2. Literature Review

2.1 Composite

2.1.1 Definition

A composite material is a product which consists of at least two distinct phases normally formed by blending together components having different structure and properties. The purpose of this is to produce a material having properties which could be achieved from any of individual component (Mc Cabe & Walls, 1998).

2.1.2 Composition

Dental resin composites comprise a blend of hard, inorganic particles bound together by a soft, resin matrix, and generally encompass three main components:

- the resin matrix comprising:
    (i) a monomer system
    (ii) an initiator system for free radical polymerization, and
    (iii) stabilizers for maximizing the storage stability of the uncured resin composite and the chemical stability of cured resin composite;
- the inorganic filler consisting of particulates such as glass, quartz, and / or fused silica; and
- the coupling agent, usually an organo-silane, that chemically bonds the reinforcing filler to the resin matrix (Peutzfeld,1997).

The nature of the resin may alter slightly from one product to another, although, essentially they all contain a modified methacrylate or acrylate. Most commonly used monomers are bisphenol A glycidyl methacrylate (Bis-GMA) and urethane dimethacrylate (UDMA) together with of triethylene glycol methacrylate (TEGMA) which is a co-monomer often used to control the viscosity of the unmixed materials.

For chemical activation, many different methods of dispensation are available. The most popular are the ‘two paste’ system. Each paste contains a blend of resin and filler. One paste contains about 1% of a peroxide initiator, such as benzoyl peroxide, whilst the other paste contains about 0.5 % of a tertiary amine activator, such as N,N’dimethyl-*p*-toluidine or *p*-tolyl dimethanolamine.

Light activated materials are generally supplied as a single paste which contains monomers, co-monomers, filler and an initiator which is unstable in the presence of either ultraviolet (uv) or high intensity visible light. For uv-activated materials, the most commonly used initiator is benzoin methyl ether. The use of uv-activated materials has diminished greatly since the possible dangers of long-term exposure to ultraviolet radiation were highlighted. For visible light activated materials the initiator system comprises a mixture of a ketone and an amine.

The type, concentration, particle size and particle size distribution of the filler used in a composite material are major factors controlling properties. Fillers commonly used include quartz, fused silica and many types of glass including aluminosilicates and borosilicates, some containing barium oxide.

The filler particles are subjected to a special pretreatment prior to blending with the resin. This involves laying down a surface coating of a coupling agent on the particles to enhance bonding between the filler and resin matrix. The coupling agent most commonly used is methacryloxypropyltrimethoxysilane.

2.1.2.1 Principle Monomers

Until recently, the resins used in contemporary resins based composite (RBC) materials were generally those which were available 30 years ago. Approximately 50% of RBCs are now based on aromatic dimethacrylate system, the monomer being the reaction product of bisphenol A and glycidyl methacrylate, often called Bis-GMA or Bowen's resin. This is a highly viscous monomer which may undergo free radical addition polymerization to give a rigid cross-linked polymer (Combe & Burke, 2000).

2.1.2.2 Diluent (Lower molecular Weight) Monomers

Lower molecular weight monomers are included in many RBC formulations, especially those based on Bis-GMA to reduce the viscosity of the material, to enable proper blending with the inorganic constituents, and to facilitate clinical manipulation. Examples are ethylene glycol dimethacrylate (EGDMA) and triethyleneglycol dimethacrylate (TEGDMA).These diluent resins, being of low molecular weight, therefore contribute substantially to the overall polymerization shrinkage of the composite material.

A number of manufacturers have recently developed and introduced alternative resin systems to the 'traditional' system. For example Z250 and P60 (3M, St.Paul, MN, US), the resin utilized are Bis-EMA (bisphenol A polyethylene glycol diether dimethacrylate) and urethane dimethacrylate (UDMA).This produced a mixture which is less viscous than Bis-GMA, and this aviates the need to use the diluent resin, TEGDMA, which exhibits high polymerization contraction. This resulted in less shrinkage on polymerization of these composite materials, and overall polymerization contraction of these composite materials (Combe & Burke, 2000).

2.1.2.3 Initiator/Activator system

The activation of polymerization of RBC materials may be by chemical means or by light. In the chemically activated materials, benzoyl peroxide acts as the initiator and tertiary amine activators, or sulfinic acid type initiators may be employed. Visible light cure composites contain diketone such as camphorquinone and an amine (Combe & Burke, 2000).

2.1.2.4 Silane Coupling Agents, Polymerization Inhibitors and UV Stabilizers

To achieve reinforcement of the polymer by the filler, it is essential that the two constituent are bonded together. To achieve this, the filler is treated with a vinyl silane compound. Dimethacrylate monomers will polymerize on storage, and it is therefore necessary to add an inhibitor. The monomethyl ether of hydroquinone is now used in a concentration of a few parts per million. To prevent the discolouration which may occur with ageing composite restoration, compounds are incorporated which absorb electromagnetic radiation (Combe & Burke, 2000).

2.1.2.5 Inorganic Fillers

Early composites, term macrofilled composites, contained fillers which were generally between 5 and 10 microns. These materials produced restoration with surfaces which were difficult to polish and which therefore stained readily. Wear resistance was poor as the filler particles were readily lost from the material.

Microfilled composite was developed in 1970s.These product contain colloidal silica filler of particle size about 0.04 microns resulting in a material which was easily polished. Current materials may contain fillers of lithium aluminosilicates, crystalline quartz,or barium aluminoborate silica glasses. Many current materials are term hybrid composite, because the filler is composed of a variety of particle sizes, ranged from 1 to 1.5 microns, but the spaces between the larger particles being filled with particles which may be as small as those in the microfilled materials, i.e. 0.04 microns.

Most recently, research has been undertaken in the use of nanofillers, which are smaller than microfillers, with particle sizes below the wavelengths of visible light. These nanofillers do not scatter or absorb visible light and therefore provide a means for incorporating radiopacity without interfering with the aesthetics of the material. Additionally, these very small particles may fill spaces between larger particles and allow filler loading levels of up to 95% by weight. This, in turn, will reduce polymerization shrinkage and improve physical properties (Combe & Burke, 2000).

