CHAPTER 2

LITERATURE REVIEW
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2.1 Dental resin composite

2.1.1 Definition
A resin composite material generally consists of filler particles (a dispersed phase) that are distributed within resin matrix (a continuous phase) (O’Brien, 2001, Sturdevant, 1995). A composite resin has been defined as three-dimensional combination of two or more chemically different materials with a distinct interface separating the components (Phillips, 1991).

2.1.2 Background
Bis-GMA composite resin was introduced by Dr. Rafael Bowen in 1956 (Peutzfeldt, 1997). Composite restorative materials were developed originally to overcome the deficiencies of silicate cements and acrylics as anterior restoration. Composite resins were initially developed for Class III, IV and V restorations. These were later indicated for use in Class I restorations with moderate occlusal stress. Further improvements in the material’s properties and handling techniques have extended their use in Class II restorations. The rapid acceptance of composite resin was due to its superior aesthetics, improved wear resistance, reduced coefficient of thermal expansion, reduced polymerization shrinkage and improved mechanical properties, higher resistance to abrasion and greater range of application and ease of manipulation (Leinfelder, 1985).

In recent years, composite materials have found increasingly wide application in a variety of clinical procedures. Their wide use is made possible not only by the development of the acid-etch bonding techniques developed by Buonocore as early as
1955, but also by apparent improvements in the strength characteristic of the newer materials (Lee and Orlowski, 1977).

2.1.3. Composition

There are three phases combined to make a composite resin, namely:

2.1.3.1 Resin matrix (organic phase)

2.1.3.2 Inorganic fillers (dispersed phase)

2.1.3.3 Coupling agent

2.1.3.1 Resin matrix

The resin component of a cured dental resin is a polymeric matrix. A polymer is a large molecule built up by repetitive bonding together of smaller molecule called monomer. The process by which monomers are joined together and converted into polymer is called polymerization. The monomers upon polymerization are converted into solid.

The extent to which monomers are changed into polymers is termed degree of conversion (Peutzfeldt, 1997). The degree of conversion is a measure of percentage of carbon-carbon double bonds that have been converted to single bonds to form a polymeric resin. The higher the degrees of conversion, the better the strength, wear resistance and many other properties and resin performance (Anusavice, 2003). Some of the common recent monomers are discussed as follows:

a) Bisphenol A glycidyl dimetacrylate (Bis-GMA)

It is the most common oligomers used in dental composites. It contains reactive carbon double bonds at each end that can undergo addition polymerization. The viscosity of the monomer is very high that diluents such as triethylene glycol dimetacrylate (TEGMA) must be added (Craig, 2002). The lowering of the viscosity of the monomer mixture
enables filler to be incorporated into the mixture. As the Bis-GMA content is increased, the degree of conversion is decreased without affecting its strength and hardness (Bowen, 1963). Bis-GMA is superior to methyl methacrylate because of its large molecular size and chemical structure, providing lower volatility, lower polymerization shrinkage, more rapid hardening and production of stronger and stiffer resins (Bowen, 1963).

b) Urethane dimethacrylate (UDMA)

This monomer has low viscosity and do not require the use of diluent monomer although some manufacturers do blend various monomers together. The rapid increase in viscosity during setting causes a relatively high concentration of acrylate or methacrylate groups to remain unreacted after setting. This results from the reactive methacrylate groups that make it difficult for them to migrate to reaction sites as viscosity increases. Further reaction could be encouraged by heating the material to a temperature well above the ambient temperature in order to regenerate mobility of reactive groups (McCabe and Walls, 1998).

c) Bisphenol A polyethylene glycol diether dimetacrylate (Bis-EMA)

Bis-EMA is a derivative of modified Bis-GMA. The terminal hydroxyl groups present in Bis-GMA have been removed to reduce the water sorption. However, it does not result in superior mechanical properties or enhanced wear performance (Peutzfeldt, 1997).

