DEPARTMENT OF MATERIALS

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"Modification of silorane based dental resin and its chemical/mechanical characterization"

BY

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Thesis submitted for the completion of M.Phil in the field of Dental Materials.

ACKNOWLEDGMENT:

ABSTRACT:

It is desirable for a restorative dental material to have bioactive and adequate mechanical properties at the interface between the material and the tissue to prevent micro-leakage and ingress of bacteria. Current dental restorative composites, which consist of mainly polymer matrix, filler particles, and coupling agent, do not exhibit these properties. The presence of discrete zones at the interface between these three components could cause water absorption and the osmotic effect would result in swelling and residual pressure on tooth structure.

In this study, a material recently introduced by 3M ESPE with the commercial name of FILTEK Silorane was modified by incorporating nano-hydroxyapatite (HA) and fluoroapatite (FA) crystals and then evaluated for specific properties. Apatite powders have high surface area to volume, tendency to show osteoconductivity, superior chemical homogeneity and micro structural uniformity. Hence, it would be advantageous to combine these two materials to form a new dental material that would possess the above desirable properties. The requirement of a specific material differs according to the nature of the application and there are different techniques in modifying and fabricating different compositions to achieve exact requirements for clinical use

HA and FA were prepared in the laboratory by sol gel technique which involved the use of dried oven for ageing and heat treatment in furnace while silorane was dissolved in a Tetrahydrofuran (THF). Once the Silorane got completely dissolved in the solvent, n-HA and n-FA was added in different weight percentages. The mixture was left to mix for 24 hours. After the mixing films were cast from the suspension and dried. The prepared samples were tested for characterization, bioactivity and few mechanical properties.

Object of this study was to invent a bioactive restorative material with good mechanical, physical and chemical properties. Result of the study shows that addition of HA and FA by 40 to 60% weight results in the modification of chemical structure because of increase in filler size. In comparison the

spectra of 5 and 10% show the presence of fluoroapatite and hydroxyapatite without modifying the chemical structure of the Silorane Moreover fluoride ions are already present in the filler matrix of Silorane and by adding fluoroapatite it may increase the concentration of fluoride in the matrix. Bioactivity and mechanical properties were improved in modified silorane as more the fillers content in any material the more would be the strength and bioactivity of the material. It is also important that a proper balance of the matrix and filler is maintained so that the material does not become too brittle.

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CHAPTER 1

INTRODUCTION

1.1 <u>INTRODUCTION:</u>

This study is about the analysis and modification of silorane based dental resin to produce a bioactive restorative material with improved compressive strength for routine use in dentistry.

It is a requirement for a restorative dental material to possess bioactive and mechanical properties at the interface between the material and the tissue to avoid micro-leakage and access of bacteria (A.S Khan et al 2008). Current methacrylate based composites has several shortcomings, the most problematic of which was their polymerisation shrinkage and their related polymerisation stress (A.Tezvergil et al 2008).

In the recent years, 3M ESPE explored a new cationic ring opening monomer system to overcome the difficulty of high shrinkage, reactivity and to improve biocompatibility so that the restoration can be retained in aggressive oral atmosphere. (Wolfgang et al 2004).

The silorane resin was derived from the mixture of its structure blocks siloxane and oxirane. This innovative low polymerization shrinkage material recently launched to the European market had overcome the disadvantage of high polymerization shrinkage and related stress due to the ring opening oxirane monomer and increases its hydrophobicity because of the existence of siloxane species (Ilie et al 2009).

One of the shortcomings of silorane based material is their incremental bonding properties which is found to be inferior when compared to conventional dimethacrylate composites (Tezvergil 2008). Therefore, our designed experiment and aims are to improve the above mention shortcoming of the silorane based resins. This can be done by incorporating hydroxyapatite and fluoroapatite nano crystals and summarised experimental plan is discussed below.

1.2 EXPERIMENT:

Commercial Silorane will be dissolved in THF or deuterated chloroform. While for the preparation of nano HA and FA, appropriate amounts of calcium nitrate tetra hydrate, sodium fluoride and phosphoric pentoxide were required (the sol-gel will be used to synthesize hydroxyapatite/fluoroapatite as it offers homogenous composition, high product purity and low synthesis temperature in addition to applicability for surface coating).These products will be dissolved in absolute ethanol. Then solution will be mixed at a particular molar ratio followed by steps of gelation, aging, drying, sintering and crushing for preparation of nano HA and FA.

After the preparation of HA/FA incorporated silorane, samples will be prepared for the procedure and comparison and characterisation will be done in between both the silorane system using Fourier transform infrared and Raman spectroscopy.

In the second phase of experiment, experimental silorane will be prepared and immersed in SBF for specific days. Lastly, mechanical testing will be done by using universal testing machine.

In short we will incorporate hydroxyapatite (HA) and fluoroapatite (FA) crystals in to the silorane based resin. As HA/FA are considered to be acid resistant and believe to be hardest substances of the body (J.Norton et al 2006) and they also has been established as an osteoconductive material that binds chemically to enamel and dentine (A.S Khan et al, 2008).

1.3 AIMS AND OBJECTIVES:

The aim and objective of this study was to modify and analyze the silorane based dental resin to produce a bioactive restorative material with improved compressive strength. Fluoride ions are known to add strength to the tooth structure by creation of fluorohydroxyapatite (Tencate 1999). Incorporating these crystals in a restorative material has an advantage of being a reservoir for fluoride release. Addition of hydroxyapatite (HA) crystals can also improve bonding properties as it

is identified as an osteoconductive material forming chemical bonds with tooth structure (A.S Khan et al, 2008). The aim was to incorporate hydroxyapatite (HA) and fluoroapatite (FA) crystals in to the silorane based resin (J.Norton et al 2006).

In Summary our objective of this study is to investigate the effect of incorporating hydroxyapatite (HA) and fluoroapatite (FA) crystals in silorane based resins and to evaluate the compressive strength of silorane based resins. Analysis are to be conducted in conditions as similar to oral cavity and currently we need a material with fluoride leaching property for the posterior restoration which should last for adequate time.

Therefore it is possible that modified silorane based resin could be the next material for the posterior application with fluoride release and enhanced strength as currently available commercial materials exhibits less strength as compared to Dimethacrylate composites (A.Tezvergil et al 2008).

Of necessity relevant literature survey has been carried out and given in the next chapter.

CHAPTER 2

LITERATURE SURVEY

2.1   INTRODUCTION:

2.1.1   Tooth structure:

Apart from their mandatory role in digestion through chewing, teeth are important for phonetics, aesthetics and protection of the tongue. It's hard, calcified constituents and whitish colour compliments its functions. A tooth can be anatomically divided into two parts: the crown, which refers to the portion that is visible in the oral cavity; and the root, which is concealed by the alveolar socket it is ingrained in, thus effectively anchoring the tooth in situ. (Tencate, 1998)

The two substructures that are consistent throughout the tooth structure are the inner most dental pulp; and the more externally located dentine. The dentine is covered by enamel in the crown region and cementum in the root. The periodontal ligament connects the cementum to the alveolar bone. The specialized tissue that supports the tooth structure is termed the Periodontium. (Anusavice, 2003)

Figure 2.1 Structure of Tooth (Ten Cate, 1988)
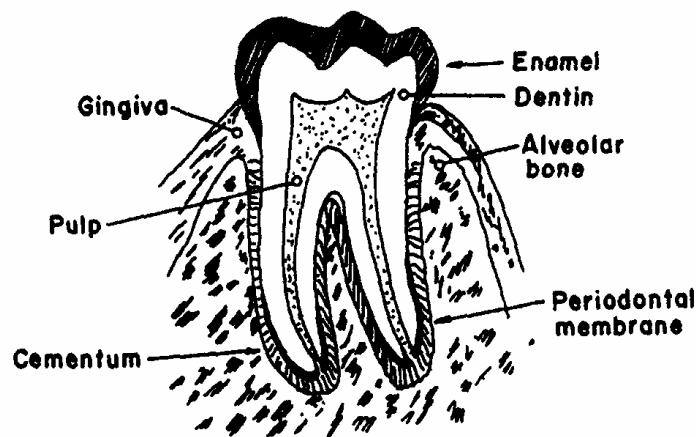
2.1.2 Composition:

Pulp:

Tooth is a sensory tissue as well. The sensations arrive from a soft connective tissue containing nerve fibres identified as PULP. (Lin, Xu et al. 2010) Dental pulp can be defined as unmineralized, soft, loose connective tissue. Its chief constituents are: Cells (odontoblasts, fibroblasts, and stem cells.); extracellular matrix (nerve fibres, blood vessels and irregularly arranged collagen type 3 and type 1); and ground substance (fibronectin, glycoprotiens, proteoglycans, and 75-80% water.)

The dental pulp is accountable for pain experienced by dental caries through subodontoblastic plexus of Raschkow, which consists of nerve fibres. It consists of myelinated type A delta fibres which transmit a sharp, fast, acute pain; whereas the unmyelinated type C fibres transmit a dull, aching, chronic pain. Once tooth decay is restricted to enamel, the pulp does not respond; however, if dentine gets exposed by the development of decay, dentin becomes sensitive. This is explained by the hydrodynamic theory. The dentinal tubules (within dentin) transmit signals such as differences in temperature or pH, to the odontoblastic layer of the pulp. A simple filling suffices as a restoration when the decay is limited to enamel and dentin. However, the concentration of the response increase once the decay has reached the pulp, since the C fibres offer a diffused, chronic pain, which is difficult to confine. One of the responses may also include inflammation of the pulp, known as pulpitis. At this stage, a root canal treatment or tooth extraction is essential. It should also be considered that since the pulp is bounded by mineralized dentin, an inflammation external to the pulp can cause compression of the pulp. (Roy and Basu 2008) (Tencate, 2003)

Enamel:

Enamel is the hardest tissue in the body; it is highly mineralized, protective, translucent covering encompassing coronal dentin and is the outer most part of the tooth that covers the anatomical crowns of teeth. Mature enamel is composed of the Inorganic phase with approximately 92–96%

made of mineral content.(Zaslansky, Friesem et al. 2006) Its pigmentation ranges from yellow to white and it is more mineralized than any other extracellular matrix within the body, which renders it hard, but brittle.

The mineral part are principally made up of calcium phosphate in the shape of either hydroxyapatite (HA) (Ca_{10} $(PO_4)_6(OH)_2$) or fluoroapatite [FA] (Ca_{10} $(PO_4)_6F_2$) crystals that are both carbonated and defective. Such an elevated mineral substance makes teeth the hardest and the toughest biological object within the human body. (Zaslansky, Friesem et al. 2006)

- **1–2% of organic material**

- **3–4% of water by weight**

The microstructure of enamel consists of aligned prisms or rods, running just about perpendicular from the DEJ in the direction of the tooth surface. The arrangement of the rods is keyhole-like with an average width of about 5 μm. (Roy and Basu 2008) Each of these rods consist of closely packed carbonated hydroxyapatite crystals, enclosed by a nanometre-thin layer of enamelin and oriented next to the rod axis. (Low, Duraman et al. 2008) Enamel tufts and enamel lamellae, though of no clinical significance, are also found within enamel. Enamel tufts originate from the dentino enamel junction and contain more protein than the remaining structure. It is suggested that they play a role in anchoring enamel with dentin. Enamel lamellae are formed as a result of failure of maturation process. (Tencate, 2003)

<u>Dentine:</u>

Dentine is defined as a pale yellow, calcified tissue that is denser and harder than bone and is comprised of dentinal tubules, water, both organic and inorganic constituents. It provides the tooth with bulk, rigidity and shape. It also serves the purpose of protecting the underlying pulp. It is a soft a tough layer of tooth providing the tooth with the strength vital to oppose catastrophic fracture when put under the masticatory stresses. (Zaslansky, Friesem et al. 2006; Roy and Basu 2008; Lin,

Xu et al. 2010) It encloses dentinal tubules lengthening throughout its thickness. These tubules spread out from the pulp cavity to the DEJ. (Roy and Basu 2008; Lin, Xu et al. 2010)

Table 2.1 Composition of dentine by weight and volume (Ten Cate, 1998)

Composition	By weight (%)	By volume (%)
Inorganic material	70	45
Organic material	20	33
Water	10	22

The types of dentin can be distinguished according to their location, mineralization and age. Primary dentin is deposited before and during the course of tooth eruption. Although mantle dentin and circumpulpal dentin are types of primary dentin, the latter is known to be more mineralized of the two and forms most of the dentin surrounding the pulp. Secondary dentin formation initiates once the root of the tooth has been produced, the dentinal tubules within it are in continuity with those of the primary dentin deposited earlier, but fewer in number.