Inorganic fillers play an important role in the properties of a resin composite material. The roles are:

- Improve mechanical properties such as compressive strength, modulus of elasticity and hardness
- Reduce the coefficient of thermal expansion
- Reduce the setting contraction
- Reduce the heat evolved during polymerization
- Contribute to the aesthetic of the restoration
- Produce a radio-opaque material if barium or strontium glasses are used

2.1.3 Properties of direct restorative composites

2.1.3.1 Setting and working time

The setting time for chemically activated composite resin ranged from 3 to 5 minutes. These short setting times have been accomplished by controlling the concentration of initiator and accelerator. The changes in viscosity that occur in chemically activated composites during the setting procedure are related to the resin matrix and are not influenced by the particle size or volume fraction of the inorganic filler.

Setting time for the photoinitiated composites is related specifically to the application of the light beam to the material, and approximately 75% of the polymerization takes place during the first 10 minutes. The curing reaction continues for a period of 24 hours. All the available unsaturated carbon-carbon bond do not react, and studies reported that about 25% remain unreacted in the bulk of restoration .If the surface of the restoration is not protected from air by a transparent matrix, inhibition of polymerization occurs, and the number of unreacted carbon double bonds may be as high as 75% in the tacky surface layer. Although the restoration can be finished with abrasives and is functional after 10 minutes, the optimum physical properties are not reached until 24 hours after the reaction is initiated (Craig & Power, 2002).

2.1.3.2 Thermal properties

The thermal expansion coefficients of composite range from 25-38 X 10 $^{-6}$/°C for fine composites and 55-68 X 10 $^{-6}$/°C for microfine composites. The values more closely approach those for dentine (8.3 X 10 $^{-6}$/°C) and enamel (11.4 X 10 $^{-6}$/°C) than has been possible with previous unfilled resin restorative materials. The high values for the microfine composite are related mostly to the greater amount of resin present.

Thermal stresses place an additional strain on the acid-etch bond, which further compounds the detrimental effect of the polymerization shrinkage. Thermal changes are cyclic in nature, which can lead to material fatigue and early bond failure. However, for highly transient temperatures, the composites do not change as fast as tooth structures, and this difference does not present a clinical problem (Craig & Power, 2002).

2.1.3.3 Polymerization shrinkage

Polymerization shrinkage ranged from 1.0-1.7% for fine composite and 2-3 % for microfine composite. The free volumetric polymerization shrinkage is a direct function of the amount of oligomer and diluent. This shrinkage creates polymerization stresses as high as 130 kg/cm^2 between the composite and the cavity of the tooth. These stresses severely strain the interfacial bond between the composite and the tooth, leading to a very small gap that can allow marginal leakage of saliva. The potential for this type of failure is even greater with microfine composites, in which there is a much higher volume percent of polymer, and polymerization shrinkage is greater. The net effect of setting contraction can be reduced by incremental addition of a light curing material and polymerization of each increment independently, which allows for some contraction within each increment before successive additions (Craig & Power, 2002).

2.1.3.4 Water sorption

Water sorption range from 0.3-0.6 mg/cm^2 for fine composite and 1.2-2.2 mg/cm^2 for microfine composite and hybrid lays intermediate**,** therefore fine composite exhibit less expansion**.** Water sorption of microfine composite is greater because of the higher volume fraction of polymer. The quality and stability of the silane coupling agent are important in minimizing the deterioration of the bond between the filler and polymer and the amount of water sorption. It has been postulated that water sorption is not all detrimental and that the corresponding expansion associated with the uptake of water from oral fluids could counteract setting contraction. In the measurement of hygroscopic expansion starting 15 minutes after initial polymerization, most resins required 7 days to reach equilibrium and about 4 days to show the majority of expansion (Craig & Power, 2002).

2.1.3.5 Solubility

The water solubility of composite varies from 0.01 to 0.06 mg/cm^2**.** Inadequately polymerized resin has greater water sorption and solubility, possibly manifested clinically with color instability. However, during the storage of fine composite in water, the leaching of inorganic ions can be detected, and such ions are associated with a breakdown in interfacial bonding. The breakdown and leakage can be a contributing factor to the low resistance to wear and abrasion (Craig & Power, 2002).

2.1.4 Classification of composite

Lutz and Ralph, 1983 classified composite based on their fillers:

- Traditional macrofillers
- Microfillers
- Microfilled complexes

2.1.4.1 Traditional composite resins

Traditional composite resin contained average particle size of filler. The differences in hardness of the two phases and the high visibility of the rather large macrofillers, which in general are larger than the wavelength of the visible light, make it difficult to finish the resin to a smooth surface.

The modern traditional composite resins contain smaller, more rounded, softer macrofillers, coupled with an appropriate size distribution. Furthermore, these fillers are frequently radiopaque. Examples of the traditional composite resins are Clearfil, Concise (1970s), Adaptic (1970s), Profile, Simulate and Smile (Lutz & Ralph, 1983).

2.1.4.2 Hybrid composite resins

These materials contained inorganic macrofillers of an optimized traditional type of composite resin plus pyrogenic silica. A further improvement can be anticipated with the use of even smaller macrofillers, which would have an average size of approximately 1 micron. Apart from the common hybrid type of composite resin, there are some rather rare constructions of this kind that combine the elements present in a hybrid with microfilled complexes. Examples of the hybrid composite resins are Adaptic (1980s), Concise (1980s), Aurafil, Miradapt and Command Ultrafine (Lutz & Ralph, 1983).

2.1.4.3 Homogenous microfilled composite resins.

Homogenous microfilled composite resins are combination of an organic matrix and directly admixed microfillers. They are considered optimal with regard to at least two properties. First, a composite resin exclusively containing inorganic fillers, which are smaller of the visible light, visually appears homogenous. Consequently this result in high degree surface polishes ability. Second, the homogeneity and the extremely small particle size provide only a minimal working surface for wear plucking-out process. This has raised expectations for superior wear properties. However, the inorganic loading with such small particles, approximately 0.04 to 0.2 micron, is still limited because of the viscosity effect resulting from the large surface area they present. Therefore, other technologies were required to incorporate the microfillers in a higher concentration without effecting viscosity (Lutz & Ralph, 1983).