2.1.3.2 Inorganic fillers

The fillers employed influence the properties of composite restorative materials. The fillers used in dental composites directly affect the material’s radiopacity, wear
resistance, flexural modulus and thermal coefficient of expansion. Incorporation of filler particles into resin matrix significantly improves the properties of the matrix material if the filler particles are well bonded to the matrix. The amount of filler that can be incorporated into resin matrix generally is affected by the relative filler surface area. To ensure acceptable aesthetics of a composite restoration, the translucency of the filler must be similar to the tooth structure. Quartz has been used extensively as filler, particularly in the first generation of composites. The radiopacity of filler materials is provided by glasses and ceramics that contain heavy metals such as barium (Ba), strontium (Sr), and zirconium (Zr). The most commonly used glass filler is barium glass (Anusavice, 1996). Filler loading also affected the flexural strength and modulus, microhardness and fracture toughness. An increase of filler loading up to 55% of filler volume will increase the fracture toughness.

2.1.3.3 Coupling agents

Coupling agents, an organosilane (silane) contains functional groups that react with inorganic filler, as well as unsaturated organic groups that react with oligomer during polymerization. Silane forms a bond between the inorganic and organic phase of the composite. A properly applied coupling agent can improved physical and mechanical properties and provide hydrolytic stability by preventing water from penetrating along the filler-resin interface (Anusavice, 1996). Accelerator and initiator are the chemicals that promote the hardening or polymerization and reaction in the composites. An initiator (camphoroquinone) and amine are added to accelerate the reaction for light-cured composites. For self-curing system, an initiator (benzoylperoxide) is added to one paste and an activator (amine) is added to the other. In the light-cured material, the visible light causes the camphoroquinone to become reactive, whereas in self-curing
system, the amine causes the amide to become reactive. The polymerization of the self-curing material is brought about by mixing the two paste components (Ferracane 2001).

2.1.4. Classification

Dental composites generally are classified based on components, amount or properties of filler or matrix phases. The most common classification method is based on filler content, filler particle size and method of addition. The first classification system was introduced by Lutz and Phillips (1983) and was based on average size of filler particles, manufacturing technique and the chemical composition of filler particles.

Currently composites used as restorative materials that are available in the market can be widely divided into microfilled, microhybrid and nanocomposites.

2.1.4.1 Microfilled composites

The average size of the filler particles of these types of composites is approximately 0.05-0.1µm. Filler loading in these composites is between 20% to 55% by volume or 35% to 60% by weight, and low-molecular-weight organic diluents of low viscosity are often added to give the composite a workable clinical consistency (O’Brien, 2001). Unmodified microfills are called homogenous microfills and the blend of precured microfills composite with uncured material. The precured particles were generated by grinding cured composites to a 1 to 20µm sized powder. The precured particles become chemically bonded to the new uncured material that will provide better properties and can be finely finished. These variants are known heterogeneous microfills (Sturdevant, 1995).
2.1.4.2 Hybrid composites

Typically hybrid composites have a combination of colloidal and fine particles as filler. The colloidal particles fill the matrix between fine particles, resulting in a filler content of around 60% to 65% by volume. Hybrid composites currently dominate the dental market (O’Brien, 2002). Hybrid composites contain a mixture of small and microscopic particles. The most common are the minifills with the largest particles are either 1 to 2 μm. Hybrid with larger particles are called midifills which contain particles with size 3 to 8μm. Generally materials with larger particles have greater amount of fillers and consequently higher strength (Ferracane, 2001). Later it was realized that highly filled (microfilled composites) were difficult to use, dental composites were then formulated with a mixture of particles in microfiller range from 2 to 5μm. These bimodal distributions allowed higher filler levels and still permitted good finishing. Currently the principal particle size for newer materials is in the range of 0.1 to 1μm (Anusavice, 2003) and has been described as microhybrid composites.