Tertiary dentin is formed as a reaction to an external stimulus such as caries, attrition or an invasive restorative dental procedure. Reactionary dentin and reparative dentin are both types of tertiary dentin. The difference between the two lies in their formation; reactionary dentin is formed by odontoblasts, whereas reparative dentin is formed by odontoblast like cells. (Tencate, 2003)
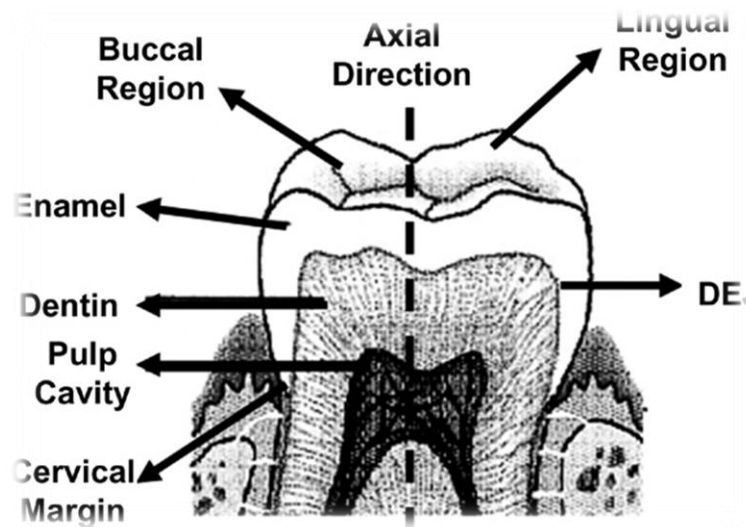
Figure 2.2: Schematic of a tooth section cut perpendicularly. (Roy and Basu 2008)

Dentine-enamel Junction:

As the name suggests, this junction is found between enamel and dentin, and is shell-shaped or scalloped. This shape increases surface area which results in a more uniform distribution of masticatory forces and acts as a shock absorber. It is a distinctive junction among highly mineralized tissues of diverse embryogenic origins, matrix composition and physical properties. (Roy and Basu 2008) It has the potential of arresting crack proliferation (Low, Duraman et al. 2008) and allows enamel and dentine to work mutually over long periods, during numerous cycles of load. (Zaslansky, Friesem et al. 2006)

Periodontium:

The Periodontium is a tooth – supporting connective tissues system that contains four mineralized tissues: The gingiva, periodontal ligament, alveolar bone and cementum are collectively referred to as Periodontium.

Cementum and alveolar bone interface with an elastic fibrous tissue known as the periodontal ligament (PDL). The periodontal ligament (PDL) is accountable for connecting the cementum with the alveolar sockets; it is thinnest near the centre of the root. It constituents comprise osteoblasts, fibroblasts, osteoclasts, cementoblasts and most decisively mesenchymal cells which allow differentiation into cementum or alveolar bone. Though cementum is connected to root dentine via

hydrophilic fibrous cementum-dentine junction (CDJ). (Ho, Marshall et al. 2007) (B.K.B. Berkovitz 2009)

Cementum is the calcified material which envelops root dentin. Its inorganic constituents (45-50%) contain hydroxyapatite and fluoride (which is most profuse in the cementum), whereas the organic constituents (50-55%) include type I collagen and proteoglycans. Since there are both cellular and acellular types of cementum based on their cellular contents and both extrinsic and intrinsic types based on their fibres. Acellular cementum is located around the root adjacent to dentin and cellular cementum is more commonly found in inter-radicular areas. A clinically important feature is the thickness of cementum which may increase to compensate for loss of tooth structure incisally caused by attrition etc. Additionally, the cementum is avascular, has no innervations and is less readily resorbed than bone which highlights its importance in tooth movement in orthodontics.

The alveolar bone is responsible for supporting the root in the maxilla and the mandible, and comprises of alveolar sockets which contain the tooth. (Tencate, 2003) (B.K.B. Berkovitz 2009)

Dental Caries and Restoration:

Dental caries is a multifunctional disease linking interaction among the diet, saliva, the plaque micro-flora and a vulnerable tooth surface. (Marsh, 1995) It is a pathogenic progression, which occurs due to precise acidogenic microorganisms found at the tooth surface which produces high concentrations of organic acids from nutritional carbohydrates, which results in demineralization of enamel and dentine. (Castioni, Baehni et al. 1998)

The course of dental caries starts with the demineralization of the mineral section of enamel and dentine and then grows with the breakdown of the organic material. Caries results primarily from a discrepancy between demineralisation and remineralisation of the tooth structure. (Thylstrup et al., 1994)

The management of caries depends on the step of caries progression. The following four approaches are promising to avoid the carious lesion. (Kidd and Smith 1991; Bjørndal 2008)

- Non-operative and anticipatory approach for initial lesion

- The operative method is the treatment alternative when caries has advanced into a clinical breakdown of the enamel surface and with carious dentine revelation

- Endodontic treatment is considered when pulp has been occupied. It includes elimination of infected pulp and restoring it with a restorative material.

- The ultimate approach is removal of the tooth if the carious lesion is not controllable by any of the above stated three alternatives.

The operative approach is considered when the carious lesion has advanced from enamel to dentine but has not infected the pulp yet. This method involves the drilling and filling of the cavity, thus giving the tooth back its structure and function that it has lost due to caries. The key goal of restorative dentistry is the avoidance of secondary caries. (Jones 2001)

2.2   DEVELOPMENT OF AESTHETIC RESTORATIVE MATERIALS:

2.2.1 Introduction:

The science of dental materials discusses the development, characterization, use and evaluation of the materials used to restore or replace the teeth. (Jack L, 2001) The history of dental restorative materials begins from the 500 B.C. There are four different classes of restorative materials, which include metals, ceramics, polymers and composites. (Jack L, 2001) All of above mentioned categories have characteristic microstructures and properties. (Roberson et al 2002) All of these different classes have certain applications in the everyday dentistry. Restorative dental materials comprises of all synthetic components which can be employed for fixing or restoration of tooth structure, including primers, bonding agents, cement bases, liners, amalgams, resin based

composites, hybrid ionomers, compomers, cast metals, metal-ceramics and denture polymers. (Anusavice, 2003)

Historically, the three earliest materials to achieve recognition as direct filling materials were cohesive gold foil, dental amalgam and silicate cements. (McCabe 2008)

The characteristics of the ideal restorative materials are that these should be biocompatible, mechanically stable and durable, resistance to corrosion or chemicals, dimensionally stable, match the usual appearance of tooth composition and other visible tissues, easy to manipulate, adherent to tissue and cost effective. (Jack L, 2001)

Despite the latest enhancements in the physical properties of the dental materials, none of the category of the dental material can be classified as an ideal restorative material. Dental clinicians and materials researcher will carry on the search in the 21st century for the principle restorative material. (Anusavice, 2003)

2.2.2 Early Development of Restorative Materials:

2.2.2.1 Development of Resin based dental composites:

In early 1960s, dental silicate cement was considered as the principal restorative material, but later in the mid 60s defects or problems were distinguished in the silicate cement. (Wilson 1988) Their physical properties were questioned raising the question for new development. New material should be developed with acceptable physical properties, biocompatibility, adhesion etc. (Wilson 1988)

The era of dental resin composites was initiated in 1956 by the synthesis of BisGMA. (Bowen 1962)

During the past few decades, adhesive dentistry has developed significantly, greatly because of the invention of 2,2-bis[4-(2-hydroxy-3-methacrylyloxypropoxy)phenyl]propane (BisGMA) based composites in the late 1950s. (Braga et al 2005, Bowen et al 1962)

The advancement was completed when Bowen (1962) of the American dental association research unit at the national bureau of standards and Buonocore discovered a new type of composite

material. (Jack L 2001) These innovations were Bisphenol A glycidyl methacrylate (bis-GMA), a dimethacrylate resin and an organic silane coupling for the development of a bond between the filler particles and the resin matrix. (Anusavice 2003) Still today, the monomer system of most resin composites are based on BisGMA or BisGMA derivatives. (Peutzfeldt & Asmussen 1998)

In 1974 Foster and Walker developed the commercial composites by incorporating the UEDMA or UDMA, which is reported to have low viscosity as compare to BisGMA. (Charton et al 2007)

The incorporation of monomers like UEDMA (1,6-bis[methacrylyloxy-2-ethoxycarbonylamino]-2, 4, 4-trimethylhexane) and BisEMA, new initiation systems and filler technologies extensively enhanced the physical properties of these materials but the polymerization shrinkage and the stresses produced by the composite remained a question. (Braga et al 2005)

The first invented composites were cured by a chemically activated polymerization reaction. This is also termed as cold curing or self-curing. Chemically activated polymerization is started by manipulating two pastes just before use. (Anusavice 2003)

Later for dental procedures applications, light activated resin composites substituted the chemically activated resin composites to overcome few shortcomings. One of the short coming was the rapid polymerisation reaction and need of greater control in timing the commencement of polymerisation. This 'setting on command' permits the dentist to position and contour the restoration with relative ease. (Dauvillier et al 2003)

2.2.2 Development of Glass ionomer cement:

While work on different modifications of composite resin was carried out, Wilson and Kent developed Glass ionomer cements from original work by D.C.Smith (1968) on poly carboxyl cement. Glass ionomer cement resulted when phosphoric acid in dental silicate cement was substituted by organic chelating acids. (Wilson 1988) The original invention was termed as ASPA I. (Aluminosilicate polyacrylate) (Wilson and Kent reported in 1971, 1972 & 1973) (Wilson 1988)

Efforts were made to improve cements properties so that it could be regularly used in dentistry for restorative purpose. Modifications were also done to improve and widen the range of application as early inventions were not workable and their setting times were too slow. (Wilson 1988)

In 1969, Wilson, Kent and Lewis proposed novel glass formulations which permit stable cements to be formed. (Wilson and Kent 1973) In 1972, an important modification was proposed by Wilson and Crisp (1976) who established that addition of tartaric acid could modify the reaction which gave improved manipulation, increased working and reduced setting time. This modified cement was termed as ASPA II and was the first practical glass ionomer cement. (Wilson 1976)

It was a satisfactory material but its poor aesthetics appearance and low mechanical properties made it less successful. (Crisp et al 1975) Further improvements were required to overcome the deficiencies of the glass ionomer cement. Development and modification results in the cement where the poly (acrylic acid) was vacuum dried powder mingled with the glass powder. The cement formation took place by incorporating powder with water or tartaric acid. (Prosser et al 1984)

Table2.2: Components of fluoroaluminosilicate glass and their role. (Mount and Hume, 1998; Wilson and McLean, 1988)

Component	Percentage	Effects
SiO_2	29.0	
Al_2O_3	16.6	These three essential components of the glass fuses to form the Calcium fluoroaluminosilicate glass. Al_2O_3/ SiO_2 ratio should be 1:2 or more for correct cement formation. However alteration may result in more
CaF_2	34.2	translucent or radiopaque cement.
Na_3AlF_6	5.0	It reduces fusion temperature.
$AlPO_4$	9.9	For Improving translucency.
Sr, Ba, La, Salts	-------	Used to replace calcium fully or partially which results in radiopacity.

2.2.2 Later development of Glass ionomer cement:

Further Development to enhance the strength of glass ionomer cement was carried out by addition of metallic oxide and metal alloys. (Wilson 1980 & Simmons 1983) The accumulation of silver-amalgam alloy powder to usual materials improved the physical strength of the cement and offer radiopacity. Consequently, silver particles were sintered onto the glass and numeral of products then appeared where the amalgam alloy substance had been fixed at a point asserted to generate most favourable mechanical properties for glass cermet cement. (Anusavice 2003, McCabe 1998)

Development to overcome the deficiencies was carried out by addition of resin in the glass ionomers. In 1992, resin-modified glass ionomer cements were modified that can be light cured. In these materials, the elementary acid-base reaction is complemented by a subsequent resin polymerization typically commenced by a light-curing process. In their simplest type, they are glass ionomer cements that include a small amount of a water-soluble and polymerizable resin component. More composite materials were innovated by altering the polyalkenoic acid with side chains that may well polymerize by light-curing mechanisms in the existence of photo initiators. (Anusavice, 2003) Resin based materials are extensively utilized in restorative dentistry because of their exceptional aesthetic properties and for the enhanced wear resistance. (R.Labella et al 1995)

A further class of light-cured restorative materials, which include GIC components and liberate fluoride, was launched to market. These materials branded as "polyacid-modified composite resins" (PMCR) or "compomers" may not be tagged the same as conventional glass ionomer cements, they are offered as one-component resin-based products and do not encompass an acid-base reaction which happens without photo activation and diffusion of water. Upon setting they also do not demonstrate the characteristic properties of true GIC. (Anusavice, 2003)

A detail comparison table is discussed on next page which would help in differentiating and compare the different modifications of Glass ionomer cement.