2.1.4.4 Heterogeneous microfilled composite resins.

Heterogeneous microfilled composite resins are combinations of an organic matrix, directly admixed microfillers, and microfiller-based complexes. Heterogeneous microfilled composite resins fall into three different subclasses. Those with:

- splintered prepolymerized particles
- spherical prepolymerized particles
- agglomerated microfiller complexes

2.1.4.4.1 Heterogeneous microfilled composite resins with splintered prepolymerized particles

At present this is the most common type of mirofilled composite resin. The admixture of splintered, prepolymerized complexes to a microfiller-reinforce organic matrix is one of a three methods that are technically feasible for augmenting the inorganic loading and volumetric filler content without further increasing the viscosity and jeopardizing the handling characteristic of the composite resin.

If compared to a homogenous microfilled resin, this type of resin has excellent polishability, a permanent surface smoothness, excellent aesthetic and good wear resistance, provided that two crucial conditions are fulfilled:

1. The concentration of the dispersed silica microfillers must be equal in the prepolymerized particles and in the polymerized organic matrix in order to provide a uniform distribution throughout the composite resin following polymerization and
2. The bond between the reinforced organic matrix and the partially organic complexes should be as strong as the cohesive forces within the phases.

Polymeric interfacial bond is not adequate under certain circumstances and may occasionally contribute to failure. This lack of a perfect polymeric interfacial bond is the main reason for the technique sensitivity seen with microfilled composite resin.

Apart from their sensitivity to the finishing technique, heterogeneous microfilled composite resin systems also demand additional modifications of other clinical procedures. They should be used in combinations with long-beveled cavity preparations, the enamel etch technique, and bonding agents in order to reduce polymerization shrinkage. Examples of these types of resins are Estic Microfill, Isopast, Phaseafill, Silar and Superfil (Lutz & Ralph, 1983).

2.1.4..4.2 Heterogeneous microfilled composite resins with spherical prepolymerized particles

Spheres with a specific size distribution allow dense packing, so can reduce polymerization shrinkage. However, such a heterogeneous microfilled composite resin has not been marketed yet (Lutz & Ralph, 1983).

2.1.4.4.3 Heterogeneous microfilled composite with agglomerated microfiller complexes

Agglomerated microfiller complexes are similar to traditional macrofillers in size and chemistry, but not in structure. Furthermore, they allow a substantial increase in the microfiller content when admixed to a microfiller reinforced organic matrix. Not much is known about the *in-vivo* performance of this filler type and consequently of the resins. Those essential clinical studies are not available (Lutz & Ralph, 1983).

2.1.4.4.4 Nanofilled Resin Composite

A nanometer (nm) is 10 Angstroms or 0.001 µm. True nano-composites include true nano-sized fillers. The nanofillers in use today in dentistry have dimensions that are typically 10-to-25 nm or an order-of-magnitude bigger than the typical nanometer range. These fillers could be just as easily described in terms of microfiller sizes. For the time being, these particles would be referred as “near-nano” sizes (Bayne, 2006).One example is Filtek Supreme (3M) introduced in early 2003.It is formulated with nanomer and nano cluster filler particles. It’s nanomer are discrete non-agglomerated particles 20-70 nm in diameter. The combination of nanomer sized particles and the nano cluster formulation reduces the interstitial spacing of the filler particles. This will increased filler loading, better physical properties, and longer retention of surface polish compared to composites containing only nanoclusters.

2.1.5 Technique to overcome shrinkage and improve marginal leakage

Polymerization shrinkage creates contraction stresses in the resin composite restoration and internal stress and deformation in the surrounding tooth structure. Reduction of the polymerization shrinkage has been an important issue since the use of dental resin composites. Non-shrinking resins and modified filler particles have been developed to tackle this problem, but are not commercially available yet. Factors that can affect the shrinkage are inorganic filler content, the molecular weight of monomer system, and the degree of conversion of the monomer system (Peutzfeldt, 1997).

The polymerization of the resin matrix produces a gelation in which the restorative material is transformed from a viscous-plastic into a rigid-elastic phase. The gel point is defined as the moment at which the material can no longer provide viscous flow to keep up with the curing contraction. Therefore the results of shrinkage determinations are dependent on the flow ability of the material in the experimental set-up. In a situation where a curing material is bonded on all sides to rigid structures, bulk contraction cannot occur, and all, yet unavoidable, shrinkage must be compensated for by some kind of volume generation. This can come from a minimal strain on the material and mainly from dislodgement of the bond, increase in porosity or internal loss of coherence. In this particular case, the contractile forces come into action when the reaction is initiated, at the very start of the contraction. Therefore, all shrinkage must be regarded as a possible contribution to stress (Davidson & Feilzer, 1997).

Shrinkage stress occurs when the contraction is obstructed and the material is rigid enough to resist sufficient plastic flow to compensate for the original volume. Stress relief can be obtained in various ways. One approach involves the design of the restoration, in other words, the ability of the restoration to contract freely to the adhesive interface. The less the restoration is bonded to opposing walls, the less obstruction there is for the shrinkage. This explains why the adhesive Class IV restoration has proved so successful, while other classes often display marginal defects.
The use of linings for polymerization shrinkage stress reduction is now widely accepted and employed. As the bondings usually have a low filler loading, their modulus of elasticity is substantially lower than that of the restorative material. Stress reduction generated by means of the use of a lining has been demonstrated experimentally by Davidson and Feilzer (1997).

It has been hypothesized that contraction stress could be partially relieved by introducing nanofiller silica particles that were not surface treated, or treated with a non-functional (no carbon–carbon double bonds) silane coupling agent, thereby minimizing the interaction between the filler surface and the forming polymer. Studies verified this hypothesis, though the extent of stress relief was maximized at between 30 and 50% for hybrid and microfilled composites (Condon & Ferracane, 1998).