2.1.4.3 Nanocomposite

New composites with nano-fillers that range in size from 0.005 to 0.01μm, which is below the wavelength range for visible light (0.02 to 2μm). Nanofillers are so small that they fit between several polymer chains. These characteristics permit the opportunity to achieve very high filler loading levels (up to 95%) in composites while still maintaining workable consistency (Moszner and Klapdohr, 2004). Nanofillers are very different from traditional fillers and require a shift from top-down to bottom-up manufacturing approach. Nanofillers such as pure silica glass fillers synthesized via sol-gel process and have the advantage of producing very homogenous and highly pure glass powder. The sintering temperature was decreased due to nanoscopic structure of the condensate, which provides a large surface area. The optical properties of nanofillers were good
because it has low visual opacity. This allows clinician to construct a wide range of shades and opacities, thus providing highly aesthetic restoration. Nanotechnology allow the dental restorative composite system to offer high translucency, high polish and polish retention similar to microfills while the wear resistance is similar to hybrid composites. Thus nanocomposites would be useful for all posterior and anterior restorative application (Mitra and Holmes, 2003). Moreover, well designed nano and micro structured sol-gel components can be used for producing protective and wear resistant coating for teeth, metal alloys and glass fillers of special compositions. The materials used in the preparation of “sol” are usually inorganic metal salts or metal organic compounds such as metal alkoxides. The precursor is subjected to a series of hydrolysis and polymerization reactions to form a colloidal suspension or a “sol”. Further processing will make the ceramic materials in form of thin films that can be coated. When the coated film cast into mould, a wet “gel” will form. With further drying and heat-treatment “gel” is converted into dense ceramic or glass particles. (Moszner and Klapdohr, 2004).

2.1.5 Polymerization of composite

Light curing provides high degree of polymerization. Visible light cured composites are the most popular today, but their successes depend on the access of high-intensity light to cure the matrix material. The adequate light intensity is important to produce complete curing if the thickness of the composite does not exceed 1.5 to 2mm. Access to interproximal areas is limited and requires special approaches to guarantee adequate light-curing energy. Because of these problems, more composites are dual-cured or staged-cured. Dual cured are combining the self-curing and light-curing. The self-curing rate is slow and designed to cure only those portions not adequately light-cured. Stage cured done by filtering light from the curing unit during initial cure that produce a soft,
partially cured material that can be easily finished. After the filler is removed, the composite curing is completed with full spectrum light (Sturdevant, 1995). About 75% of the polymerization takes place during the first 10 minutes. The curing reaction continues for a period of 24 hours. If the surface of the restoration is not protected from the air by a transparent matrix, polymerization is inhibited; the number of unreacted carbon double bonds may be as high as 75% in the tacky surface layer. Although the restoration can be finished after 10 minutes, the optimum physical properties are not reached until about 24 hours after the reaction is initiated (Craig, 2002).

The light source is usually from quartz bulb with a tungsten filament in a halogen environment (QTH). More recently, other types have been introduced with the advantages such as light-emitting diodes (LEDs), plasma arc curing (PAC) and laser lamps. Light source generate different light intensities over time, depending on the quality and age of the lamp, the presence of contamination such as composite material residue on the light tip and the distance between light tip and restoration. The light source should be checked regularly and the operator should always place the light tip as close as possible to the restorative material (Anusavice, 1996).

2.1.6 Finishing and polishing of composite resin restorations

The finishing and polishing procedures influence the quality of composite surface. Finishing usually commenced by using diamond or carbide-finishing burs, finishing disks or strips of alumina for gross reduction and later continued with abrasive impregnated rubber rotary instruments or rubber cup with various polishing pastes for final finishing. Polishing is the final step of finishing and usually performed with aluminium oxide abrasive and progressively to finer grit sizes. Polishing the composite
is important, because a smooth surface is desired to prevent retention of plaque and is needed to maintain good oral hygiene (Craig, 2002).

Tjan and Chan (1989) showed that composites that were finished with aluminium oxide coated Sof-Lex (3M ESPE Dental products, St. Paul Minn USA) discs showed smoother surfaces than those finished with silicon dioxide impregnated rubber polishers. The cutting abrasive particles must be harder than the filler materials for the finishing system to be effective. The correlation between the hardness value (Rockwell Hardness Number-RHN) and the surface roughness value (Ra) were shown to be statistically significant. It was shown in this study that composites with higher hardness value produced a correspondingly higher roughness value.

On the other hand, Marigo et al., (2001) showed that abrasive impregnated disks followed by polishing pastes (Prisma Gloss and Prisma Gloss extra-fine aluminium-oxide pastes) for the Enhance system (LD Caulk/Dentsply) and finishing burs followed by silicon points followed by diamond polishing pastes for multi-step system provided a considerably smoother surface than the other systems. Diamond finishing burs when used routinely in clinical practice, followed by secondary finishing procedures and final polishing (with diamond polishing pastes), results in a surface smoothness and gloss superior to that obtained with an abrasive impregnated disc or aluminium oxide discs alone.