	CONVENTIONAL GIC	METAL REINFORCED GIC	RESIN MODIFIED GIC	COMPOMERS
Composition	Powder: Sodium Aluminosilicate glass + 20 % CaF Liquid: Aqueous solution of Polyacrylic acid	1.Powder of GIC with physical incorporation of Silver alloy known as Silver Alloy Admix 2.Fusing particle of conventional GIC with silver particles through sintering .They are known as Cermet	Powder: Fluoroalumino Silicate glass + initiator for light curing Liquid: a)Methacrylate Resin b) Polyacid c) HEMA d) Water	One Component(Single paste): Silicate glass particle, NaF and polyacid modified monomer without water. Activation via light curing
Setting Reaction	Exothermic with temperature rise of 2-5º C	Same as conventional GIC	Highly Exothermic because of polymerization leading to temperature rise of 10º C	Same as resin modified GIC
Fluoride Release	Significant amount of fluoride release which decrease the susceptibility of caries	Lower fluoride release than conventional GIC because of replacement of glass by metal	Behave similar to conventional GIC	Less fluoride release than conventional and Resin modified GIC
Resistance to Fracture	Low resistance to fracture.	Brittle, subject to chipping on filling edges, but good bulk strength in larger high-load restorations.	Low to moderate resistance to fracture.	Moderate resistance to fracture in high-load restorations
Moisture Sensitivity	High and should protected from contamination by varnish application	Same as conventional GIC	Presence of resin protects the cement from effect of contamination by moisture. No varnish needed	Same as resin modified GIC
Aesthetics	Matches natural tooth colour, but lacks natural translucency of enamel	Silver or grey metallic colour does not match tooth colour	Matches natural tooth colour, but lacks natural translucency of enamel	Matches natural tooth colour more closely as compare to any other modification of GIC
Setting Mechanism	Acid base Reaction	Acid base Reaction	Initially by polymerization followed by acid base reaction	Initially by photo polymerization and then after water absorption –Acid base reaction

Table 2.3: Comparison of different modifications of Glass ionomer cement (Anusavice 2003, McCabe 2008 & Jack L.Ferracane 2001)

2.2.3 Further development in the Aesthetic restorative materials (Resins):

Dental resin composites were invented as an aesthetic option to amalgam in the 1960/1970s and since then these have been regarded as the most accepted and far most commonly applicable direct restorative materials in the routine dental applications. (Ralf Beugers et al 2007)

The history of resins in dental restoratives composites saw an uninterrupted advancement during the last three decades. (Wolfgang et al 2004) The modern history of dental composites started with Bowen's resin (BisGMA), which was modified by various additions keeping in view the different properties of dental resins. Different co monomers like triethylene glycol dimethacrylate (TEGDMA) or urethane Dimethacrylate (UDMA) were added over time to improve the clinical application of the dental composites. (Wolfgang et al 2004)

2.2.4 Recent Advances in Dental resins:

All composites resins were based on the radical polymerisation reaction of dimethacrylate. (Wolfgang et al 2004) To overcome the disadvantages exhibited by the methacrylate based resins, there was a need of introduction of new resin system or alteration in the previous system.

As dental resins are the preferred choice of clinicians for most of the restorations, we needed some alterations to overcome the deficiencies of methacrylate based resins. (D.Truffier et al 2003) Despite of constant modifications in formulation to advance the clinical performance, methacrylate based resins can not be considered ideal as they exhibit few shortcomings. (A.Tezvergil et al 2008) One of the short coming is polymerisation shrinkage, which can lead to generation of stress at the tooth and restoration interface. This stress relates to introduction of cuspal deflection and marginal gap. (W.M Palin et al 2005) Clinically this may results in marginal leakage and bacterial ingression leading to pulpal irritation, postoperative sensitivity and secondary caries, which directly affect the longevity of the restorative materials. (W.M.Palin et al 2005)

As polymerisation shrinkage of the methacrylate resin composite remained a major hindrance, dental researchers have introduced a novel ring opening monomer, which is a blend of siloxane and oxirane moieties. This invention is named as Silorane. (Guggenberger et al 2003)

These silorane based resin have revealed low polymerisation shrinkage, low polymerisation stress, good colour stability and insolubility in biological fluid stimulants. (Adilson 2008) Their marginal integrity and micro leakage is found to be superior than the methacrylate based resins. (J.David Eick 2007)

One must remember the first expansion of the organically modified ceramic (Ormocer) material, advertised by Degussa AG, by the brand name of Definite. (Whitters et al 1999) In this ceramic filler particles were incorporated, creating the product still classifiable as composites.

2.3 CLASSIFICATION & COMPOSITION OF DENTAL RESINS:

2.3.1 Composition:

Composite resins materials are composed of few components in addition to the resin matrix, inorganic filler particles and a coupling agent. The reaction mechanism or activator initiator system is based upon the conversion of resin paste from a soft, mouldable filling material to a hard, long lasting restoration. (Anusavice 2003) They also contain chemicals to initiate the hardening process and pigments to create the different shades for matching the range of the natural teeth. (Jack L 2001)

In summary the dental composites are generally made up of an organic resin matrix loaded with a delicately dispersed glass or silica filler which is linked to the matrix polymer through a coupling agent that is silane. (Yoshida et al 2002) Each of the components is discussed on the next page:

2.3.1.1   Resin Matrix:

Per definition dental filling composites are a combination of an organic matrix and inorganic fillers. (Moszner et al 2001) The resin matrix itself is comprised of three main components which are: a monomer system, an initiator system for free radical polymerization and lastly stabilizers which maximizes the storage stability of the uncured resin composite and the chemical stability of the cured resin composite. (Peutzfeldt 1997) Normally, the organic monomer system is based on methacrylate chemistry, whereas particularly cross linking dimethacrylate like Bis-GMA, UDMA or TEGDMA are used. (Moszner et al 2001) The type of monomer significantly influences the reactivity, viscosity and polymerization shrinkage of the restorative paste, plus the mechanical properties of the cured restorative material. (Klapdohr and N.Moszner 2005)

The common types of monomer used in the resinous matrix phase are bisphenylglycidyl dimethacrylate (BisGMA), triethylene glycol dimethacrylate (TEGDMA) and urethane dimethacrylate (UDMA). While the photoinitiator system is mainly camphorquinone coupled with a tertiary amine. (Bernardi et al 2008)

2.3.1.2 Fillers:

The properties of resin based composites are extensively predisposed by the fillers which are used. Generally the filler used are the ground glasses or pyrogenic silica or mixture of both. (Klapdohr and N.Moszner 2005)

These radio opaque fillers are one of the key components of the dental composites. Radiopacity in dental composites is primarily accomplished by means of ground glasses, which include heavy metals such as barium oxide or strontium, which take up or reflect X-ray. (Moszner et al 2001)

2.3.1.3 Coupling Agents:

It was essential to develop an agent which could strengthen the interface between the inorganic phase and the polymer matrix. In recent times much consideration has been given to the improvement of a coupling agent for a specific structure, which has two dissimilar functional group: one involved with the matrix and the other with the surface of the filler, directing to configuration of covalent bonds linking the reinforcement and the matrix. (Chao et al 2009) An organo-silane (3-methacryloyloxy-propyl-trimethoxysilane) is applied as a coupling agent to attain an adequate bond between the resin matrix and organic particles. (Manhart et al 1999)

Compounds referred to as silanes belong to a class of inorganic hydrides of silicon which have the general formula. The number of Silicon atoms (n) determines the size of the silane compound, where every individual Silicon atom forms four bonds, either with another silicon atom, or with a
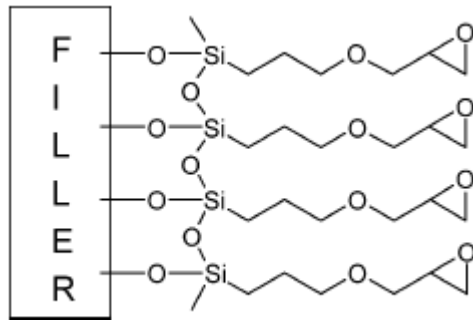
Figure 2.3: Silane Molecule (Anusavice 2003)

hydrogen atom. The term organosilanes refers to a class of organic compounds (due to the Carbon-silicon bonds within them) with general formula: X-R-Si $(OR')_3$. The symbols X, OR', and R indicate non hydrolyzable organic, hydrolyzable organic, and spacer groups respectively. This combination of constituents allows it to react with both organic and inorganic compounds along with other silanes. These silanes are termed functional silanes, as opposed to the non-functional silanes, which contain a single functional group, thus limiting their reactivity to only inorganic substrates. The above mentioned difference highlights the chemical basis for the use of functional

silanes in enhancing adhesion of two chemically different materials (organic with inorganic). The non-functional silanes are used as a cross linking agent, since it effectively binds two silane molecules together, forming a strong meshwork which is less permeable to water and has increased bond strength (Chao et al 2009).

In the series of reactions explained below, Y refers to an organic group, which reacts with organic constituents, and OR implies an alkyl group- R (Carbon and hydrogen chain) bonded to oxygen- O. The reactions describe the hydrolysis of silane, which activate the functional groups in the silane coupling agent, so that a bond can be established with the –OH groups of the substrate to which it is applied (Anusavice 2003).
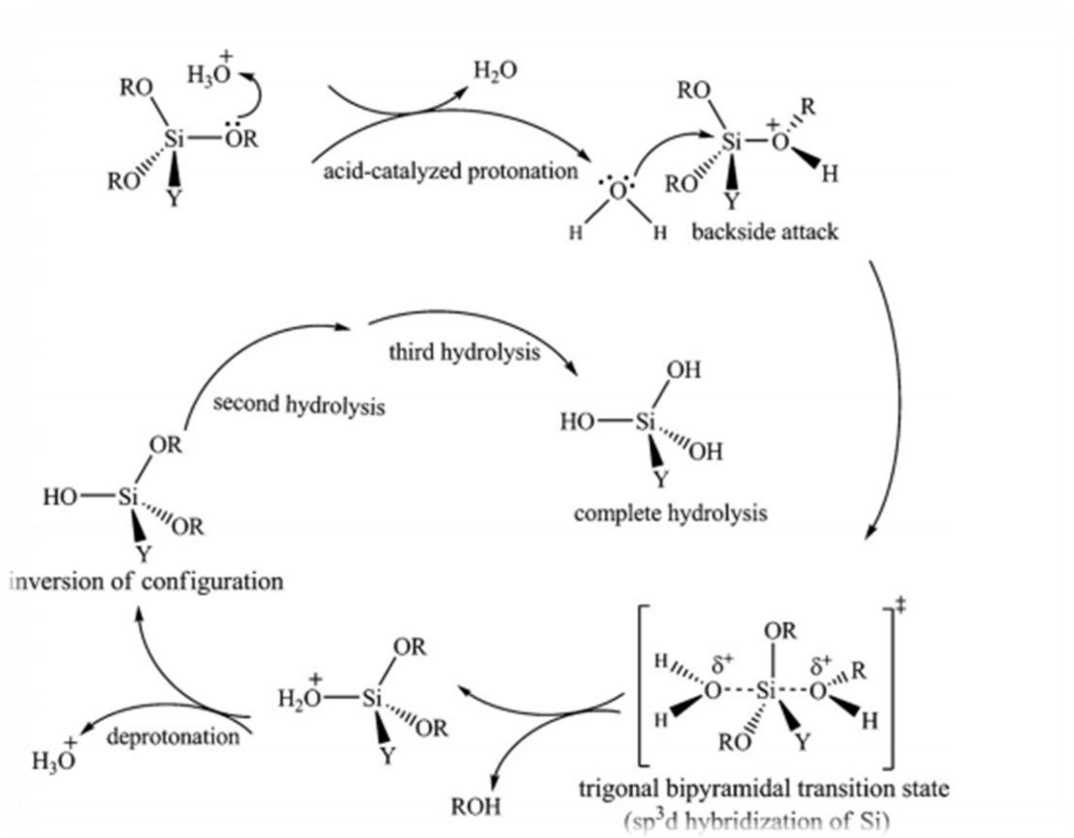
Figure 2.4: Mechanism of activation (Anusavice 2003)

2.3.1.4 Colour pigments:

Lastly, colour pigments are also supplemented in adequate quantities of 0.001 to 0.05% by weight in order to achieve the aesthetic requirement for composite fillings. Generally a mixture of different inorganic pigments which are yellow, red, white and black are most frequently used to replicate the colour of the normal teeth. Oxidic pigments like ferric oxide (red) or ferric hydroxide (yellow) are most commonly used. (Klapdohr and N.Moszner 2005)

2.3.2 Classification:

Filler particles differ significantly in value of their chemical composition, morphology and dimensions. Lutz and Phillips categorized composite resins based on their filler particle size: (Kahler et al 2008)

a) Macro-filled composites: It contains filler particles from 0.1-100 um

b) Micro-filled composites: It contains filler particles of 40 nm

c) Hybrid composites: It contains inconsistent filler sizes normally ranging from 0.6 to 1 um and contains 40 nm sized colloidal silica.