Modified light-curing protocols involving lower initial irradiance, pulsed light applications, delays between exposures, stepped or ramped light applications have been suggested as a means to reduce contraction stress in dental composite restorations. Lim et al, in 2002, showed that an approach involving an initial low radiant exposure (2 s at 290 mW/cm^2) followed by a delay of 5 minutes subsequent to an exposure of 60 s at 330 mW/cm^2 produced a significant reduction in contraction stress compared to a single, continuous exposure of 60 s at 330 mW/cm^2, despite producing identical volumetric contractions. It was suggested that the delay provided time for polymer relaxations and flow to relieve stresses forming during the initial exposure.

Reductions in contraction stress have also been verified for composites placed *in-vitro* with multiple adhesive layers (Choi et al, 2000). It is hypothesized that the thick layers serve as stress absorbers during the polymerization contraction of the composite by virtue of their low modulus of elasticity that allows them to increased deformation as the composite shrinks. This effect is dependent upon the composite establishing a strong bond to the adhesive layer. Attempts to use flowable composites to provide the same effect have met with mixed results, with some composites being effective due to their low modulus of elasticity, while others were ineffective due to a higher concentration of fillers that resulted in higher stiffness and less stress relieving capacity (Braga et al, 2003).

2.2. Microleakage

2.2.1 Definition

Microleakage is defined as the clinically undetectable passage of bacteria, fluids, molecules, or ions between a cavity wall and the restorative material applied to it (Kidd, 1976a). Trowbridge (1987) defined microleakage as the ingress of oral fluids into the space between tooth structure and restorative materials.

2.2.2 Causes of microleakage

One of the major causes of microleakage is poor adaptation of restorative materials to tooth structure, which may be due to inferior adaptability on the part of the material or inexpert insertion of the material by the operator. Another major cause is shrinkage of the material resulting from chemical or physical changes after it is inserted (Trowbridge, 1987).

All restorative materials are more or less sensitive to manipulation, so the skill of the operator is a critical factor in determining the extent of microleakage. Thus the surface quality of the cavity walls and the method by which the material is inserted will affect the sealing properties of the restorative material.

The restoration’s environments also play importance roles in determining the extent of microleakage. In the oral cavity, both restoration and surrounding are subjected to mechanical loading and temperature variation and are in contact with food, saliva and microorganism. Gaps around restoration may provide pathways for the ingress of oral microorganism and/or their metabolic product (Trowbridge, 1987).

Location of the cavity walls may also influences microleakage, particularly if the margin of the cavity is located in cementum. Acid etching can reduce leakage where composite restorations in enamel, but it have little effect on leakage at the cementum margin (Causton et al, 1984). Bauer and Henson, 1984 stated that factors contributing to microleakage include the interfacial space, inadequate physical properties of the restorative material, and improper restorative technique or procedures.

2.2.3 Biological effects of microleakage

Microleakage at the tooth/restoration interface is considered to be a major factor influencing the longevity of dental restoration. It may lead to staining at the margins of restoration, hastening of the breakdown at the marginal areas of restorations, recurrent caries at the tooth/restoration interface, hypersensitivity of restored teeth, and the development of pulpal pathology (Going, 1972).

Clinically, microleakage can increase the breakdown, dissolution, and discoloration of certain materials. These clinical effects can often lead to postoperative hypersensitivity of the tooth as well as to bacterial penetration of the interfacial space. Bacteria penetration can contribute to recurrent caries, which may lead to pulpal damage. Further, it has been reported that manifested pulpal irritation and pathosis are related to the diffusion of bacterial toxins into the pulp than to toxicity from the restorative material itself (Brannstorm & Nordenvall, 1978).

2.2.4 *In- vitro* testing of microleakage

Many techniques have been devised to test the cavity sealing properties of restorations both *in-vivo* and *in-vitro*. *In-vitro* studies include the use of dyes, chemical tracer, radioactive isotopes, air pressure, bacteria, neutron activation analysis, scanning electron microscopy, artificial caries technique and electrochemical method.

2.2.4.1 Dyes

The use of organic dyes as tracer is of the oldest and most common methods of detecting leakage *in-vitro*. In general this method involves placing a restoration in an extracted tooth, immersing it in a dye solution, after coating the unfilled parts of the tooth with a waterproof varnish. After an interval of time the specimen is removed, washed and sectioned before visual examination to establish the extent of penetration of dye around the filling (Alani & Toh, 1997).

There have been wide variations in choice of dye used, either as solution or particle suspensions of different particle size. Some of the organic dyes used include basic fuchin, methelyne blue, eosin, aniline blue, crystal violet and erythrosine (Gonzales et al, 1997). The concentration of dye used ranged between 0.5%-10% while the time of immersion of the specimens in the dye varied between 4 hours to 72 hours or more.

2.2.4.2 Chemical tracers

The usual method involves the use of two colourless compounds to produce an opaque precipitate; usually a silver salt using established photographic techniques. In all cases these methods rely upon the penetration of both chemicals, hence precipitation will not occur when only the smaller of the two molecules can penetrate. In practice silver halids particles have been shown penetrating dentinal tubules with ease, often making interpretation of results difficult (Taylor & Lynch, 1992).

2.2.4.3 Radioactive tracers

The use of isotopes permits detection of minute amount leakage, as the smaller isotope & molecules measure only 40nm compared to the smaller dye particles 120 nm (Going, 1964). Isotopes used have been as diverse as ^{45}Ca, ^{131}I, ^{35}S, ^{22} Na, ^{32}P, ^{86}Rb and ^{14} C (Taylor & Lynch, 1992).

This method involves the use of extracted restored teeth. The roots and crowns of the teeth are painted with varnish except for the surface immediately adjacent to the experimental restoration. This is to prevent leakage through the root canal, cracks in enamel or exposed dentine, which can obliterate the true picture of marginal adaptation. The seal teeth are immerse in the isotope solution for several hours. After removal from the isotope, the teeth are subjected to prolong rinsing before ground longitudinal sections are made through the restoration. The cut surfaces are applied to photographic film. The resulting auto radiographs indicate the presence and location of any radioactive isotope that has penetrated between the restoration and cavity wall (Alani & Toh, 1997).