The surface roughness of composite resin is highly dependent on the size and type of filler particles. Smooth surface of finished composites should have the maximum size of the filler particles less than 6µm (Van Noort and Davis, 1989). Proper finishing and polishing are important steps to enhance both the aesthetics and the longevity of
restored teeth. Rough, poorly polished surface contribute to staining, plaque accumulation, gingival irritation and recurrent caries. The surface layer, which is rich in resin, need to be removed. Rubber polishing instruments and aluminium oxide disks provided a smooth finished surface (Gedik et al., 2005)

2.1.7 Hardness of composite

Hardness is the ability of a material to resist forces of indentation or resistant to wear and abrasion. Surface hardness is the result of the interaction of numerous properties: strength, proportional limit, ductility, malleability and resistance to abrasion and cutting (Ferracane, 2001). There are several types of surface hardness tests. Most are based on the ability of the surface of a material to resist penetration by a point under a specific load. The tests are Barcol, Brinell, Rockwell, Vickers and Knoop. Brinell hardness test is one of the oldest tests for determining the hardness of metal.

Brinell hardness number is related to the proportional limit and the ultimate tensile strength of dental gold alloys. In Brinell test, a hardened steel ball is pressed under a specific load into the polished surface of a material. Rockwell hardness test is similar to Brinell but instead of measuring the diameter of the impression, the depth of penetration is measured directly by a dial gauge on the instrument. The Rockwell hardness number is designated according to the particular indenter and load employed. Brinell and Rockwell test are not suitable for brittle materials. Vickers hardness test employs the same principle of hardness testing in Brinell test but instead of a steel ball, a diamond in the shape of a square-based pyramid is used. The Vickers hardness number is computed from the load divided by projected area of indentation. The length of the diagonal indentations are measured and averaged. The test is suitable for determining the hardness of brittle materials and tooth structure. The Knoop hardness test employs the
use of a diamond-indenting tool that cut in the geometric configuration. The project area is divided into load to give the Knoop hardness number. Vickers and Knoop are classified as microhardness tests. Both Vickers and Knoop tests employ loads less than 9.8N. The results are small and are limited to a depth of less than 19µm. Therefore, they are capable of measuring the hardness in small regions of very thin objects. Other less sophisticated measurement methods, such as the Shore and the Barcol tests sometimes is used to measure the hardness of rubber and plastic dental materials (Anusavice, 1996).

2.1.8 Vickers microhardness test

The Vickers microhardness test was developed in early 1920s and uses a pyramid-shaped indenter made of diamond with a square base and an angle of 136 degrees between opposite faces subjected to a load of 1 to 100 kgf. The full load is normally applied for 10 to 15 seconds. The two diagonals of the indentation left in the surface of the material after removal of the load are measured using a microscope and their averages were calculated. The area of the sloping surface of the indentation is calculated. The Vickers hardness is obtained by dividing the kgf load by the square mm of the indentation.
(a) Typical microhardness indentation

(b) Diagrammatic illustration of diamond indentation made by microhardness tester.

(b) Diamond indentation under magnification

\[ F = \text{Load in kgf} \]

\[ d = \text{Arithmetic mean of the two diagonals, } d_1 \text{ and } d_2 \text{ in mm} \]

\[ HV = \text{Vickers hardness} \]

\[
HV = \frac{2F \sin \left( \frac{136^\circ}{2} \right)}{d^2}
\]

There is now a trend towards reporting Vickers hardness in SI units (MPa or GPa) particularly in academic papers. Vickers hardness number value expressed as a number only (without the units kgf/mm²).
2.1.9  Factors affecting microhardness of composite

Composites had to have good physical and mechanical properties to be able to function well in the oral environment. The satisfactory clinical performances of composite restorations depend on their resistance to degradation, resistance to wear and mastication strength in the oral environment. The hardness of composites are influence by their filler volume fraction, chemical composition, polymerization degree, surface finishing and polishing and the environment which they are exposed to such as water and chemicals in dental plaque, food and oral hygiene products.

