or converted into an "expansion stress" by hygroscopic expansion. Expansion resulting from water sorption can be a clinically desirable phenomenon if it fully counteracts the effects of shrinkage. However, Martin & Jedynakiewicz (1998) showed that the volumetric expansion for a dental composite after two years in water was 0.5%, compared it to a value of 1.1% for composite cement and 2.26% for a compomer.

Two patterns are generally known for the diffusion of water through polymeric materials (Bellenger et al., 1989). First, the pattern following the “free volumetric theory,” in which water diffuses through microvoids without any mutual relationship to the polar molecules in the material. The second pattern is called “interaction theory,” in which water diffuses through the material binding successively to the hydrophilic groups. In connection with that, the voids trapped in the bulk polymer contain oxygen that may inhibit polymerization and consequently facilitate solubility (Bellenger et al., 1989; Gerdolle et al., 2008).

Excess water sorption may lead to hydrolytic degradation of the polymer matrix and deterioration of mechanical properties (Ferracane, 2006). This is mainly due to a hydrolytic breakdown of the bond between silane and filler particles, filler–matrix debonding or even hydrolytic degradation of the fillers (Söderholm, 1984). Chemical erosion may also result in the release of unreacted monomers and degradation by-products into the oral environment (Örtengren, et al., 2001; Ferracane, 2006).

Water absorption is the amount of water that a material absorbs over a time per unit of surface area / volume. When a restorative material absorbs water, its properties change, and therefore its effectiveness as a restorative material is usually diminished. A number of factors will determine the diffusion coefficient for this type of polymer based materials. These include types of resin, filler fraction, filler size, reactivity of the glass, presence of silane and non-silane coupling agents (Örtengren et al., 2001).

The chemistry and structure of the polymer network are important in determining the extent to which the material will be affected by an aqueous environment. Important chemical characteristics include the hydrophilicity of the polymer, and the differences in solubility parameter between the polymer and the solvent. Important structural parameters include the crosslinking density and the porosity of the network. In addition, the presence of reinforcing filler may significantly influence the solubility and sorption of the structure (Ferracane, 2006). The amount of the released (elution) components is related to the degree of double bond conversion, the chemistry of the solvent, and the size and the chemical nature of the released components (Ferracane, 1994). In cured materials, some C=C units are present as pendant methacrylate groups, covalently bonded to the polymer network, and are incapable of leaching or evaporating. Other C=C units are unreacted monomers, capable of leaving the cured material (Bagis and Rueggeberg, 1997).

Polydoroua et al. (2007) found that Tetric Flow$^{®}$ (31.5%) contains a higher amount of monomer compared to Tetric Ceram$^{®}$ (20.2%) when the material is not polymerized. However, the results were exactly the opposite for polymerized samples. The amount of monomers released from Tetric Ceram$^{®}$ after polymerization was higher compared to Tetric Flow$^{®}$. These results were the same for all polymerization and storage times used. They attributed this to the fact that the efficacy of polymerization was higher for Tetric Flow$^{®}$ compared to Tetric Ceram$^{®}$.

The wide variations in filler and resin compositions between the various brands may be helping to obscure the dependence of water sorption and water solubility on resin formulation and chemistry, Toledano et al. (2003) found that Z100 (3M, USA) showed much more water sorption than Prodigy (Kerr Co, USA). This variation between these Bis-GMA-based composites may be the result of using different proportions of diluent resins, such as triethylene glycol dimethacrylate, and a larger number of air voids was observed in the Z100 specimens.

The decreased water sorption and associated diffusion coefficient of Filtek Z250 compared with Z100 specimens was suggested to be partly attributed to a decrease in structural heterogeneity of the polymer. Furthermore, the ether groups of BisEMA and the urethane groups of UDMA (predominant in Filtek Z250) are known to form weaker hydrogen bonds with water molecules than the hydroxyl groups of BisGMA and TEGDMA molecules (predominant in Z100) (Peutzfeldt, 1997; Sideridou et al., 2003) thus, reducing the hydrophilic nature of the constituent monomer units.

The polar nature of such a polymer matrix and the presence of ether linkages are of importance for water sorption and hygroscopic expansion of composite resin materials (Peutzfeldt, 1997). Braden (1984) found that composites based on TEGDMA alone exhibited higher diffusion coefficients than composites based on a blend of UEDMA and TEGDMA. The difference was explained by a higher degree of cross-linking in the latter case. As cross-linking of the matrix is often correlated to the degree of conversion, it would also be expected that the water sorption will increase with a decreased degree of conversion of the material. Therefore, the matrix compositions of ethylene glycol dimethacrylates (constituting ether linkages) increased water sorption in composite resin matrices (Braden and Davy, 1986).