2.2.4.4 Bacteria

Bacteria have also been used in the study of microleakage. Probably the earliest such study was in 1929 when Fraser tested cements and restorative materials to determine whether they would allow bacteria to pass through or around them. A few decades' later researches have been done to investigate the marginal seal of acrylic restorations (Ross et al, 1955; Seltzer, 1955) placed on filled teeth in broth cultures. The filling materials were subsequently removed and dentine shavings from the base of the cavity were cultured.

This method provided purely qualitative results, depending mainly upon the presence or absence of bacteria in part of the dentine shaving examined (Alani & Toh, 1997). Marginal gaps allowing the leakage of bacteria would be expected to be in the region of 0.5-1.0 µm or larger. These techniques do not therefore take into account gaps which are smaller than this and while not allowing bacterial penetration, allow the passage of toxin and other bacterial products which could be detrimental to the tooth (Taylor & Lynch, 1992).

2.2.4.5 Air Pressure

Harper introduced air pressure for detection of microleakage in 1912. He constructed class II amalgam restorations in a steel dye, delivered air under pressure to the floor of the cavity, and examined the restoration under water. Several investigators (Pickard & Gayford, 1965; Granath & Svensson, 1970) have also used air pressure to evaluate restorative materials. Microscopic examination of the release of air bubbles from the margin of the submerged restoration provided a subjective view of the marginal seal. This method proved to be a valuable technique for comparing the sealing properties of different amalgams as well as cement (Moller et al, 1983; Alani & Toh, 1997).

Air pressure tests otherwise treat the restoration as leaking equally along the entire margin when this is unlikely to be the case. They do not represent the clinical situation nor is the drying effect of compressed air passing through the restoration taken into account. It is also possible that some leakage may occur through clinically sound tooth tissue (Taylor & Lynch, 1992).

2.2.4.6 Artificial caries

Artificial secondary caries-like lesions have been produced *in vitro* using either bacterial cultures or a chemical system-acidified gel technique. In 1967 Ellis and Brown, using a bacterial technique to produce artificial secondary caries at the interface of the amalgam restoration and the tooth, linked the development of carious lesions to microleakage. Microleakage has also been associated with spread of secondary (recurrent) caries (Hals & Nernaes, 1971; Grieve, 1973).

The first investigators to describe the production of caries like lesions by the acid-gel technique were Muhlmann (1960), Von Bartheld (1961), and Silverstone (1968).The acidified gel technique developed for the production of secondary caries-like lesions around amalgam fillings by Hals and Nernaes (1971) has also been applied to the study of composites by Hals and Kvinnsland (1974), Kidd (1976b) and Kidd et al (1978). The lesions produced by this technique were studied in polarized light, and two parts were described: an outer lesion and a cavity wall lesion. The outer lesion results from primary attack of the enamel surface adjacent to the restoration, while the cavity wall lesions were formed by microleakage of ions from the acidified gelatin around the restorations.

Using polarizing light microscopy, Jensen and Chan (1985) determined the extent of demineralization of cavity walls adjacent to composite resin restoration following application of an acidified gelatin to the tooth surface to simulate caries. The used of this technique in evaluation of microleakage has the advantage that microleakage may be linked directly with one of its possible consequences, namely the development and spread of secondary caries. Quantification of results is possible where depth of lesion penetration is chosen as a measurable parameter (Kidd, 1976b) and the degree of mineralization may also assess quantitatively (Kidd, 1976b) or semi quantitatively (Grieve, 1973; Alani & Toh, 1997).

2.2.4.7 Scanning Electron Microscopy (SEM)

The use of scanning electron microscopy (SEM) provides a means of direct visual observation of the adaptation of restorative materials to cavity margins because of its high magnification and depth of focus (Boyde & Knight, 1969). It has been pointed out that the SEM technique can be criticized for its potential for introducing errors and artifacts related to drying, cracking, distortion, and sectioning (Kidd, 1976a). The technique is limited to the evaluation of teeth outside the oral environment and is not oriented to diffusion and penetration as are most studies (Going, 1972). However, many workers have used SEM to measure gap formation that occurred between the restorations, walls and floor of the preparation (Davila et al, 1986, 1988; Van Dijken & Horsted, 1989; Alani & Toh (1997).

2.2.4.8 Neutron Activation Analysis

Neutron Activation Analysis has been used to study microleakage both *in vitro* and *in vivo* (Going et al, 1968). It involves the immersion of restored teeth in an aqueous solution of non-radioactive manganese salt. All of the salt adhering to the outside of the tooth was then removed and the whole tooth placed in the core of nuclear reactor. This resulted in the non-radioactive Mn^{55} being activated to Mn^{56} and the X-ray-emission of Mn^{56} formed during irradiation was then measured. The number of radioactive counts is proportional to the uptake of Mn per tooth (Alani & Toh, 1997).

2.2.4.9 Electrochemical Method

The electrochemical method was adapted for use in restorative research from endodontic research. Jacobsen and Von Fraunhofer (1975) described the technique as one that permits accurate detection of the onset of leakage and provides quantitative results over a period of time. The principle of the technique involves insertion of an electrode into the root of an extracted tooth, so that it makes contact with the base of the restoration. The restored tooth is sealed to prevent electrical leakage through the normal structure, and immersed in an electrolyte bath. A potential is then applied between the tooth and the bath and the leakage is assessed by measuring the current following across a serial resistor (Gonzales et al, 1997).

2.2.5 Thermocycling and micoleakage testing

If the coefficient of thermal expansion of a restorative material differs significantly from that of tooth structure, the dimensions of the space around the filling material will change as the tooth is subjected to temperature variations. Together with thermal expansion of fluid occupying the crevice between the tooth and the restoration, this difference in the coefficient of thermal expansion will result in fluid exchange between the tooth and the restoration (Nelson et al, 1952). For this reason, in microleakage studies, it has become common practice to subject specimens to thermocycling.