2.1.9.1  Filler fraction and chemical composition of resin composite

The study by Oberholzer et al., (2003) showed that highly filled materials (Z250 and Dyract AP) were harder than the flowables (Filtek Flow and Dyract Flow). Schulze et al., (2003) concluded that for chemical cured composites, higher hardness value was found in Bisfill II due to higher filler content (80wt%) compared to Isopast Variant which exhibit low hardness value due to the low filler content (39.4wt%). While a light cured composite (Vitalexence) was found to be the hardest material having 75% filler content and average size of filler particles was 0.7µm compared to Hellioprogress with 73.7% filler content and smaller filler size 0.01-0.1µm. However, after aging process the hardness are almost similar. This emphasized that high hardness values is not related only to high filler content but the more important factors that affect hardness are filler size and composition of composites.

Schwartz and Söderholm (2004) found that composites with average filler particles 1.5µm showed least decrease in hardness value than composite with coarser filler particles (3.0 µm and 10.0 µm) after immersion in water or ethanol-water. The changes were most pronounced for composites stored in ethanol-water solution. The decreases in
hardness value can be related to the plasticizing effects pH water and ethanol on the matrix material. The reason the surface hardness of coarser composite decreased more than finer composite may be related to differences in diffusion through the matrix. Diffusion into deeper layers of finer composite was likely slower than into the composite with coarser filler particles. They also found that smaller particles result in higher wear resistance. The hardness and wear result suggest a reverse relationship between surface hardness and wear of composites. However, the differences in hardness value for all composites with different filler particles were not significant when tested dry.

In a review by Peutzfeldt (1997), it was concluded that performance of a resin composite is the result of interplay between all the components present in the material, a change in monomer system will be reflected in the performance of the resin composite. The use of low-shrinking monomers lead to reduced marginal leakage and significantly improved longevity of resin composite restorations. Monomer systems displaying increased conversion of methacrylate double bonds and high strength would render the polymer less susceptible to degradative reactions and result in improved wear and fracture behaviour. These factors also tend to increase the longevity of resin composite restorations.

BisGMA monomer is a large molecular size and chemical structure providing lower volatility, lower polymerization shrinkage, more rapid hardening and produced stronger and stiffer resin. The high viscosity of BisGMA is lowered by a mixture with EGDMA and TEDGMA. The lower the viscosity of the monomer mixture, the more filler may be incorporated into the mixture. An increased filler content will improved several properties of the polymerized material, e.g. strength, stiffness and coefficient of thermal
expansion. However, dilution of BisGMA also has negative effect such as increased polymerization shrinkage (Bowen, 1963).

According to Ferracane and Greener (1986), and Asmussen (1982), the degree of conversion in BisGMA and TEDGMA copolymers will decrease with the increasing content of BisGMA however this does not result in reduction in strength or hardness. Due to the polar nature of dimethacrylate resins in particular those containing dialkyl ether linkages, all resin composites absorbed water from the oral environment and undergo hygroscopic expansion. Water sorption has been found to weaken the resin matrix and cause filler / matrix debonding and hydrolytic degradation of fillers with a subsequent reduction in mechanical properties and wear resistance.

Pereira et al., (2005) found that microhardness value of all tested materials (BisGMA/TEGDMA, BisGMA/CH₃ BisGMA and BisGMA/CF₃ BisGMA) was increased with the filler content. CH₃ BisGMA and CH₃ BisGMA are the low viscosity monomers that synthesized to replace TEDGMA. They also found that resin containing high concentration of TEDGMA as diluents showed lowest microhardness value. Higher microhardness value was found in resin containing higher BisGMA analogue concentration and the best performance was the resin which contains CH₃ BisGMA.

2.1.9.2 Polymerization degree

The depth of cure or degree of polymerization is strongly affected by photo-activation methods. The higher degree of cure will improve the final properties of the material. The intermittent light showed the highest depth of cure compare to continuous, exponential, plasma arc curing (PAC) and light-emitting diodes (LED). After
polymerization, residual monomer will lead to a decrease in hardness. Hardness of the inorganic fillers has a direct effect on the overall hardness of the materials. The Knoop hardness test showed that, up to a depth of 2 mm, all light-activated methods provided similar values, but at depths greater than 2 mm, the differences was observed between different methods of light activation. It was explained that the differences may be due to the characteristic of each method such as the light intensity, exposure time and heat generated. It showed that thickness greater than 2 mm should not be used clinically and possibly resulting in poorly polymerized material at deeper regions of restoration (Obici et al., 2004).