Important structural parameters include the cross-linking density and the porosity of the network. In addition, the presence of reinforcing filler may significantly influence the solubility and sorption of the structure (Ferracane, 2006). Barron et al. (1992) found the relationship between monomer conversion and inorganic filler loading was inversely proportional. While, there is no considerable absorption of water by the filler particles themselves, composites take up more water than estimated on the copolymer content, and the most probable site for accommodation of additional water is the interface between the inorganic filler particle and the polymer matrix (Toledano et al., 2003).

2.6.3 Mechanical properties

Restorations in the oral cavity are subjected to various stresses and, thus, are required to have adequate strength to function under appropriate physiological loads. ADA Specification No. 27 requires that the strength of both self-cured and light-cured materials be not less than 80 MPa when used for occlusal restorations and not less than 50 MPa when used for anterior restorations. Flexural strength has been suggested as criterion of durability and longevity of composites (Gladys et al., 1997).

Flexural strength is more clinically relevant test of material strength and is especially important if the material is used for Class I, II and IV cavities, which are usually subjected to high forces. Materials with higher flexural strength are less prone to bulk fracture as well as fracture of the margins (Yap and Teoh, 2003; Ersoy et al., 2004).

The modulus of elasticity is a measure of the stiffness or flexibility of a material. A stiff material has a high modulus of elasticity, and a flexible material has a low modulus of elasticity (O'Brien, 2002). Generally, when the modulus of elasticity increases, the maximum deflection decreases and the resin becomes more brittle (Tanaka et al., 2001).

Toughness is the resistance of material to fracture, which is an indication of the amount of necessary energy to cause fracture. The area under the elastic and plastic portions of stress-strain curve represents the toughness of a material (Craig and Powers, 2002). It has been assumed that toughness is the key property for predicting clinical fracture resistance (Bayne et al., 1998). The issue with restorative composites is to increase their flexural strength and fracture toughness, and thereby lengthen their service life in the oral cavity, while still maintaining their esthetic value (Shenoy, 2008).

To evaluate the ability of materials to resist fracture or deformity, the transverse bending test can be conducted including fracture strength, yield strength, displacement and elastic modulus. In the transverse bending test, both tension and compressive events can occur and flexural stress is developed which can be used to represent the ability of a material to resist deformation or fracture (Ho et al., 2001). They concluded that the flexural behaviour was found to be influenced by matrix resin, type, and filler content and size. In their study, microhybrid formulations showed superior flexural properties in comparison to microfilled materials.

Kawano et al. (2001) found that the hybrid composite exhibited significantly higher flexural strength and flexural modulus than the microfine composite type, which indicated that the hybrid composite type is more brittle and more prone to bulk fracture. Changes in both the organic and inorganic phases of the composites can alter the properties in order to fulfill clinical requirements. Since mastication involves many cycles of stress during the life of a restoration, fatigue properties should be taken into account in restoration design (Papadogiannis et al., 2007). Fatigue caused by cyclic loading is thought to be responsible for the failure of composites restorations described by chipping, localized or generalized wear and fracture (Abu Kasim et al., 2006).

The results of the work of Ikejima et al. (2003) clearly demonstrated the effects of filler content, filler particle size and filler silanation on mechanical properties. With the increase of filler volume fraction, flexural strength, flexural modulus and shear strength increased up to about 50% by volume. Any further increase in the filler volume above 50% did not cause an increase in the flexural strength and shear strength. There was some evidence that strength begins to decline at very high filler levels (>60 vol %). However, the modulus of elasticity continued to increase as more filler was incorporated.

The composites with considerably low or high filler content (< 60% or > 80% by weight) were significantly low in fatigue resistance. Htang et al. (1995) revealed that an inverse linear relationship tended to exist between filler level and fatigue resistance of the composite materials beyond a certain level of filler content. Increased filler level does not necessarily improve the fatigue resistance of a resin composite as determined by applying a repetitive impact load (Htang et al., 1995).