Thermocycling is defined as the *in-vitro* process of subjecting a restoration and tooth to temperature extremes that conform to those found in the oral cavity (Alani & Toh, 1997). The use of repeated thermal and/or mechanical stressing of restorations now has a wide spread role in the demonstration of marginal adaptation and leakage (Taylor & Lynch, 1992).

In 1978, Kidd et al suggested that thermocycling may not be of clinical importance in relation to composite resin. Wendt et al (1992) determined the effect of thermocycling on dye penetration in the *in-vitro* assessment of microleakage composite resin. There was no increase of microleakage in restoration when thermocycling was used.

The temperatures used for *in-vitro* thermocycling have ranged from 0°C to 68°C (Shortall, 1982). Many investigators used temperatures of 15°Cand 45°C for their thermocycling (Peterson et al, 1966; Glyn Jones et al, 1979). These figures were based upon *in-vivo* work carried out by the authors using thermocouples to measure the temperature on the surface of the tooth during imbibitions of hot and cold drinks. Others utilized temperature changes from 4°C to 60°C (Morley & Stockwell, 1977; Kidd et al, 1978), while some cycled between 5°C and 55°C (Grieve et al, 1993). Harper et al (1980) suggested that the temperature variation in the mouth was quite small. Rossomando and Wendt (1995) determined that the need for thermocycling is dependent on the restorative material's ability to conduct heat in relation to its mass. They also concluded that the dwell time should be clinically relevant, e.g. 10 seconds.

Crim et al (1985) found that the extent of penetration by dye or tracer in the detection of microleakage of composite restorations was independent of dwell time in the thermal baths. Rossomando and Wendt (1995) found that the extent of the leakage increased with the increase in dwell time for amalgam restorations, although there were no significant differences in dye penetration for thermocycled composite restorations. It was recommended that microleakage tests on composite restorations be carried out only after 24 hours of specimen's storage to permit water sorption of resin to occur first. It was further suggested that as thermal stresses act rapidly to produce microleakage, prolonged cycling was not necessary (Crim & Garcia-Godoy, 1987).

The number of temperature cycles employed has ranged from 1 to 2,500. It was reported that microleakage increased with an increase number of cycles when resin restorative materials were tested (Peterson et al, 1966). Mandras et al (1991) have shown that the difference in a microleakage of composites thermocycled at 250 and 1000 cycles was not significant.

2.3 pH and saliva

pH is related to the actual hydrogen ion concentration by the formula:

$$\text{pH} = \text{Log}\ \frac{1}{(\text{H}^+)} = -\log(\text{H}^+)$$

pH is inversely related to the hydrogen ion concentration, therefore a low pH corresponds to a high hydrogen ion concentration, and a high pH corresponds to a low hydrogen ion concentration (Guyton & Hall, 2000).

The pH of oral saliva ranged at 5.2-6.2 in unstimulated (resting) condition and 6.5-8.0 in stimulated condition (Jenkins, 1978). The acidity or alkalinity of fluid in the oral cavity as measured by pH varies from around pH 4 to pH 8.5, whilst the intake of acid fruit juices or alkaline medicament can extend this range from pH 2 to pH 11 (Mc Cabe & Walls, 1998). Experiments with saliva and buffer solutions saturated with calcium phosphate have confirm that tooth substance dissolve in saliva below a pH varying from saliva to saliva (depending on their calcium phosphate concentrations) but usually between pH 5.5 and 6.5 (Jenkins, 1978).

Mandell, 1987 stated that saliva is effective in maintaining pH in the oral cavity, contributes to the regulation of plaque pH, and helps neutralize reflux acid in esophagus. Salivary buffers consist of bicarbonates, phosphates and proteins. In the oral cavity and in the esophagus, the major regulation of pH especially during eating or drinking is the salivary bicarbonate, the level of which varies directly with flow rate. At rest, histidine-rich peptides and phosphates contribute to the buffering action as bicarbonate content is low. The value of saliva in protecting against acids in the oral cavity is being put to a severe test by the large increase in the intake of acidic soft drinks.

In the bacterial plaque, where acid production is the natural product due to bacterial metabolism of carbohydrates, saliva helps regulate pH in several ways. Bicarbonate, phosphate and histidine-rich peptides act directly as buffers once they had diffused into the plaque. Urea from saliva is converted by bacterial urease to ammonia, which can neutralize acid. Amino acids and peptides can decarboxylated to form mono-amines and polyamines, a process which consumes hydrogen ions.

Bashir et al (1995) in their study of salivary clearance of citric acid after oral rinse concluded that the clearance was very rapid during the first minute, eliminating more than 90% of the ingested acid. However, the clearance pattern was a highly individual property that was not significantly dependent on the unstimulated salivary flow rate or the residual volume of saliva swallowing.

Several attempts have been made to find a correlation between saliva pH and caries experiences. Stephan (1944) used an antimony electrode directly in the floor of the mouth, reported a wide variation from an average of pH 7 in caries free groups to an average of pH 6.4 in an extremely caries active group. The plot of plaque pH against time has become known as the Stephan Curve. Within 2-3 minutes of eating sugar or rinsing with a sugar solution, plaque pH falls from an average of about 6.8 to near pH 5.5, took about 40 minutes to return to its original value. Below pH 5.5 demineralization of the enamel occurred, this is known as the critical pH.