Discacciati et al., (2004) found that Filtek Z250 (3M, St.Paul, Mn, USA) showed lower values of hardness (VHN) and degree of conversion when low light intensity values (200mW.cm$^{-2}$) with short irradiation times (5, 10 and 20s) were used to polymerize it. The VHN values increased when the amount of energy introduced increased up to 8J but no further increased of VHN values were found when test composites were exposed to energy more than 8J. However, they also found that materials produced by the process combination of low light intensity and long irradiation times were able to reach maximum degree of conversion among all experimental groups.

Sobrinho et al., (2000) found that hardness value for composites tested was significantly higher when light curing tip was placed directly on the composite (0mm distance) compared to 6mm distance and 12mm distance for specimens of 2.5mm thickness. They found that polymerization of resin composites depend greatly on the distance of curing tip from the composite surfaces. The light also must be capable of generating sufficient intensity to cure through the entire thickness of the mass or increment. Fan et al., (2002)
reported that the ISO technical specification 10650 (2000) suggested that the minimum intensity of commercial curing lights is 300mW/cm².

According to Cavalcante et al., (2003), microhardness of composites tested was higher on the top cured surface followed by the middle and bottom surfaces. This was also supported by Oberholzer et al., (2003) who found that microhardness values at the top cured surface of composite was significantly harder compared to the bottom surface (at the depth of 2mm) when cured with continuous light with 800mW/cm² compared to light intensity of 400mW/cm².

2.1.9.3 Polishing and finishing that affected the microhardness

The purpose of polishing and finishing of the surface of composite restorations was to remove the resin-rich or oxygen-inhibition layer that developed during the polymerization process (Peutzfeldt and Asmussen, 1989 and Rueggeberg and Margesson, 1990). Chung and Yap (2005) found that the sequential polishing of specimens was needed to remove or reduce the plastically abrasion-deformed layer, which occur during polishing. They found that upon polishing, the abrasive effects caused debonding of filler particles and/or plastic deformity of resin matrix resulting in ‘peak and valley’ or asperities as observed in the SEM micrographs. The surface roughness of F2000 (3M, St.Paul, Minn, USA) that had the largest filler particles (3-10µm) was significantly greater than Z100 and A110 (3M, St.Paul, Minn, USA) with filler particles 0.01-3.50 µm and 0.01-0.09 µm (Chung and Yap, 2005). They also found that the difference in microhardness and indentation modulus of the experimental composites were not significant with varying surface roughness. This suggests that the indentation load utilized and corresponding penetration depth in their study was appropriate to overcome surface defects on the indentation test accuracy. They
concluded that surface finish has no effect on measured indentation modulus and hardness of tested composites. However, surface finishing is crucial to aid in identification of indentation via the eyepiece of hardness testing equipments.

### 2.1.9.4 The oral environment

Mechanical properties of composite resins are influence not only by chemical composition but also by the environment that they are exposed to. The degradation process promoted by water in the presence of a constant load on the surface of the resin will propagate the interfacial debonding, matrix cracking, superficial flaws, filler dissolution and filler particle dislodgement (Martos et al., 2003).

Water causes hydrolytic degradation and chemicals may affect the surface hardness of composite. Wu and McKinney (1982) showed that wear resistance of composites were significantly lower when immersed in chemicals such as pure cyclohexanone and ethanol–water mixture with different concentration. These chemicals soften the BIS-GMA matrix copolymer. Assmussen (1983) later found that not only ethanol but acetic and propionic acid have softening effect on Bis-GMA-based polymers. The softening effect decreases with increasing content of TEGMA up to 50mol% and is small for contents of TEGMA above this limit. McKinney and Wu (1985) also found that softening of microfilled composite (Silar, 3M) was more severe than conventional composites (Adaptic-Johnson and Johnson and Prisma-Fil -L.D.Caulk) based on same polymer base (Bis-GMA).

Yap et al., (2001) found that organic solvents (heptane and 75-25% ethanol-water solution) and water/weak acids (0.02N citric acid and 0.02N lactic acid) degraded the surface of composite resins. They concluded that effects of chemical media on surface
hardness and thickness of degradation layer was material dependent. All the test composites (Silux Plus, Z100, Surefil and Ariston pHc) were softened by 75-25% ethanol-water solution.