Lately, nanotechnology has led to the invention of a new class of resin composites which contains nanoparticles measuring approximately 25 nm and nanoaggregates of approx. 75nm. (Kahler et al 2008)

Resin based dental can be classified according to activation mode as well. Resin cements are typically separated in three groups: chemically-activated (self-cured), photo-activated or light activated and dual cured cements. (Braga et al 2002)

Chemically activated composites are supplied as two pastes system. These were cured by a chemically activated polymerization process when the two pastes are mixed together before use. This type of composites is also known as cold curing or self-curing. (Anusavice 2003)

Light activated resin composites were established to the commercial world in the 1970s. The first product was cured by UV light and later version by visible light. (Peutzfeldt et al 2000)

Dual-cured composites were improved to reconcile encouraging features of both types that are self cured and light activated cements. The objective was to invent a material with increased working time and capable of achieving a high degree of conversion whether the light is present or absent. (Braga et al 2002)

Figure 2.5: Complete Kit of dental composite (McCabe 2007)

2.4 SETTING SYSTEM:

2.4.1 Activator-initiator system:

The methacrylate based monomers polymerized or cured by the addition polymerization system which is commenced by the free radicals. These free radicals can be produced by chemical activation or by outside energy source like light, heat or microwave. (Anusavice 2003)

2.4.1.1 Chemically activated resins:

These types of resins are supplied as two paste system; one of the components contains the benzoyl peroxide initiator and the second component an aromatic tertiary amine activator which is N-N-dimethyl-p-toluidine. When these both components are mixed, it results in the formation of free radicals and beginning of additional polymerization reaction. Nowadays, due to advantages presented by light cure composites like (setting on command, controllable working time etc) when compare to chemical cured ones, these are used for limited applications only.

2.4.1.2 Light activated resins:

These types of resins were developed for UV light to initiate free radical polymerization. Later, with time UV light-cured composites were replaced by different light sources which will be discuss in detail. The commonest type of light source is visible blue light which offer advantages over chemically activated materials. (Anusavice 2003)

Light cured resins are dispensed as a single paste stored in a light proof syringe. These components of resins do not react with each other until they are shown or exposed to energy source. This single paste contains photosensitizer and an amine initiator, which on exposure to light produces an interaction of photosensitizer with the amine to form free radicals which initiates addition polymerization. The commonly used photosensitizer which is present in light curable dental composites is camphorquinone which absorbs the blue light at the wavelengths in between 400 and 500 nm. A small amount of amine initiators like dimethylaminoethyl methacrylate (DMAEMA) are also incorporated to interact with camphorquinone. (Anusavice 2003)
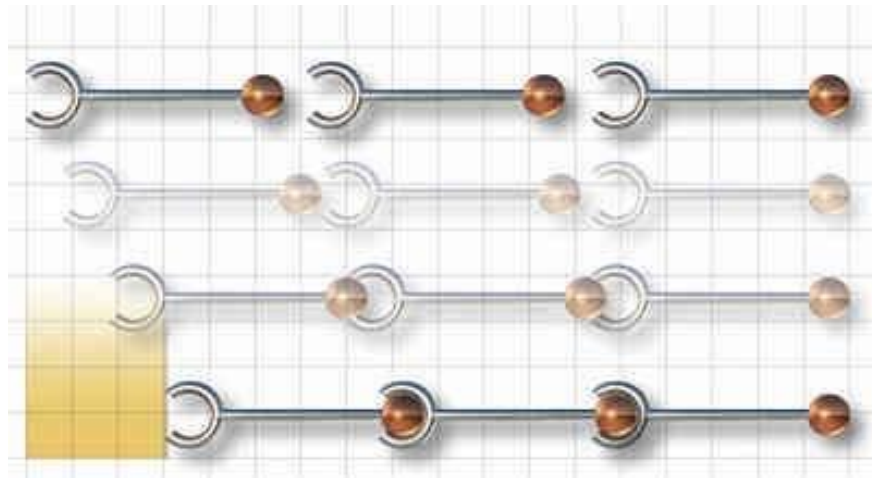
Figure2.6: Polymerization Shrinkage of methacrylate based composites (3M ESPE Catalogue)

2.4.2: Bonding of resin based materials:

The bonding of resin to enamel and dentine gives the link between the filling material and tooth. If the strength or affectivity of this link or bond is reduced in any way, it can lead to micro leakage at restoration-tooth margin with additional symptoms like introduction of sensitivity, recurrent carries and can finally lead to pulpal necrosis. (Hogan and Burrow 2001) Therefore establishing a strong and permanent bond with enamel and dentine is a highly demanding property of a dental composite (resin).

In 1955 Buonocore first introduced the acid-etch technique which results in the bonding of dental resin to enamel. In this technique phosphoric acid treatment is been done on enamel surface which results in the formation of micro porosities. As resin is placed, it penetrates these micro porosities and after polymerization it is reliably attached to the enamel via micromechanical retention. (Anne Peutzfeldt 1997)

Another challenge in early times was bonding of resin with dentine. Dentine was considered to be one of the difficult tissues to bond when compared to enamel. Dentine is mainly composed of hydrophilic calcium phosphate and collagen with adequate quantity of water. So an agent was

required which should contain hydrophilic and hydrophobic groups in order to allow them to compete with water for penetration and infiltration into dentine and also to copolymerize with dental monomers. Therefore dentine bonding system was invented and it was applied before the placement of filling material. (Anne Peutzfeldt 1997)

2.5 CURING OF RESIN BASED DENTAL COMPOSITES:

Resin based dental composites can be cured by two different ways. The polymerization may be activated chemically or by an external ultraviolet or visible light source. (McCabe 2008)

2.5.1 Chemical activation:

As discussed above that one of the method of curing or polymerization is through chemical activation which initiates by mixing two components, one of which typically consists of an initiator and other an activator. The result reaction is free radical addition polymerization. (McCabe 2008)

2.5.2 Light activation:

For the dental resin composites light activation at the ambient temperature is a organized and suitable cure system and extensively used in preparation of dental filling material. (Minhui et al 2008) Light activated resin based composites are generally dispense as a single paste which consists of monomers, comonomers, fillers and initiator. (McCabe 2008) The properties of light curing composites are primarily influenced by the quantity of energy delivered to the composite during exposure (curing) that is energy density. (Benetti et al 2009)

2.5.2.1: Types of curing sources:

As discussed previously that first product of the resin composites were cured by UV light and soon after by visible light. (Peutzfeldt 2000) Generally many of available commercial dental resin composites are polymerized by light source with the wavelength in the range of 400-500nm.

(Christian et al 2000) The purpose of the light is to activate the polymerization reaction by delivering high intensity radiation of the desired wavelength to the surface of material. (McCabe 2008) With time different curing sources were discovered and are discussed below:

2.5.2.1.1: Ultraviolet curing light:

The first ultraviolet cured dimethacrylate composite resins were introduced in 1973. In this type of light activation, the molecules of composite absorbs radiation upon exposure to ultraviolet light and undergo decomposition to form free radicals, which initiate polymerization.

The use of ultraviolet activated materials has reduced significantly because the possible dangers of long term exposure to ultraviolet radiations were highlighted. (McCabe 2008)

2.5.2.1.2: Visible Halogen Light:

This is the conventional type of blue visible light activation unit and been used in dentistry since the early 1970s. This type of light source is based upon the light produced by a quartz tungsten halogen bulb. This bulb is able to produce the required power of light output and is relatively cheap. (McCabe 2008) For the past numerous years, light emitted from a halogen light bulb has been applied to cure the resin based dental composites. Normally this type of light source cures or polymerized a restorative material within 40 seconds. (Christian et al 2000) The high intensity halogen bulb in the light unit generates light that is passed through a blue filter to maximize the light energy at suitable wavelength of 470nm. (Jack L 2001)

2.5.2.1.3: Plasma arc curing unit:

Long curing time was uncomfortable and inconvenient for both the patient and the operator. Therefore a more efficient light source with short curing time was invented, which was termed as Plasma arc curing units. This light is produced from glowing plasma (Xenon bulb), which is

aggregate of a gaseous mixture of ionized molecules and electrons. They have a wavelength of 470nm. (Peutzfeldt 2000)

PAC units were established to shorten the time used up by the dentist at curing resin composites but few disadvantages are associated with it. One of the disadvantages of PAC units is that they are really expensive and could make the treatment more expensive. Certain other issues related to common use of PAC are needed to be addressed as curing by PAC occurs very fast which influence the uncontrolled high polymerization contraction as well. (Peutzfeldt 2000)

2.5.2.1.4: Argon Lasers system:

One of the alternate light delivery system is the Argon lasers. This type emits a blue light which also can activate polymerization reaction. Argon lasers have the advantage of emitting the radiation beam which can travel longer distance without dispersion which suggests that the intensity of light stays the same (McCabe 2008). Both the plasma arc curing and laser systems were invented to reduce the light activation time from 40 to 60 seconds down to 10 seconds or less but they are generally several times more expensive than the conventional halogen bulb unit. (Jack L 2001)

2.5.2.1.5: Light emitting diode (LED):

Light emitting diodes have been successfully used in many areas of technology and certain LEDs emit blue light. The curing units based on LEDs have the advantage of low power consumption with battery power which makes them a workable option. LEDs have a long service life as there is no need to change the bulb and are comfortable for patient because they are quiet as there is no need of cooling fan in this device. (McCabe 2008)

In summary light emitting diodes (LEDs), lasers and plasma arc curing (PAC) units presents quite a few advantages over the visible halogen light system but it is quite expensive and with other offsetting drawbacks. (Anusavice 2003)

PRECAUTIONS:

The light emitted from curing units can result in retinal damage if an operator or patient looks directly at the beam constantly or for an extensive period or even for a shorter period in case of lasers. For avoiding such an incident or damage, one must never look directly into the light tip and minimize observation of the reflected light for longer episode. Protective eyeglasses or other various types of shields that filters the light are offered for enhanced protection of the patient and clinician. (Anusavice 2003)

| During curing, the substrate is exposed to visible **_blue light (470nm)_** | this results in decomposition of the initiator component of composite resin and subsequent **_formation of free radicals_**. | These free radicals then form **more _reactive new free radicals_** as a result of their reaction with the C-C bonds present within either the silane molecule or the resin monomer. | A **_covalent bond_** between the substrate and composite resin is formed once the free radicals undergo addition amidst the monomer (present in the composite resin) and silane molecules. |

2.6 PROPERTIES OF RESIN BASED DENTAL COMPOSITES:

The properties of resin based composites rely on several factors, related to the polymer matrix, the filler particles and the coupling involving filler and matrix. (Peutzfeldt & Asmussen 1998) The common type of dental resin composites are hybrid materials comprising of polymer groups that are reinforced by an organic phase of glass fillers which may have diverse compositions, particles sizes and filler percentages. (Kahler et al 2008)

One of the other important factors which influence the mechanical and physical properties is the degree of conversion. In short, the higher the double bond conversion better will be the mechanical properties. Insufficient cure and the existence of unreacted chemicals in the dental composites can give rise to liberation of residual or unreacted monomers, which is the reason of weak mechanical properties. (Du et al 2008)

However, in general resin based dental composites have certain beneficial properties like excellent aesthetics and erosion resistance but their mechanical properties are variable and discussed below:

2.6.1: Aesthetics:

This property of dental materials has increasingly become very important as the new teeth colored materials are continually introduced. Better aesthetics is considered to be one of the advantages of dental composite. Infact, originally resin composites were modified in the wake of an aesthetic filling material for anterior restorations. (Demirel et al 2003)

Their colour stability is one of the important physical characteristic of the dental composites if these are placed and finished smoothly in the cavities as rough surfaces have a natural tendency to adapt stains quickly. (Ferracane, 2003)

2.6.2 Biocompatibility:

Generally composites are accepted as the biocompatible material for use in oral cavity but these should be handled with caution. There is uncertain and controversial evidence that methacrylate based resins have been considered to release unpolymerized monomers into the tissue. Leaching of this residual monomer from composites can result in hypersensitivity, cytotoxicity, genotoxicity, estrogenicity and alteration of immune response. However there is a suggestion that it is a low biological risk from leached component. (Brackett et al 2006)

2.6.3 Depth of cure:

In case of the light activated dental composites it should be remembered that operator has a longer working time as compared to chemically activated ones. The reason is that a light activated material only begins to set upon exposure of light. This property of material setting after light exposure is termed as command setting. But one of the slighter disadvantages associated with light activated composites is its limited depth of cure. This suggests that the operator should not try to polymerize or cure a greater depth of material than recommended. The composites should be restored and cured in increments to guarantee appropriate curing. The increment of 1-2.5 mm can be placed depending upon their shade. (McCabe 2008) This incremental technique overcomes the limitation of curing depth but it increases the time and difficulty of restoration placement.