Lohbauer et al. (2006) concluded that flowable materials with reduced filler content exhibited the lowest Young's moduli, compared with those measured for higher filled materials. A linear relationship has been found between elastic moduli and filler loading (r (2) = 0.798). Correlations of flexural strength and fatigue data to different filler fractions could not be proved. Flexural strength ranged between 61.3 and 124.9 MPa. After 10(4) cycles of fatigue loading, the flexural strength suffered from a decrease between 45.2 and 61.7%. However, materials with high initial strengths do not obviously reveal the best fatigue resistance. Bayne et al. (1998) conducted a study with the mechanical property tests (ISO 4049: 1988) of eight flowable composites and two hybrid composites. They found that the mechanical properties were generally about 60 to 90 percent of those of conventional composites.

It has been shown by Asmussen & Peutzfeldt (1998) that the replacement of Bis-GMA and TEGDMA by UEDMA causes an increase in both the tensile and flexural strengths of the resin matrix. Abu Kasim (1995) found that Clearfil Photo Posterior (Kurary, Japan) and Heliomolar (Vivadent, Liechtenstein) which consisted of both Bis-GMA and UDMA were more fatigue resistant when compared to P50 (3M, USA) and Silux Plus (3M, USA), both based on Bis-GMA and TEGDMA resin.

Papadogiannis et al. (2007) assessed the fatigue properties of four dental resin composites, Alert (Jeneric/Pentron Inc., USA), Filtek P60, Admira (Voco, Germany) and Synergy (Coltene Whaledent, Germany). Among the four composites, Filtek P60 exhibited the best behavior under fatigue and when compared to the others, its stress to failure versus the log of the number of cycles was the highest, with a statistical significance ($p < 0.001$). Filtek P60 belongs to the Compact-Filled group of composites and because it is more heavily filled than Synergy and Admira it was expected to have better fatigue properties. However, it also showed significantly higher fatigue properties than Alert, which is the material having the highest percentage of fillers. However, in Filtek P60 there is also a difference in the composition of the matrix. The basic component is Bis-GMA, but part of the diluent monomer TEGDMA is replaced by UEDMA and Bis-EMA. It has been shown by Asmussen & Peutzfeldt (1998) that the replacement of Bis-GMA and TEGDMA by UEDMA causes an increase in both the tensile and flexural strengths of the matrix. This may be explained by the degree of conversion of the polymer matrix or it can be associated with the ability of the urethane linkage to form hydrogen bonds in the copolymer, which presumably results in restricted sliding of the polymer segments relative to each other. With the correct proportion of the content of UEDMA, Bis-GMA and TEGDMA the resin composite may satisfy the needs of use and this may be the case with Filtek P60.

2.6.4 Biocompatibility

Biocompatibility is perhaps the most critical requirement for dental materials. If these materials adversely affect the oral environment, then all the attempts to treat the tooth decay are, at best, questionable (Tiba and Culberson, 1999).

Biomaterials do not usually intend to have the same therapeutic effect as drugs, as they should be "biologically neutral", i.e., should not elicit adverse reactions in the tissues with which they are in contact. In that regard, attempts are usually made to make biomaterials inert and insoluble. However, biological reactions which favor the healing of the involved tissues or enhance the function of the device do not preclude their classification as biocompatible materials (Major, 1992).

The objective of *in vitro* biocompatibility tests is to simulate biological reactions to materials when they are placed on or into tissues of the body. These methods offer less expensive ways to survey newly developed materials, reducing the probability of surprises when animal usage tests or clinical trials are performed. Without prior laboratory testing of materials, using animals to test materials could become very time-consuming and expensive (Hanks et al., 1996).

An *in vitro* test has several advantages over animal or usage tests. They are relatively fast, inexpensive, and easily standardized. Furthermore, they may be used for larger-scale screening than can be used in either animal or usage tests. Conditions for these tests can be tightly controlled to provide the highest quality of scientific rigor. The tests of *in vitro* are performed outside of an organism and *in vitro* tests have been used as the first screening test to evaluate a new material (Anusavice, 2003).

Cell culture methods are frequently used to test the cytotoxicity of dental materials (Schmalz and Schmalz, 1981; Schmalz, 1994). Cytotoxicity can be assessed by different methods, e.g. cell counting, determination of proliferation rates, synthesis of different cell products or determination of enzyme activities (Schmalz, 1994).

Cytotoxicity tests involved the evaluation on cell cultures of enzyme activities, membrane integrity, alteration of cell morphology, determination of cell growth inhibition, and determination of the effective dose that causes 50% reduction of cell proliferation (Goldberg, 2008).