Wongkhantee et al., (2006) found that hardness value of microfilled composite and resin-modified glass ionomer significantly reduced after immersion in cola-based soft drink. However, hardness values of universal composite and conventional glass ionomer did not significantly change. The higher resin content of microfilled may be the reason for greater hardness reduction in comparison to universal resin composite.

Previous studies have shown that alcohol-containing products can affect selected physical properties of composite restorative materials such as Adaptic, Prisma-Fil, Silux Plus, Z100, Surefil and Ariston pHc (Lee et al., 1998). Surface hardness, diametric tensile strength and shear bond strength will be decreased when exposed to ethanol. In clinical situation, even in absence of fluid uptake, the dental restorative material may absorb some component or solute from surrounding fluid phase. If one component of the dental material dissolves in the storage solution, the materials will be porous due to leaching of monomers. These effect influence the behaviour of material despite the absence of externally applied mechanical stress and obvious shape changes. As the storage solvent penetrates the matrix and expands the opening between polymer chains, unreacted and leachable monomers may diffuse out. The organic solvents are more efficient in extracting these components than water, probably because of enhanced ability to penetrate the cross-linked resin matrix of the composites. The oral cavity probably presents an environment somewhere between the more aggressive solvents and water. The amount of leachable species is related directly to the extent of polymerization reaction, the resin based composition, chemistry of the solvent and the
size and chemical composition of leachable species itself. The leaching of the components or degradation byproducts from dental composites has a potential impact on both the structural stability and the biocompatibility of the material (Lee et al., 1998).

Okada et al., (2001) found that surface hardness of the composite resin and the polyacid-modified composite resin showed slight increases after one day storage in saliva. Polyacid-modified composite resin had matrix that would not absorb metal ions from saliva. In this study they also found that surface hardness of glass ionomer cement after 40 days storage in saliva increased significantly because of the absorption of some organic ions.

2.1.10 Surface analysis

There are several methods currently available which are used as a research methodology to measure the texture of the surface; these include contact stylus tracing, laser reflectivity, non-contact laser stylus metrology, scanning electron microscopy and compressed air measuring. More recently, atomic force microscopy has been evaluated for use in assessing the surface texture (Marshall et al., 1993).

Atomic Force Microscope (AFM) was developed in 1986 by Binnig, Quate, and Gerber as collaboration between IBM and Stanford University (Marshall et al., 1993). This technique includes scanning tunnelling microscopy. The microscope uses a microfabricated tip assembly consisting of a sharp tip, which is mounted on a cantilever. The sample is placed on a piezoceramic tube that can provide three dimensional motions to the sample with sub-nanometer accuracy. The sample is brought in contact
with the tip, which exerts a force of $10^{-8}$ N on the sample and the tip is scanned such that no change in cantilever deflection is detected. The three-dimensional motion of the piezoceramic tube corresponds to the surface morphology of the scanned area (Marshall et al., 1993). AFM is highly complex method and the equipment is very expensive and sensitive.

Surface roughness parameter Ra was measured to describe the overall roughness of a specified surface area and can be defined as the arithmetical value of all absolute distances of the roughness profile from the centre line within the measuring length. It is a true amplitude measurement. This is the most commonly tested parameter.

2.2. Mouthrinses

Generally, U.S. Food and Drug Administration (FDA) classify mouthrinses as cosmetic and therapeutic. Traditionally mouthrinses are used to freshen bad breath. Dental professionals should advise patients that have bad breath to improve the oral hygiene by using mouthrinses. Oral malodour or halitosis is cause for concern, embarrassment and frustration on the part of public. It can lead to social isolation, divorce proceedings and even ‘contemplation of suicide’ (Harris and Garcia-Godoy, 2001). However, the effectiveness of most mouthrinses is limited to dislodging gross debris, temporarily reducing micro-organism and providing a feeling of freshness. It is only recommended as adjuncts to and not replacement for mechanical plaque control.

2.2.1 Composition

Most commercially available mouthrinses contain alcohol. Other ingredients are water, flavouring, colouring and sweetening agents and active ingredients such as;
antimicrobials to reduce and inhibit microbial activity, oxygenating agents to debride and release oxygen, astringents to shrink tissues, anodynes to alleviate pain, buffering agents to reduce acidity, deodorizing agents to neutralize odours and fluorides (Darby and Bushee, 1991).