2.6.4 Polymerisation shrinkage and setting contraction:

One of the significant disadvantages of composite material is said to be its polymerisation shrinkage and related setting contraction. Polymerisation shrinkage during the curing reaction can found to be in the range of 2.6-7.1%. This shrinkage stress which is produced during the curing reaction can result into the beginning and development of interfacial defects. (Kahler et al 2008) These defects can effect the longevity of the restoration and said to be related with clinical symptoms such as micro-leakage, post-operative sensitivity and micro bacterial contamination with recurrent carries. (Kahler at al 2008)

When looking into the chemistry of the resin, the single resin molecules move towards each other and are linked by chemical bonds to form a polymer network and this results in a significant volume contraction. (3M ESPE)

2.6.5 Thermal properties:

One of the important aspects of consideration for dental resins is its thermal properties. They generally have low thermal conductivity but the thermal expansion coefficient which reflects the amount of expansion upon heating and contraction when cooled is higher for dental composites when compare to tooth structure. This mismatch in thermal expansion coefficient may lead to high stress concentrations which plays a significant role in producing conditions for micro-crack initiation. In short the difference in the thermal expansion coefficient can produce higher stresses and also can be believed as a main cause of the fatigue damage. (Kahler et al 2008)

2.6.6 Abrasion resistance:

Surface roughness can be resulted by abrasive forces applied on the materials after their placement. Food stuffs and dentifrices can be the common factors. Inadequate wear resistance under masticatory load is often cited as one of the main problem of dental composites because excessive abrasion can result in change of anatomical form of the restoration. Abrasion resistance could be considerably enhanced with reduced average filler particle size and increased filler loading. (Manhart et al 2000)

2.6.7 Hardness:

Hardness values of the materials are use to specify the relative ability to resist scratching and abrasion. Higher the value of hardness, easier it is to finish and polish the material. Hardness values in dental composites are associated with few factors. One is the amount of filler content, increase in the amount of filler content leads to higher surface hardness. (Demirel et al 2003)

Hardness values indicate an excellent correlation with degree of conversion. In case of light activated dental composites, it depends on the amount of light shown or exposed on the filling

material. Light activated resins shows lower hardness values as compare to other activation modes. (Braga et al 2002)

2.6.8 Bonding strength:

Composites itself does not make a long lasting bond with the tooth structure. There are factors or agents which greatly influence the bonding strength and minimize the chance of micro leakage. Oxygen inhibition layer, acid etch technique and dentine bonding agents are mainly responsible for bonding composites with tooth and are already discussed above. (McCabe 2008) These all factors contribute to increase bond strength of dental composites.

2.7 CLINICAL APPLICATION:

The cement has a range of uses, which includes:

- Restoration of Class III, IV and Class V cavities.

- Esthetical repair material for fractured or chipped tooth or porcelain restorations.

- Restoration of Class I where extensive tooth structure is intact.

- Inlays and Onlays.

- Bonding orthodontic brackets.

- Core build-up.

- Fissure sealant

2.8 SILORANES:

As discussed earlier that history of dental restorative composites has seen continuous modifications in many ways since its introduction with Bowen's resin, BisGMA. (Weinmann et al 2005) The attempts to improve the clinical performance and the affectivity of the restorative dental resin material are primarily centred on reducing the polymerization shrinkage, in addition to improving

the biocompatibility, wear resistance and the processing properties. (Moszner et al 2001) Ring opening polymerization is one of the ways of reducing polymerization shrinkage.

2.8.1 Introduction and history of silorane:

History of polymeric material begins from 1901 with the introduction of methyl methacrylate. But the age of dental resin composites was initiated in 1956 by the synthesis of BisGMA. (Bowen 1962) The early materials were chemically cured, but this tooth-colored material promised improved aesthetics as compared to other available materials. All composites in previous decades utilize dimethacrylate such as TEGDMA, BisGMA or UDMA, which were radically polymerized as the primary resin. Despite the decade of improvements, polymerization shrinkage still remained a major challenge for the material scientist. (3M ESPE)

As mentioned earlier two major complains that needed to be addressed were their polymerisation shrinkage and the related polymerization stress. (Weinmann et al 2005) Chemically the translation of monomer molecules into the polymer network, termed as sol-gel conversion is accompanied with closer packing of the molecules, which results in volume contraction. This shrinkage value ranges from 2 to 6%. (Charton et al 2007)

In the past few years, 3M ESPE introduced a new cationic ring opening monomer system to avoid the deficiency of high shrinkage, reactivity and biocompatibility which maintains it integrity in the aggressive atmosphere of the oral condition. (Wolfgang et al 2004)

2.8.2 Structure and chemistry of silorane:
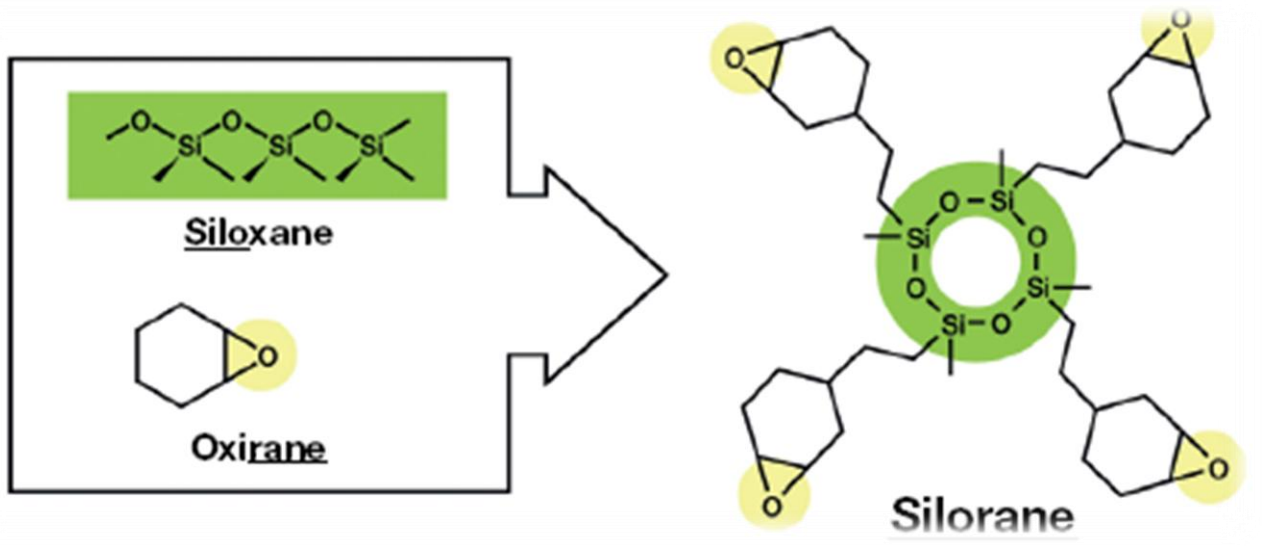
Figure 2.7: Chemical Building blocks of Silorane & A silorane molecule (3M ESPE Catalogue)

The silorane resin was innovated from the blend of its building blocks siloxane and oxirane. This new low polymerization shrinkage material recently launched in the European market have overcome the disadvantage of high polymerization shrinkage and related stress due to the ring opening oxirane monomer and increase in hydrophobicity because of the presence of siloxane species. (Ilie et al 2009)

Siloranes are different from the traditional composites. These are completely new class of compounds available for use in routine dental practise. As mentioned earlier the term silorane is derived from its chemical building blocks siloxane and oxirane.

Siloxanes are very commonly used in industries for their known hydrophobicity. Therefore by incorporating this in resin based composites makes it hydrophobic. While oxiranes are well known for their technical field application where there is a need of high forces and expectation of tough physical environment. The common examples are tennis rackets or skis. Oxirane polymers are

recognized because of their excellent low shrinkage and the exceptional stability toward several physical and chemo physical forces and authorities. (3M ESPE)

The mechanism of reduction in stress in this system is accomplished by the opening of the oxirane ring during polymerization. Apart from the usual radical polymerisation initiation in traditional dimethacrylate based dental resin/composites, the silorane composites polymerizes by a cationic ring opening method which is not sensitive to oxygen. (Ilie et al 2009)
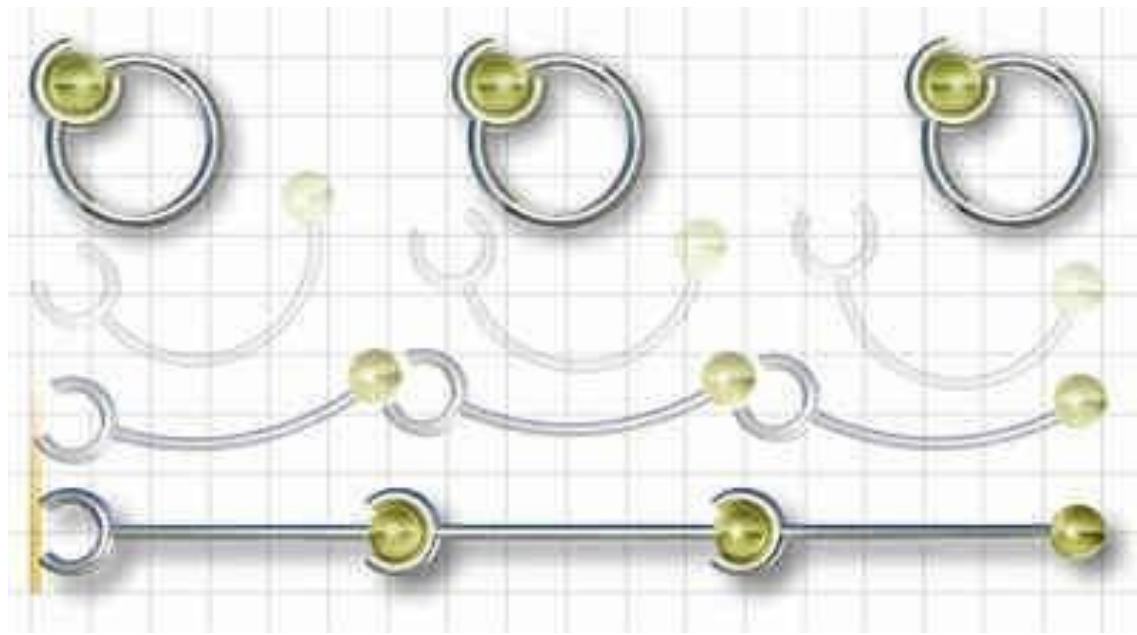
Figure 2.8: Polymerization Shrinkage of Silorane based composite materials (3M ESPE Catalogue)

The silorane resin is developed from the blend of its chemical building blocks siloxane and oxirane. The purpose of siloxane is to introduce hydrophobicity in the composites, which is very essential as high water sorption restricts the extensive physical strength of composite in the oral environment. Where as oxirane are responsible for low polymerization shrinkage and stability. The key difference among them and methacrylate is curing reaction. Methacrylate set by radical polymerization where as silorane polymerize via cationic polymerization. (Weinmann et al 2005)
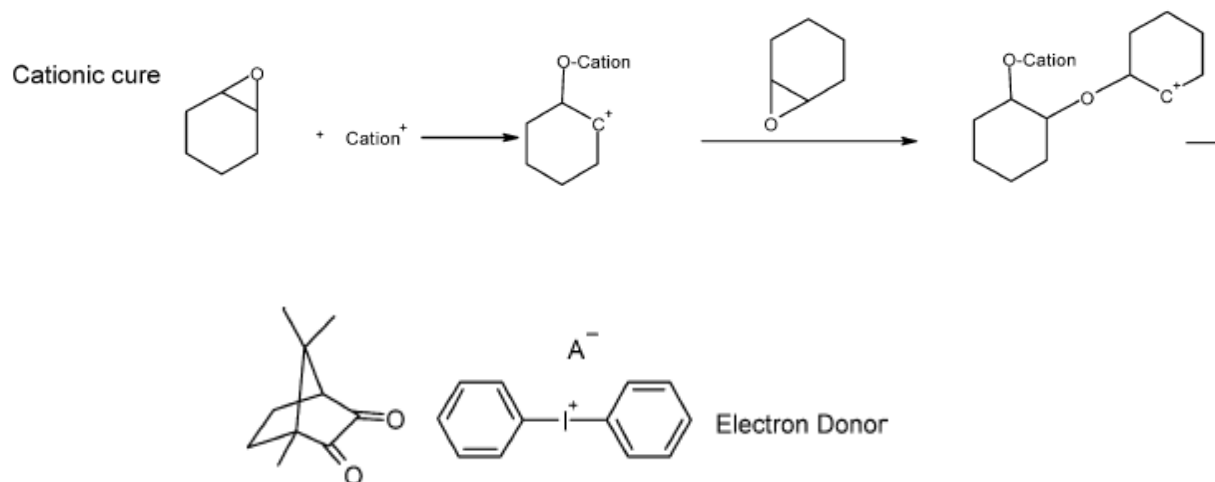
Figure 2.9: Polymerization of cation curing ring opening epoxies (3M ESPE catalogue)

The initiating system of silorane is made up of three components system, camphroquinone which is the photoinitiator, an iodonium salt and an electron donor. During this reaction the donor breaks down the iodonium salt to an acidic cation, after which commences the ring ion polymerization. This three component system gives a very good balance of the high polymerization reactivity with the excellent light stability. (W.Weinmann. et al. 2005)

The aesthetic quality and the mechanical stability of the silorane depend on the usage of the fine quartz particles. The silane layer formed is very much like the methacrylate based restoratives and this layer is modified by epoxy functionality, introduced by the silanization process. The hydrophobic property of the filler surface is enhanced by silane and it is a transitional interface between the filler and resin matrix. Another key function of the silane in silorane is to avoid the attack of silicon and the hydroxyl groups, which may reason for any unnecessary polymerization process. (W.Weinmann. et al. 2005)

The adhesive system of the Silorane is the methacrylate based, two-step self etch system. First the polymerizable self-etching primer is placed, pursued by the application of hydrophobic

dimethacrylate monomer and photo polymerization of the adhesive resin. This encourages association and covalent bonding to the hydrophobic oxirane-based composite. (Navarra et al 2009)

2.8.2.1 Composition of Silorane:

Table 2.4: Constituents of the silorane resin composites (Shawkat et al 2009).