Toxicity *in vitro* is a negative or deleterious effect of an agent on normal cellular biochemical functions, i.e. a disturbance of cellular homeostasis. This may assume a spectrum of changes from frank loss of cellular vitality to very subtle alterations in cellular function, which can be detected only by biochemical means (Kirkpatrick and Mittermayer, 1990). The TC50 can be calculated for quantification of the toxic reaction as the concentration which results in a 50% reduced cell survival under given experimental conditions. With this method mainly the effect of soluble single resin components can be determined (Pelka et al., 2000).

Fibroblasts are used for cytotoxicity testing since they are an ISO-approved cell type (Wataha et al., 2003). The methylthiazol tetrazolium (MTT) test has been used extensively to assess cytotoxicity of dental materials, which is a well-established method for dental material testing (Issa et al., 2004; Wataha et al., 2003). In this MTT test methylthiazol tetrazolium is metabolically reduced to coloured formazan. Factors that inhibit dehydrogenase activity will affect the associated colour reaction. It has been shown that activated cells produce more formazan than resting cells; therefore it is possible to measure cell activity or enzyme activities (Issa et al., 2004).

Al-Hiyasat et al. (2005) demonstrated that the change in the chemical structure of the composite and the variation in the ratio of filler and monomer have a significant effect on the element release and cytotoxicity level of the materials. In terms of biocompatibility of dental composite, the fillers do not seem to play a major role in the biocompatibility of the material. The organic polymerized matrix seems to be responsible for most of the reported undesirable effects (Goldberg, 2008).

Issa et al. (2004) reported that the *in vitro* cytotoxicity of some resin monomers were quantitated by the release of cytotoxic enzyme lactate dehydrogenates (LDH) into cell culture medium as the marker for membrane integrity, and the MTT assay representing the metabolic and mitocondrial activity of treated cells.

The cytotoxicity of dental composite components hydroxyethylmethacrylate (HEMA), triethyleneglycoldimethacrylate (TEGDMA), urethanedimethacrylate (UDMA), and bisglycidylmethacrylate (Bis-GMA) was investigated on human gingival fibroblasts (HGFs) at two time intervals. The following range of increased toxicity was found for composite components (24 and 48 h): HEMA < TEGDMA < UDMA < BisGMA (Franz-Xaver Reichl et al., 2006).

When reducing the amount of unreacted monomeric double bonds it is critical to limit the risks associated with leaching of small molecules (Anseth, et al., 1996). The degree of cure of restorative composites has been shown to be directly related to the level of cellular biocompatibility *in vitro*. As the degree of monomer of the conversion of composites decreases, protein synthesis by gingival fibroblasts also decreases (Caughman et al., 1991). Partially reacted monomer units which are attached to the polymer network are not a concern for subsequent leaching and toxicological effects in the body (Anseth et al., 1995). Bland & Peppas (1996) calculated the conversion of multifunctional methacrylate with a conversion of 33% a monomer with three reactive double bonds, makes it is possible for essentially all the free monomer molecules to have reacted via at least one double bond, and are, therefore, attached to the polymer network.

Many *in vitro* studies have shown that the polymerization reaction that produces the cross-linked polymer matrix from the dimethacrylate resin monomer is never complete and adverse reactions are due to the release of nonpolymerized monomers such as TEGDMA or HEMA (Schedle, 1998; Issa et al., 2004; Al-Hiyasat et al., 2005). Unbound free monomers seem to be directly responsible for the cytotoxicity of resin composites on pulp and gingival cells, and they are probably also implicated in the allergic potential of the material (Ferracane, 1994). Recent progress of dental composites did not change the occurrence of cytotoxic effects, and in this context, similar toxic levels were obtained with packable and nonpackable dental composites (Franz et al., 2003). It is clear that resin-containing restorative materials release unbound free monomers, immediately after setting and throughout its life span as a restorative material. These monomers were found to be cytotoxic for pulp and gingival cells and leaching of some ions seems also to be implicated in cell alterations (Goldberg, 2008).

An *in vitro* study has reported that leached TEGDMA is considerably cytotoxic in various cell cultures (Issa et al., 2004). It has also been observed that TEGDMA can easily penetrate membranes and may subsequently cause detrimental reactions with intracellular metabolic system (Geurtsen and Leyhausen, 2001).

Low degrees of conversion during resin polymerization are responsible for the loss of mechanical, chemical and physical properties. TEGDMA release has been mainly studied and the quantity released was sometimes higher than the cytotoxic limit. The cytotoxic effects became less important when the curing time of the resin was increased and with preincubation periods in a biological medium (Schedle, 1998).