2.2.2 Types of mouthrinses
Darby and Walsh, 1995 divided mouthrinses into:-

i) antiplaque/antigingivitis rinses that can be used as therapeutic antiseptic

ii) cosmetic antiplaque rinses

iii) therapeutic anticavity fluoride rinses

iv) cosmetic breath freshening mouthrinses, and others which are topical antibiotic rinses, enzymes rinses, artificial saliva rinses and rinses that control tartar

2.2.3 The effect of alcohol-containing mouthrinses on restorative materials.
The commonly used alcohol in mouthrinses is ethyl alcohol that acts as solvent and taste enhancer. The percentage of alcohol content is between 11% to 27%, however, there are also alcohol-free mouthrinses available in the market. Alcohol-containing mouthrinses can be dangerous to small children, recovering alcoholic and clients taking medications (for example-metrodinazole) (Darby and Walsh, 1995). Besides that, alcohol in mouthrinses also has an effect on restorative materials placed in the oral cavity.

Penugonda et al., (1994) carried out a study to evaluate the effects of alcohol-containing mouthwashes on hardness of composite resin-APH (LD Caulk Co.). They found that alcohol content in mouthwashes can affect composite hardness and the softening effect was directly related to percentage of alcohol in mouthwashes.
Gurgan et al., (1997), later performed a study to investigate the effect of alcohol-containing and alcohol-free mouthrinses on microhardness of three different restorative materials (Composite-Amelogen, Ultradent Pro.Inc.USA, Glass Ionomer Cement -Fuji II LC®, GC Dental Ind., Japan; Fissure Sealant-Ultra Seal XT®, Ultradent Pro.Inc.USA). They reported that both alcohol-containing and non-alcohol containing mouthrinses affect the microhardness of restorative materials compared to distilled water. The differences in microhardness were not significant. However, it was suggested that in clinical situation, the alcohol content may not be the only factor that has softening effect on composites. Saliva may dilute or buffer the mouthrinses thus reducing the softening effect.

Gurdal et al., (2002) studied the effect of mouthrinses on microhardness and colour stability of restorative materials. Three mouthrinses of different pH and alcohol content were used. One composite (Brilliant Dentin), one conventional glass ionomer cement (Chelon-Fil) and one poly-acid-modified resin composite (Compoglass) were tested. They reported that mouthrinses with various pH and alcohol contents has no significant effect on the microhardness and colour stability of all restorative materials tested. It was suggested that the difference observed might have originated from the structure of materials themselves and not from the test solution. However, this suggestion was not clearly explained.

Yap et al., (2003) reported that effects of mouthrinses on hardness and wear were material dependent. Two composites- Estet-X (minifilled) and Dyract Posterior (posterior compomer) were immersed in three alcohol containing mouth rinses, two non-alcohol mouthrinses and distilled water as control. Dyract Posterior was significantly softened by Listerine, while Esthet-X was significantly softened by
Listerine and Chloropharm. No significant difference in hardness was detected between specimens for Dyract Posterior when immersed in Chloropharm and distilled water. This is probably due to the composition of Chloropharm. Chloropharm contain eugenol and other herbal oils that may soften the polymer matrix. The actual alcohol concentration in all alcohol-containing mouthrinses was not stated. It was concluded that clinically the effect of alcohol in the mouthrinses may be modified by many factors that cannot be replicated in their study.

2.2.4 Plant extract and herbal base mouthrinses.

Plant extract and herbal base mouthrinses were the alternative mouthrinses for treatment of gingivitis and other periodontal problems. These mouthrinses was proved to have similar effect of inhibiting the growth of pathogens and also can improve periodontal diseases compared to mouthrinses containing chlorhexidine gluconate (Moran et al., 2000). Pistorious et al., (2003) found that subgingival irrigation with herbal extract mouthrinses led to significant reduction of sulcus bleeding index and gingivitis index. They also concluded that these mouthrinses be recommended as adjunctive procedure to reduce gingival inflammation.

Herbal mouthrinses may contain purely plant extract or in combination with other antimicrobial agent. Essential oils such as clove oil (eugenol), thyme oil (thymol), chamomile, cetylperidium chloride, quartenary ammonium phenols and phenolic compound and several plant extracts were the main composition of herbal mouthrinses. Although the effect of herbal mouthrinses on antimicrobial effect has been proven but the effect of these mouthrinses on restorative materials had not been done and studied.