Commercial Resin brand	Resin matrix	Filler
Filtek Silorane 3M	TEGDMA	Quartz
	ECHCPMS	0.1-2.0 um (76%)

ECHCPMS= 3, 4-epoxycyclohexylcyclopolymethylsiloxane
TEGDMA= Triethylene glycol dimethacrylate

Table 2.5: Composition and technical guide of the silorane adhesive solutions (Navarra et al 2009).

Brand	Composition (wt %)	Application mode
Silorane adhesive 3M	**Self-Etching/Primer** 2-Hydroxyethyl methacrylate (HEMA)15% Bisphenol A (BisGMA) (15-25) Water (10-15) Ethanol (10-15) Phosphoric acid-methacryloxy-hexylesters mixture (5-15) (Dimethylamino) ethyl methacrylate (<5) Silane treated silica (8-12) Copolymer of acrylic and itaconic acid (<5) dl-Camphorquinone (<3) 1,6-Hexanediol dimethacrylate (5-10) Phosphine oxide (<3) **Bond** Substituted Dimethacrylate (70-80) Silane treated silica (5-10) Triethylene glycol dimethacrylate (TEGDMA) (5-10) Phosphoric acid methacryloxy-hexylesters (<5) dl-Camphorquinone (<3) 1,6-Hexanediol dimethacrylate (<3)	Apply on tooth surface and brush for 15 seconds Expose to gentle air stream and then cure for 15 seconds. Agitate the bottle Apply on tooth surface Expose gentle air stream Cure for 10 seconds

2.8.3 Properties of Silorane:

The introduction of silorane leads to remarkable improvements in the properties of traditional composites. Silorane based composites exhibits excellent mechanical properties and also appealing aesthetics. (Weinmann et al 2005)

2.8.3.1 Polymerization shrinkage:

Two major shortcomings of conventional dimethacrylate composites were polymerization shrinkage and the related polymerization stress. Silorane based resin composites is known to overcome these shortcomings because of the presence of their chemical building block. It exhibits low polymerization shrinkage because of the ring-opening oxirane monomer while other component siloxane is accountable for increased hydrophobicity. (Ilie and Hickel 2009)

2.8.3.2 Ambient light stability:

The high ambient light stability of silorane can be clarified by the ternary initiating system. As in case of silorane a distinct balance of high ambient stability and high reactivity is possible at the same time, which is not achievable for the two component initiating systems of methacrylate. (Weinmann et al 2005)

2.8.3.3 Solubility:

Siloranes are introduced as a substitute to conventional methacrylate based composites because of their hydrophobicity and low polymerization shrinkage. Usually compounds containing oxirane as their chemical building blocks are known to be reactive with water and it questions the stability of silorane based composites in the oral environment. (Eick et al 2006)

But silorane based composites are extremely hydrophobic like other silicon containing monomers in which siloxane (one of chemical building block of silorane composite) makes the oxirane groups

unreachable to water attack. It suggests that these silorane composites are more stable for use in the oral environment as compared to conventional methacrylate. (Eick et al 2006)

2.8.3.4 Bonding properties:

This is one of the properties of silorane based composites which needs improvement. Absence of Oxygen inhibition layer of silorane composites along with the cationic polymerization questions the adequacy of bond strength in between the incremental layers of these composites. (Mutluay et al 2008) Oxygen inhibition layer in the conventional methacrylate based composites are responsible to aid superior interfacial adhesion of the resin layers along with other factors. (Eick et al 2006) It is suggested that that silorane based composites shows inferior bonding properties when compared to conventional dimethacrylate composites. But Shawkat et al in their recent study suggest that incremental bond strength is not completely dependent on surface oxygen inhibition layer as after the immediate placement in large restorations, the bond strength between the consecutive increments of silorane is similar to conventional methacrylate materials. (Shawkat et al 2009)

2.8.3.5 Longevity:

The vulnerability of direct restorative materials to adhere normal flora or other micro organisms in the oral cavity is considered to be of prime significance for their longevity. Silorane based resin composites shows excellent biocompatibility characteristics with low mutagenic potential. (Buergers et al 2009) As mentioned earlier silorane based composite resins are hydrophobic in nature which leads to lower quantity of streptococcal (bacteria) adhesion as compared to conventional methacrylate resin. Even fungus like Candida albicans which is the most widespread fungus in the oral environment can adhere to restorative materials and can promote oral candidosis but due to hydrophobic siloxane backbone of silorane based resins; it shows low adherence values than any other composites. (Brachert et al 2008) This low adhesion prospective of the silorane based

composite resin could be reason of improved longevity of the direct fillings or restorative procedures and can also results in reduce secondary caries. (Buergers et al 2009)

2.8.3.6 Aesthetics:

The aesthetical appearances of the restorative material are needed to be ideal or close to natural dentition in appearance. Many factors like gloss, colour stability and smoothness contributes to pleasing aesthetics. Increased gloss and decrease roughness will give a more aesthetically pleasing tooth and will match with the neighbouring teeth. While reductions in gloss and smoothness with aging could possibly results in plaque accumulation, discoloration and poor aesthetical appearance. (Furuse et al 2008) Roughness will also take up stains from exogenous sources like tea or red wine, which also promotes discoloration.

But when compared to conventional dimethacrylate, silorane based resin composites exhibited better overall colour stability and should be considered a more aesthetically pleasing material. (Furuse et al 2008)

2.8.3.7 Biocompatibility:

Some studies suggested that bis-GMA is a recognized skin contact sensitizer as identified on guinea pig models and human skin patch tests. Skin contact to unpolymerized bis-GMA and other methacrylate have been recognized to initiate skin sensitization and allergic contact dermatitis in vulnerable individuals. (Kostoryz et al 2006)

The silorane contain Tet-Sil and Ph-Sil as their resin matrix components which have been found to be non-sensitizing. However, the patients who have been found to be allergic from bis-GMA, can be restored with silorane based resin. Therefore, silorane based restorative materials could become the choice of material for the patients who exhibits methacrylate sensitivity. (Kostoryz et al 2006)

2.8.4 Applications of silorane based resin in dentistry:

These new silorane based materials are invented to replace amalgam restorations in posterior regions. It can be indicated for the following applications:

- They can be used in Class I and Class II posterior restorations.

- They can be use with Glass ionomer cements as cavity liners or bases. (3M ESPE)

2.9 BIOACTIVE HYDROXY APATITE/FLUOROAPATITE CRYSTALS:

In addition to special fillers and monomer, FA/HA could be added to the composite either to decrease bacterial growth or to encourage remineralisation and avoid demineralization of the tooth. (Moszner et al 2001)

2.9.1.1 Introduction:

There is a requirement and high demand of a material that hinder the growth or production of secondary caries. Bioactive materials have a promising prospective of fulfilling this demand. (Moszner et al 2001)

Fluoride ions are identified as one of the alterations to the tooth structure by resulting in the formation of fluorohydroxyapatite crystals. (Ten Cate 1999) Fluoride release could be achieved by the addition of fluoroapatite crystals.

While incorporation of hydroxyapatite (HA) crystals in the silorane based resin can also improve the bonding properties of the silorane as it is known to be an osteoconductive material and it also binds chemically to enamel and dentine. (A.S Khan et al, 2008)

2.9.1.2 Hydroxyapatite crystals and its properties:

In the past decades there was always a need for replacing bone substances and human teeth which have been missing because of traumatic or non-traumatic injuries. The lost tissue can be restored by endogenous or exogenous bone tissues or grafts. The implantation of endogenous replacement includes the additional surgery; while they are only available in restricted quantities. The most questioning demerit of exogenous bone implants is hypersensitivity type II reaction i.e. rejection of the implant by human body, transmission of disease along with implant and inferior performance of exogenous implants when compared to endogenous ones. (Suchanek and Yoshimura 1998)

Several metallic and non metallic materials have been extensively used for the medical and dental applications. Metals have been commonly used but there were various problems associated with use of metallic materials in the human body like corrosion, tissue reaction and wear. However continuous development in the biomaterials industry saw clinical application of several ceramic materials. Among titanium alloys have been widely used in the world but problem of loosening of implant and stress concentration remains a question for metallic implants. (Suchanek and Yoshimura 1998)

The need for the superior materials for the medical and dental purposes is among the one of most essential continuing modern materials engineering advancement. The most capable prospective for bone alternates is revealed by materials based on non metals like hydroxyapatite(HA), Ca_{10} $(PO_4)_6$ $(OH)_2$.Hydroxyapatite can create strong bonding with bone tissue, shows brilliant osteoconductive behaviour and does not demonstrate any undesirable effects on human organisms. (Orlovskii et al 2002) The human teeth are natural composites which are composed of nano hydroxyapatite crystals. These crystals are characteristically sized lesser than 100 nm and are set in lamellae. (Sanosh et al 2009) Hydroxyapatites are one of the extreme biocompatible materials and have resemblances like

the mineral constituents of teeth and bones. They display admirable properties like satisfactory biocompatibility with hard tissues and also with skin and muscle tissues. (Suchanek et al 1996) Hydroxyapatites are termed as bioactive because they have the ability of promoting bone growth with swift fixation competent of direct bonding osteogenesis and this property is termed as osteoconductive process. (Han et al 2007) Its bioactivity results in a direct bond with a bone tissue without any fibrous encapsulation. (Cheng et al 2001) Calcium phosphate exhibits adequate bioactivity and biocompatibility because of its chemical and crystallographic similarities to the mineral components of bones and teeth. The dissolution rate of hydroxyapatite in human body is around 15-30 um per year and they are not believed as health hazardous. (Suchanek et al 1998)One of the disadvantages which question the long term stability of HA is its solubility. They possess high solubility value but it can be controlled by its chemical composition and crystallinity. (Han et al 2007) They also exhibit low fracture toughness, strength, density and modulus of elasticity but again this can be controlled by combining with other materials which results in greater mechanical properties. (Tkalcec et al 2001 and Sygnatowicz et al 2009)

2.9.1.3 Processing methods of HA:

As discussed earlier hydroxyapatite are bioactive ceramic material which are found naturally in the mineral portion of human bones and teeth. This bioactive material can be used as a bony substitute in the human body to treat bony defects. (Norton et al 2006)

There are number of methods which have been introduced for the chemical production of hydroxyapatite. These processing methods have been tried to synthesized fine hydroxyapatite powder. There are several methods which include precipitation and co precipitation, pyrolysis of aerosols, sol-gel synthesis and few other routes. (Norton et al 2006)

Among all above mentioned methods, precipitation and sol gel method are the most commonly used for the homogeneous preparation. (Manjubala et al 2001)

<u>Precipitation and co-precipitation method:</u>

Many hydroxyapatite synthesis techniques have been developed during the 20th century and these includes various wet chemistry techniques. Among all, the two most commonly used techniques for preparation of hydroxyapatite powder are precipitation technique and sol-gel technique. (Feng et al 2005)