Caughman et al. (1991) concluded that for each studied composite; P-50, Prisma-Micro-Fine (Dentsply Caulk, USA), and Multifil (Kulzer, USA), as the percentage of monomer conversion increased, cellular toxicity decreased. As measured by inhibition of cellular protein synthesis, cellular toxicity decreased as the curing time and resultant monomer conversion increased for each composite sample. Al-Hiyasat et al. (2005) found that the flowable materials, Admira Flow, Tetric Flow, Feltik Flow of the traditional composites (Admira, Z250, Tetric Ceram) were more cytotoxic than their standards. Also they determined the compounds released from these materials by high-performance liquid chromatography (HPLC) analysis, and found that Bis-GMA and TEGDMA in the eluates of all the materials, while urethane dimethacrylate (UDMA) was present in all eluates except that of Feltik Flow. TEGDMA has the largest amount of leached compounds.

Säilynoja et al. (2004) pointed out the heat curing time of a fiber-reinforced resin affected the degree of conversion of the material. This result was expected, but it was somewhat surprising that the heat curing time did not affect cytotoxicity. They also concluded that the urethane tetramethacrylate UTMA-based materials show no cytotoxic effects at low temperatures or on contact with cells, indicating that the potentially harmful molecules are released very slowly from the matrix during storage in a solution. In clinical situations, a slow release of potentially harmful molecules minimizes the chance of irritation or allergic reactions.

2.6.5 Durability of composite restoration

The factor which is generally used to assess the success or failure of a restorative material for any application is durability, which depends on the physical, mechanical and biological properties of the restorative materials (McCabe and Walls, 1998). The problems such as surface roughness and color instability, which are primarily related to the composite materials, are no longer considered as serious clinical challenges for posterior composite restorations (Sarrett, 2005). This is not to say that improvements in these properties would not be welcomed, however, future research would be more profitable if directed elsewhere. The available clinical data indicates that secondary caries and restoration fracture are clinical challenges with posterior composite materials that merit further research (Sarrett, 2005).

The success rate of these posterior restorations was very high in early clinical evaluations, but started to drop after 5 years. Qvist et al. (1990) in Denmark reported that half of Class I and II restorations were replaced because of secondary caries and bulk fracture of the fillings. Collins et al. (1998) found that the bulk fracture and secondary caries at the margin accounted for 72% of the known failures of the three different types of composite resin restorations, at 8 years of clinical evaluation. A recent review of longitudinal clinical studies verified that bulk fracture of the composite was the most common cause for restoration replacement after five years (Brunthaler et al., 2003).

Fatigue caused by cyclic loading is thought to be responsible for the failure of composites restorations described by chipping, localized or generalized wear and fracture (Abu Kasim et al., 2006).The properties, and hence the performance of resin composites, are dependent upon the three basic components of the material (Peutzfeldt, 1997; Vasudeva, 2009). Wilson et al. (2002) suggested for short term clinical testing that Z250 has potential as alternative to amalgam in the restoration of selected posterior teeth after one year. Z250 (3M ESPE, St Paul, USA), is a resin composite that has been modified to exhibit lower polymerization shrinkage, higher fracture toughness and superior curing characteristics when compared to its predecessor, Z 100 (3M ESPE). The resin system in Z250 has been modified by eliminating the Bis-GMA content and reducing the amount of TEGDMA. The new resin consists of UDMA and Bis-EMA plus a small amount of TEGDMA (Filtek Z250 Technical product file, 3M ESPE).

Söderholm et al. (2001) in their study showed that resin matrix was the most significant factor affecting the wear rate. The UEDMA/TEDGMA composites showed significantly less wear compared with the BisGMA/UDMA composites. The difference was approximately 25%. There were no significant differences between the fillers or the silanization methods.

Matsumura et al. (2000) evaluated the clinical performance of Cesead composite (Kurary Co, Japan), for more than four years and this composite was considered to be clinically reliable as a prosthetic veneering agent. Cesead, a hybrid composite, is photo-activated composite material designed for prosthetic veneer, which consists of a tetrafunctional urethane methacrylate base monomer and three types of fillers.

As expected, the longer a restoration is in use, the higher the failure rate, but the failure of resin composite restorative materials is far more complicated than just the material properties. As with all dental restorative materials, the proper technique, the appropriate materials, and proper patient selection usually ensure a successful clinical restoration (Drummond, 2008).