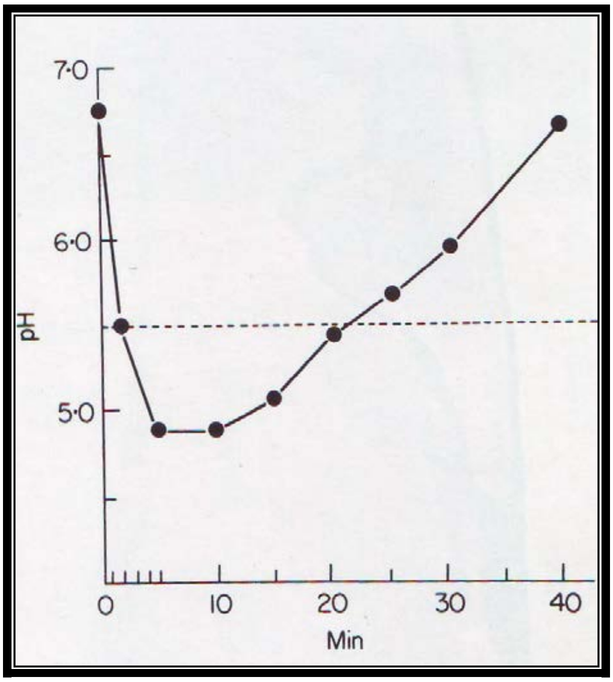

Figure 2.1: Plot of the pH of dental plaque against time (Stephan curve)

2.4 Effects of different pH on tooth structure and filling materials

The role of acids in causing dental erosion, where there is irreversible loss of dental hard tissue by a chemical process without the involvement of microorganisms, has long been established (Eccles, 1979). The acid may be derived from intrinsic sources in patients with recurrent vomiting due to anorexia, bulimia or gastro esophageal reflux (Meurmann & Ten Cate, 1996) or extrinsic sources derived from the environment, medications, lifestyle and diet (Zero, 1996).

Most all low pH foods and drinks have the potential to cause dental erosion in the human mouth. It appears that as a rule, dietary substances with pH above 4.5 have a low potential to cause dental erosion (Zero, 1996). Many drinks, fruit juices and sweet have a low pH and would be expected to dissolve enamel if taken regularly. In man, the effect of occasional acid drinks is unlikely to be important but frequent consumption of products which are held in the mouth for sometimes is damaging (Jenkins, 1978).

Hughes et al (2000) in their *in-vitro* study on effects of pH and concentration of citric, malic and lactic acids on enamel found that for each acid, a progressive linear loss of enamel was observed with successive ten minutes exposure at each condition. In their study they used enamel of unerupted third molar that were grounded using 600 grit abrasive disc before immersion in the respective medium.

Balasingam et al (2003) studied the microhardness of enamel after immersed in selected carbonated soft drinks. In their study, they used Pepsi (pH 2.95), Pepsi T (pH 3.30) and 100 Plus (pH 3.74) for 2,4,6,8 and 10 minutes. They found that enamel microhardness most reduced in Pepsi, followed by Pepsi T and 100 Plus from baseline up to 8 minutes. At the end 10 minutes, Pepsi still showed the lowest enamel microhardness.

The mechanism behind enamel erosion is basically that degree of saturation of the fluid around the enamel with respect to calcium phosphates, mainly hydroxyapatite, is shifted to under saturation due to a decrease in pH. Also some acids, like citric acid, are strong chelating agents, decreasing the free calcium ion concentration in the saliva (Lagerlof & Lindqvist, 1982).

Just like tooth surfaces, dental restorations may also be adversely affected by exposure to either intrinsic or extrinsic acids. Lower pH has been shown to affect negatively wear resistance of composite resin materials (Chadwick et al, 1990). Low acidic pH may cause erosion of materials and leaching of the principle matrix forming substances (Yip et al, 2001; Abu-Bakr et al, 2000; Lee et al, 1998).

Abu-Bakr et al (2000) studied surface hardness, compressive strength, solubility and surface integrity of compomers, resin–modified GIC and composite resin after they were immersed in acidic soft drinks. They used four different pH, which were 2.62, 3.83, 4.04 and 5.62.The specimens were immersed 3 hours every day for 60 days. They found SEM changes in surface texture when materials are immersed in low pH soft drinks. SEM revealed that the surface of resin composite was slightly affected, whereas the surfaces of the compomer and RM-GIC showed a rough surface with voids and protruding glass particles. They also found that compomers are softer then composite but harder than resin modified glass ionomer cements when immersed in acidic media.

Tahir et al in 2005 studied three different materials from Dentsply-De Trey, Konstanz, Germany, they found that the effect of pH on microhardness was material dependent, with the new generation compomer (Dyract Extra,) exhibiting lower microhardness value than the composite(Esthet-X,)and giomer (Beautiful) at various pH levels. For all the materials tested, the highest microhardness value was observed when the materials were conditioned in a medium with neutral pH 7.The critical pH at which degradation occurs varies among the three types of resin –based restorations. In their study, they used 0.3% citric acid, as base line and were adjusted to pH 2.5,3,4,5,6 and 7 by titration with 1M sodium hydroxide solution. The specimens were conditioned in the solutions for one week.

Ortengren et al (2001) studied the influences of pH and storage time on the sorption and solubility behaviour of three composite resin materials. They used Spectrum (Dentsply, Konstanz, Germany), Z100 (3M, St.Paul,USA) and ArtGlass (Heareus/Kulzer, Germany) in pH 4, 6 and 8 for 1, 7, 60 and 180 days. They found that time had a significant influence on the sorption and solubility of the materials tested and it was related to hydrophylicity of the matrix and chemical composition of the fillers. From 1 to 7 days, all materials in all pH showed increased in solubility. For more than 7 days, the difference in solubility between samples stored at different pH level was significant.

2.5 Bonding agents

2.5.1 Overview

The development of adhesive material has begun to revolutionize many aspects of restorative and preventive dentistry. The cavity design is changing and large quantities of sound tooth structure can be conserved. Microleakage which is a major dental problem may be reduced (McCabe & Walls, 1998). Strong and durable adhesion between cavity walls and restorative materials is necessary to produce well sealed and long lasting restorations (Alavi & Kianimanesh, 2002).

Enamel have smooth surface which has little potential for bonding by micromechanical attachment. Used of certain acids, usually 37% phosphoric acid can provide irregularities on the enamel surface, thus enhance bonding. Resin from the composite flows into the etched enamel and sets, forming rigid tags, typically 25 microns long, which retain the restoration. Bonding agent normally contain an unfilled resin may enhance the adhesive bond strength (McCabe & Walls, 1998).