Precipitation of HA consists of two steps: nucleation and grain growth. In nucleation the small solution molecules randomly assemble resulting in production of aggregates which are not adequate for precipitation. Grain growth takes place when the nuclei become larger which eventually leads to suspension of very tiny particles and final size of the precipitate. Precipitation of HA involves concentrated calcium and phosphates simultaneously to favour high rate of nucleation. (Kong 2002 and Harris 1991) However, it is difficult to produce HA with small grain size via conventional precipitation as it does not possess required concentration of both calcium and phosphorus. (Norton et al 2006)

Co-Precipitation is one of the potential methods for the preparation of hydroxyapatite because of its simplicity of experimental operations; reduce operating temperature and production of pure products. In this process, solution consisting of diammonium hydrogen phosphate was retained at pH value of more than 12 by incorporation of ammonium hydroxide and placed in calcium nitrate solution with the same pH value. HA formation occurs during the mixing process. (Kong and Boey 2002)

In summary chemical precipitation from aqueous solution gives a flexible and cost-effective route. The final product can be used as surface coatings or to produce HA powders with controlled morphology. (Pang and Bao 2003)

<u>Sol-gel processing method:</u>

Precipitation technique possesses some demerits like requirement of high pH value to overcome the synthesis of a Ca-deficient HA and high sintering temperature for the formation of crystalline hydroxyapatite. (Feng at al 2005)

Sol-gel process which has been considered as the method of production for ceramic materials from past 150 years is gaining importance nowadays. Sol-Gel is the type of procedure which results in the synthesis of large inorganic polymers. A 'Sol' is a scattering of colloidal units and a 'Gel' is an organized polymeric network produced by the congregation of the sol. (Aurobind et al 2006)

The sol gel processing has been gaining popularity as one of the method to produce materials at low temperatures. This route involves the controlled and polycondensation of alkoxide followed by aging and drying under ambient temperature which in turns forms a gel. Thus the main steps of sol gel processing method are hydrolysis and condensation or polymerization. This method produces a material which could be really sensitive to pH. (Valenzuela et al 1996) The low temperature processing makes it promising to manufacture novel materials by uniting organic and inorganic components. Attention should be paid to drying stage if homogeneous and crack free materials are required. (Viitala et al 2002)

This method of processing offers some advantages over other methods which includes high product purity, homogenous composition and the main advantage is the preparation at low temperature in addition to applicability for surface coating. (Norton et al 2006) This method also allows you incorporate heat sensitive materials like active proteins in porous materials (Aurobind et al 2006) and makes it feasible to manufacture different morphologies like ; monoliths, films and fibres. (Viitala et al 2002)

Other advantages include:

- the formation of organic-inorganic hybrids

- can produce a high abrasion resistant material

- gives excellent optical transparency

- It does not need costly equipments

- Chemical composition and microstructure can be controlled easily. (Aurobind et al 2006)

2.9.1.4 Substitutes of Hydroxyapatite:

There are several chemical replacements which can be done within the HA lattice without resulting in any kind of adverse effects. Various elements like sodium, magnesium, potassium, fluoride. Chloride and carbonate are found in the chemical composition of the mineral content in the hard tissues. (Norton et al 2006)

Carbonated apatite:

Bone minerals is essentially a calcium phosphate apatite phase, it also has considerable concentration of other ions like carbonate, magnesium and sodium etc. Carbonate ions are the major secondary ions in the bone minerals and play an important role in the biological/chemical behaviour of bone mineral. (Gibson and Bonfield 2002)

The inclusion of carbonated ions in to hydroxyapatite structure plays a role in maintaining the phase purity of HA but increasing the carbonate content will lead to increase material solubility without affecting the crystallinity. (Gibson 2002 and Norton et al 2006)

Magnesium apatite:

The incorporation of magnesium ions plays an important role in the hydroxyapatite since they are one of the essential in developing artificial bone. Kim et al verified that in the beginning of calcification, the quantity of magnesium coupled with apatitic phase is much higher when compared with the later stages of calcification. It showed that magnesium plays an significant role in the qualitative changes of the bone matrix which establishes the bone fragility. Deficiency of magnesium

can result in cessation of bone growth which reflects the importance of this bivalent ions association with biological apatites. (Kim et al 2003)

It is also suggested that magnesium hinders apatite crystallization in solution and destabilizes the structure of HA while supports the thermal conversion into α or β-tricalcium phosphate. (Kim et al 2003)

Silicon apatite:

The importance of silicon has been studied by many researchers. It has been indicated that silicon is localized in active growth areas and it was generally noted that silicon is necessary for the growth of tissues such as bone, teeth and some invertebrate tissues. (Kim et al 2003)

Silicon is accepted to be important for growth and development of biological hard tissues. The inclusion of silicon into HA lattice therefore is desirable to enhance the bioactivity. (Norton et al 2006)

Fluoride apatite:

Fluoride is a necessary trace element present and required for normal skeletal and dental development. Studies also suggest that fluoride presence have a beneficial effect for bone formation in the body. For dental applications, it is well known for caries avoidance. (Manjubala 2001)

The mineral phase of tooth enamel consists of apatite containing 0.04 to 0.07 wt% of fluoride, which is around 95 to 97% of dry mass. Fluoride ions are present in saliva and are essential for normal dental and skeletal development. Studies suggested that fluoride intake of 1.5-4 mg per day considerably decreases the chance of dental caries. Fluorohydroxyapatite is more acid resistant than hydroxyapatite. (Jha et al 1997)

The translation of HA to fluoroapatite needs fluoride, which result in increased pH. Norton et al (2006) suggested that incorporation of fluoride ions to solutions containing calcium and phosphate ions encourages apatite formation while enhances the hydrolysis rate. (Norton et al 2006)

2.9.1.5 Fluoroapatite crystals and its properties:

Fluoride is a necessary trace element present and required for normal skeletal and dental development. Studies also suggest that fluoride presence have a beneficial effect for bone formation in the body. For dental applications, it is well known for caries prevention. (Manjubala 2001)

Fluoroapatite is a structural analogue of HA, was first determined by Naray-Szabo in which the fluoride ions substitute readily for hydroxyl groups in the structure of Ca_{10} $(PO_4)_6$ $(OH)_2$. Fluoroapatite are more resistant and thermodynamically more stable than HA. (Orlovskii et al 2002) Natural fluoroapatite occurs in variety of colours, makes column-like or table like crystals and it is also known in the form of granules or fibres. Fluoroapatite can also be found in bones and teeth. It possesses excellent properties and can be used as a substitute for dental enamel. Enamel is the hardest component in vertebrates and contains 97% by weight (92% by vol.) of inorganic material, 1% organic material and 2% water. (Mojumdar et al 2004)

Properties:

Fluoroapatite is a very important biomaterial and for its good quality is used for replacing dental enamel. They exhibit adequate properties for e.g. hardness of tooth is 3.6 GPA while the incorporation of fluoroapatite can raise the hardness value of the composite up to the required value depending upon the type of composite/material used (Mojumdar et al 2004) which makes it a suitable substitute for dental enamel.

The solubility of apatite is one of the significant factors for its application and fluoroapatite crystals possess low solubility when compared to HA. It is really important to have adequate solubility for a bioactive material. (Cheng et al 2001)

It also possesses adequate biocompatibility when compared to HA in terms of bone fixation and growth. Incorporation of fluoride ions can also improve the stability and integrity of HA. Most

importantly fluoroapatite crystals are recognized to encourage the mineralization and crystallization of calcium phosphate in the bone forming procedures. (Han et al 2007)

2.10 CHARACTERIZATION:

Characterization and analysis of the material is an essential part of any new invention in the material sciences. Characterization will be done in the modified silorane system using Fourier transform infrared and Raman spectroscopy.

(a) Chemical/Structural/Optical Characterization:

The investigation of materials and natural tissues by spectroscopy has had a key impact on the expansion of specific structure-property relationships in biomaterials. For biomedical applications, the composition and structure of natural tissue is of immense significance, as it is essential to modify the interactions of the implant material with biological tissue. Although many spectroscopic methods have been used to the structural characterization of materials and natural tissues, infrared spectroscopy seems to be exceptionally suitable for analyzing the complex chemical and morphological structures that make up natural tissues.

In this study, structure of the composites and silorane will be investigated using Fourier Transform Infrared (FTIR) and FT-Raman spectroscopy. Photo-acoustic sampling technique in conjunction with FTIR will be applied to look at the bulk material. This technique permits the analysis of neat materials without the requirement of any sample preparation. IR and Raman spectra are corresponding techniques to each other. They describe the molecular vibrational transitions of the atom of a compound. Therefore they are also known as vibrational spectroscopy. They are commonly used for the quantification as well as quality assessment of a material. (Gotter,Faubel et al 2010) These methods are also used to study the ionic substitution of a material and are widely used for the research of phosphate minerals. (Antonakos,Liarokapis et al.2007)

Fourier Transform Infrared Spectroscopy:

Fourier Transform Infrared (FTIR) Spectroscopy is a type of infrared (IR) spectroscopy. FTIR can be used to identify the chemical structure and measured as useful mean for identifying the functional groups. IR rays are passed through a sample which absorbs some rays and some rays are transmitted, which produce a unique wavelength for each molecular structure to form a spectrum. Chemical structure and bonds can be determined by interpreting this spectrum. The spectrum produced for each molecule is so unique that they are called "molecular fingerprint".

FTIR is the qualitative technique widely used for the identification of polymers.(Chakraborty, Bandyopadhyay et al. 2007) There are a few types of FTIR, like FTIR-ATR (Fourier transform infrared attenuated total reflection) spectroscopy, FTIR-PAS (Fourier transform infrared photo acoustic spectroscopy) and FTIR-RAS (Fourier transform infrared reflection-absorption) spectroscopy. FTIR-ART technique can provide information on the process of releasing drugs in formulations and become a usual protocol to study the drug-penetration and drug release in membranes from pharmaceutical products. FTIR-PAS is capable of providing chemical information of transparent to opaque samples. FTIR-RAS is used for the measurement of thin films; up to the depth of 50 μm can be reached by certain ranges by this technique. (Gotter,Faubel et al 2010)

Raman Spectroscopy:

Fourier transform Raman Spectroscopy is one of the spectroscopic techniques developed with FTIR for the confirmation of the molecules order. It is usually used to characterize the molecular structure of the compound. (Gotter,Faubel et al 2010) It characterizes the vibrational, rotational and other low frequencies in a compound.

The phenomenon of Raman spectroscopy was invented in 1928 by Sir Chandrasekhra Venkata Raman. He used sunlight as the light source and a telescope as a collector, detected the sample with his eyes. Gradual improvements were taken place in the various components to improve the crude

instrumentation. Those developments results in the present form of Modern Raman instrument. (Navarra 2008)

Components:

Commercially available Raman spectrometer consists of following components: (Navarra 2008)

- A continuous light source

- Sample illumination and collection system

- Wavelength Selector

- Detection and computer processing system

The structure, dynamics and environment of polymeric materials can be easily characterized by Raman spectroscopy. The method is highly sensitive to polymeric structure and allows obtaining detailed information on various materials. (Navarra 2008)

(b) Mechanical Characterisation:

Strength will be measured at a constant strain rate. The stress-strain behaviour of the modified and unmodified samples will be compared with those of controls (need to find a control here) to assess the mechanical effectiveness of the HA incorporated material which will provide information about the effect of filler on matrix.

Compressive strength and Flexural Strength:

Fracture of the dental restoration due to fatigue is the main reason for the failure of restoration. 3M ESPE conducted many tests and compared the silorane samples with different methacrylate samples. The silorane filling material was found to have very good flexural fatigue limit even under different salivary conditions, much better than other methacrylate composites (Professor Braem, University of Antwerp). These tests were done on 10,000 cycles on a temperature of 35 degrees, on a three point bending test with a frequency of 2 Hertz.