Preparation cavity into dentine will form a smear layer. This layer, which is 3-15 microns thick composed of micro-organism, salivary protein and collagen from the dentine. In order to form an effective bond and seal between a restoration and tooth surface, the smear layer must be removed, disturbed or modified which allows access to the underlying dentine. The liquids used for dentine pre-treatment prior to bonding are called conditioners. Most dentine bonding system used acids as a conditioner and at the same time as an enamel etchant. After conditioning with the acid, priming agent are use to change the chemical nature of the dentine surface and to overcome the normal repulsion between the hydrophilic dentine and the hydrophobic resin. After priming, bonding agent, normally an unfilled resin will able to flow over and wet the primed surface to complete the formation of an effective bonding (McCabe & Walls, 1998).

It is now believed that efficient dentine conditioning not only remove the smear layer, but also causes a significant decalcification of intertubular dentine to a depth of a few microns. The decalcification process formed a three-dimensional collagenous network which can be infiltrated by primer and resin to form a resin infiltrated/reinforced layer or hybrid layer at the interface between the dentine and the resins (McCabe & Walls, 1998).

2.5.2 Classification

Perdigao and Swift Jr. (2006) elaborated the development of dentine adhesion in their book. During the 1950s, it was reported that resin containing glycerophosphoric acid dimethacrylate (GDPM) could bond to a hydrochloric acid-etched dentine surface (Buonocore, 1956).The bond strengths of this adhesion technique were severely reduced by immersion in water.

2.5.2.1 First generation

The development of the surface active co-monomer N-phenylglycine glycidyl methacrylate (NPG-GMA) (Bowen, 1997) was the basis for Cervident (S.S. White, Lakewood, NJ), which is considered the first-generation dentine bonding system. Theoretically, this co-monomer could chelate with calcium on the tooth surface to form a chemical bonds of resin to dentinal calcium. However, the *in-vitro* dentine bond strengths of this material were in range of only 2-3 MPa. Likewise the *in-vivo* results also were discouraging. Based on carbon-13 nuclear magnetic resonance analysis, it seems that no ionic bonding developed between NPG-GMA and hydroxyapatite (Perdigao & Swift Jr. 2006).

2.5.2.2 Second generation

Phosphate ester dentines bonding were introduced in late 1970s and in the early 1980s. Clearfil Bond System was first introduced in Japan in 1978, followed by other products such as Scotchbond (3M ESPE, St. Paul, Minn), Bondlite (Kerr Corporation, Orange, Calif), and Prisma Universal Bond (Dentsply Caulk,Milford, Del). This generation system typically had in-vitro bond strength of only 1-5 MPa. This is due to problems caused by the loosely attached smear layer and these resins were relatively devoid of hydrophilic groups and had large contact angles on intrinsically moist surface. Whatever bonding did occur was due to interaction with calcium ions. The *in-vivo* performances of these materials were found to be clinically unacceptable two years after placement in cervical tooth preparations without additional retention, such as beveling and acid etching (Perdigao & Swift Jr. 2006).

2.5.2.3 Third generation

The concept of phosphoric acid etching of dentine before application of a phosphate ester-type bonding agent was introduced by Fusayama et al in 1979. Because of hydrophobic nature of the bonding resin, however acid etching did not produce a significant improvement in dentine bond strength, despite the flow of the resin into the open dentinal tubules. Most of third generation materials were designed not to remove the entire smear layer, but rather to modify it and allow penetration of acidic monomers, such as phenyl-P or PENTA. Treatment of smear layer with primers was proposed using an aqueous solution of 2.5% maleic acid, 55% HEMA and a trace of methacrylic acid

(Scotchbond 2; 3M ESPE, St Paul, Minn). Scotchbond 2 was the first dentine bonding system to receive ‘provisional’ or ‘full acceptance’ from American Dental Association. Manufacturers combined the dentine etching philosophy advocated in Japan with the more cautious approach advocated in Europe and United States. The result was preservation of a modified smear layer with slight demineralization of the underlying intertubular dentine surface (Perdigao & Swift Jr. 2006).

2.5.2.4 Fourth generation

The use of total-etch technique is one of the main characteristics of fourth generation bonding system. This technique permits the etching of enamel and dentine simultaneously using phosphoric acid for 15 to 20 seconds. The surface must be left moist in order to avoid collagen collapse. The application of hydrophilic primer solution can infiltrate the exposed collagen network forming the hybrid layer. The formation of resin tags and adhesive lateral branches complete the bonding mechanism between the adhesive material and etched dentine substrate (Kugel & Ferrari, 2000).

2.5.2.5 Fifth generation

The fifth generation of bonding system was developed to make the use of adhesive materials more reliable for practitioners. This generation consists of two different types of adhesive materials: the so-called ‘one-bottle system’ and the self-etching primer bonding systems.

- One-bottle systems

‘One-bottle systems’ combined the primer and adhesive into one solution to be applied after etching enamel and dentine simultaneously (the total-etch technique) with 35-37 percent phosphoric acid for 15-20 seconds (Kugel & Ferrari, 2000).

- Self-etching primer

Watanabe and Nakabayashi developed a self-etching primer that was an aqueous solution of 20 percent phenyl-P in 30 percent HEMA for bonding to enamel and dentine simultaneously. The combination of etching and priming steps reduce the working time, eliminate the washing out of the acidic gel and also eliminate the risk of collagen collapse. However the self-etching primer solution also has some disadvantages. The solution must be refreshed continuously because its liquid formulation cannot be controlled where it is placed, and often a residual smear layer remained in between adhesive material and dentine (Kugel & Ferrari, 2000).

2.5.2.6 Sixth generation

Recently, several bonding systems were and proposed as the sixth generation of adhesive materials. These bonding systems are characterized by the possibility to achieve a proper bond to enamel and dentine using only one solution. These materials should really be a one-step bonding system (Kugel & Ferrari, 2000). These bonding systems are characterized by the possibility to achieve a proper bond to enamel and dentine using only one solution. These materials should really be a one-step bonding system (Kugel & Ferrari, 2000).