Any restorative material which has a high compressive and flexural strength, when used in the restorations of the posterior teeth prevents the tooth from fracture and stabilizes them. The compressive and the flexural strengths of the silorane restorative material were found to be above the ISO range which is around 80 MPa. The compressive strength was measured by applying a continuous force on the material of the measurement of 3x3x5 mm until the material fractured. The flexural strength was measured again by the three point bending test and again the force was applied till the material fractured. (3M ESPE internal data)

2.10.1 Basis and interpretation of Spectroscopy:

In recent decades the traditional techniques used for assessment of bone components includes the use of light microscopy, electron microscopy, x-ray diffraction and wet chemical analysis. These applications have some limitation which includes the certain preparation processing that may change its structure and composition. This limitation raises question for reliability of results and conclusions obtained from the above techniques. The ideal analytical method is the one which should involve minimal sample preparation and does not alter the structure of the sample. (Rehman and Smith 1995) The vibrational spectroscopic techniques, like FTIR are reasonably simple, reproducible, non invasive and requires a very small size of material. FTIR peaks are relatively narrow and in many instances are associated with the vibration of a particular chemical bond (or a single functional group) in the molecule. (Zanyar et al 2008)

In presents days the systems of Fourier transform infrared (FTIR) and FT Raman spectroscopy are becoming more applicable as analytical ways for biomedical applications. Few advantages are mentioned below:

a) In these techniques the requirement for tissue/sample preparation is minimal. (Very small amount of the tissue like micrograms even nano-grams can be successfully analyzed)

b) Molecular level information can be obtained from the both techniques, which allows us to investigate or understand the functional groups, bond types and molecular conformation. (Rehman and Smith 1995) Spectral bands in Raman spectroscopy are molecule-specific and give direct information about the biochemical composition. (Rehman et al 2007)

c) This versatile technique allows us to examine samples of complex and uneven shapes such as human skull, femur and mandible without any chemical pre-treatment. (Kirchner et al 1997)

While Raman spectroscopy is a vibrational spectroscopic technique which was first describe by Nobel Prize winner Raman in 1928. Raman spectra are a scheme of scattered intensity as a function energy difference of photons. Results are obtained by positioning a monochromatic laser beam at a minimally prepared sample. Spectra produced are characterized by shifts in wave numbers from the incident frequency. This frequency variation is measured by the machines detector and is represented as 1/cm. Raman peaks are spectrally slender and are usually represented with the vibration of a particular chemical in the molecule. (Zanyar et al 2007)

Characterization methods of Fourier transform infrared (FTIR) and Raman spectroscopy are progressively becoming the major analytical method for biomedical applications, particularly when are used collectively for analysis of surface reactions. Its minimal sample preparation in combination with high quality structural and compositional detail makes them very effective methods for surface analysis. (Rehman et al 1999)

The increasing importance of FTIR and Raman's spectroscopy can be estimated by their consideration as one of emerging biophotonic tool for recognition of different diseases. Significant progress has been made within the past decade. As we understand the different diagnostic tools like excision biopsy requires excessive tissue removal and it also increase the pathology cost and biopsy-associated risks. Therefore the need to overcome these demerits was fulfilled by these spectroscopic techniques. Few advantages of these techniques includes low cost, high molecular specificity, avoid

unnecessary tissue excision and quick results. They can be used as a diagnostic tool for different tumours, atherosclerosis, kidney stones and gall stones etc. (Krafft et al 2009)

Even though Raman spectroscopy and FTIR are appropriate methods, with their relevant spectra corresponds to one another, there are few distinctions among these two methods. The most significant difference between these methods is the kind of samples that can be investigated by the methods. FTIR principally deals with non-aqueous samples where as Raman is efficient with both aqueous and non-aqueous samples. This is because of strong absorption bands of water which creates problem for FTIR spectroscopy. Also Raman can perform confocal imaging and requires minimal sample preparation while FTIR comparatively requires more sample preparation and does not have the ability of confocal imaging. Significantly, FTIR spectroscopy is due to changes in dipole moment during molecular, whereas Raman spectroscopy involves a change in polarizability. There is also an existing difference in their resolution. (Zanyar et al 2008)

Spectroscopic analysis of HA are aimed at clarifying or understanding the mechanical and pharmacokinetic properties of HA. Before the introduction of FT Raman spectroscopy, the investigation of HA was hindered by a strong fluorescence, which was caused by organic matrix of bone mainly type I collagen. Fluorescence was the prime difficulty associated with natural materials since the excitation laser operates in the visible region of the spectrum. However, introduction of FT Raman spectroscopy offers fluorescence free Raman spectra with minimal or no sample preparation. (Dippel et al 1998 and Rehman et al 1995)

When infrared radiation is shown, absorption of specific wave length by sample takes place which marks in the dipole movement of sample. Most of the materials are infrared (IR) active except numerous diatomic molecules like Oxygen, Nitrogen and Chloride because of their zero dipole change in the vibration and rotation of theses molecules. (Paula et al 2009)

A material can vibrate in different patterns. Every vibration is termed as vibrational mode. These involve stretching, bending, twisting etc but generally there are two primary modes of vibration, which are Stretching and Bending. The change in dipole movement determines if a compound is IR active or inactive. (Furuse 2006)

V_1, V_2 etc are different vibrational modes or states of spectroscopy and indicates the energy state in a molecule. They are interpreted on the spectrum as stretching and bending modes of molecules, and represent the pattern of absorption. (Dippel et al 1998) Molecular bonds with permanent dipoles results in strong peaks. Most common range for FTIR spectra is 400-4000 cm^{-1} as the absorption radiation of most organic compounds and inorganic lie within this limit. If there is any inclusion of impurity in the sample then it will produce complex spectra. (Paula et al 2009)

As Raman functions by estimating the interactions of light with sample's chemical bond. Therefore, in order for laser to show a Raman effect it must have a change in its molecular polarizability. If there is change, the molecule will be termed as Raman active and increase in electron deformation will decide the Raman scattering intensity. (Zanyar et al 2007) Raman active bonds in the molecule cause the emission of diverse wavelength of light. The number of possible vibrations for a given molecule is determining the number of atoms present. Molecules with double, triple bonds and aromatic structure produce strong Raman signals. In short increase in bond strength leads to corresponding frequency increase. (Paula et al 2009)

CHAPTER 3

MATERIALS AND METHOD

3.1 MATERIALS AND METHODS:

In this chapter we will discuss about the materials and methods used for the preparation of nano hydroxyapatite and fluoroapatite powder. Later we will discuss the characterization of synthesized HA/FA incorporated silorane composite.

Hydroxyapatite and fluoroapatite crystals were prepared by sol gel technique. This technique involves the use of dried oven for ageing and heat treatment in furnace as we discuss in the previous chapter. The reagents used for the preparation of HA were calcium and phosphate precursors. Ethanol was used as a solvent in the preparatory method. (Feng et al 2004)

3.1.1 Materials For the preparation of HA:

Calcium Precursor:

Calcium nitrate tetra hydrate [Ca $(NO_3)_2.4H_2O$] (Grade = puriss .p.a ACS ≥ 99%) from Sigma Aldrich, UK was used a calcium precursor with ethanol as a solvent.

Phosphate Precursor:

Phosphorus Pentoxide ($P_2 O_5$) (Grade= puriss p.a ACS Reagent ≥ 98%) received from Sigma, Aldrich UK was used as phosphate precursor and ethanol from Sigma Aldrich UK was used as solvent.

Ammonium Buffer Solution:

Ammonium buffer solution (ph=10) was used for pH adjustment as supplied by Sigma Aldrich UK.

Fluoride precursor:

Ammonium fluoride (ACS Reagent ≥ 98%) was purchased from Sigma Aldrich UK and used as a fluoride precursor with ethanol used as a solvent.

3.1.2 Materials for Silorane solubility:

As we know silorane is a high molecular weight polymer and therefore we required high purity of solvents for dissolving this high mol. weight polymer. Three solvents were identified as the possible ideal solvents and were tried to obtain the desired solubility. These three were:

N-N Dimethylformamide (DMF) (Anhydrous ≥ 99.8%)

Tetra Hydro furan (THF) (Anhydrous ≥ 99.9%)

Acetone (ACS Reagent ≥ 99.5%)

All of the three showed adequate solubility for the silorane but in this project we carried our experiment with THF.
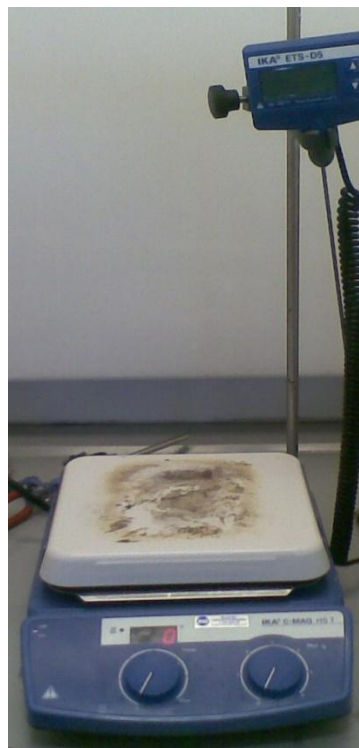
Figure 3.1: IKA C-MAG HS 7 Stirrer

3.1.3 Experimental Equipment:

Glass wares used in this experiment were washed with neutral detergents, warm water and then were placed in oven for drying at 130°C. During the project, all the stirring and heating was carried out by using IKA C-MAG HS 7 stirrer. Magnetic stirrer bars were used. PH meter HI98127 was used purchased from Hanna industries. (It is a water proof pH tester with replaceable electrodes)

Figure 3.2: PH Meter HI98127

Sol Gel method:

Sol gel method was employed for the preparation of nano hydroxyapatite and fluoroapatite. This method involves the use of oven drying and heat treatment which results in the production of homogenous and highly crystalline particles.

Fig 3.3: Schematic flow chart of sol gel method

Phosphate Precursor Solvent + Calcium precursor & Solvent

↓

Mixing and Gelation
(60°C for 24 Hours
Ammonia Buffer for pH maintenance)

↓

Ageing and Drying
(80°C for 2 Hours)

↓

Heat Treatment
(At 800°C for 48 hours)

↓

Ball Milling Treatment
(Grinding for 12 hours)

↓

Nano Hydroxyapatite and Fluoroapatite
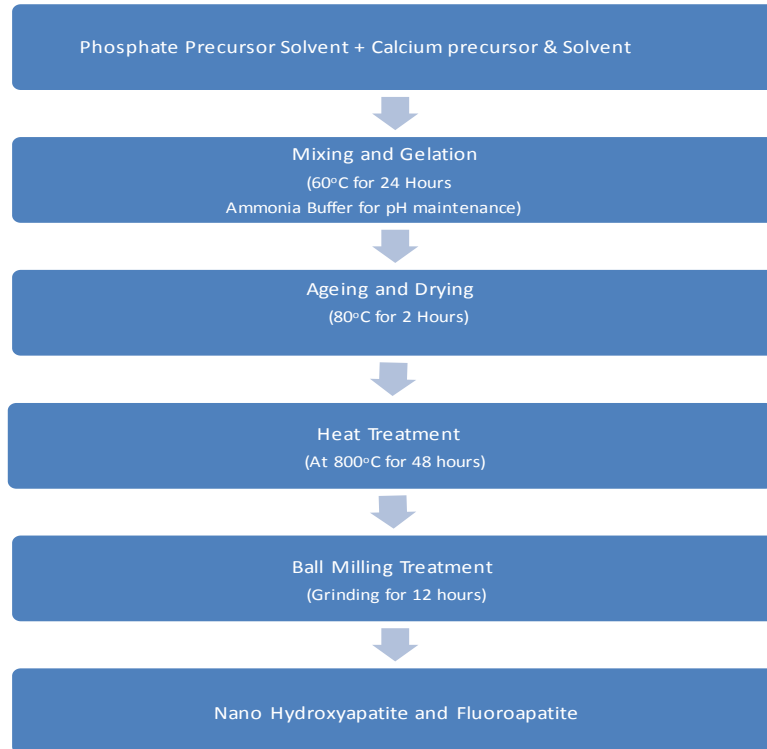
Figure 3.4: Hot Air Oven

3.2 HYDROXYAPATITE PREPARATION:

As Wang et al suggested, 1M of calcium nitrate tetra hydrate and Phosphorus pentoxide (1.67M) were measured before mixing and desired ratio of 1.67 was mixed in 50 ml of ethanol. After that both the precursors were mixed and solution was stirred at 60 ^{o}C. Ammonia buffer solution was added drop wise to maintain the pH value and pH meter was used to monitor the pH regularly.

3.3 CHARACTERIZATION:

Characterization and analysis of the material is an essential part of any new invention in the material sciences. Characterization was done in the modified silorane system using Fourier transform infrared and Raman spectroscopy.

Figure 3.5: Raman Spectroscopy Apparatus

(a) Chemical/Structural Characterization:

The chemical and structural information for these materials will be studied using conventional techniques to assess materials.

In this study, structure of the composites and silorane will be inspected using Fourier Transform Infrared (FTIR) and FT-Raman spectroscopy. Photo-acoustic sampling technique in combination with FTIR will be applied to check the bulk material. This method permits the analysis of neat materials without the want of any sample preparation. Surface properties will be assessed by using Attenuated Total Reflectance (ATR)-FTIR spectroscopy.

Figure 3.6: Fourier Transform Infra Red (FTIR) Apparatus

(b) Mechanical Characterisation:

Strength and ductility will be measured via tensile tests at a constant strain rate. The stress-strain behaviour of the modified and unmodified samples will be compared with those of controls (need to find a control here) to assess the mechanical effectiveness of the HA incorporated material which will provide information about the effect of filler on matrix.

3.4 SAMPLE PREPARATION AND TECHNIQUE:

Commercial Silorane were dissolved in THF or deuterated chloroform (Eick et al 2005 in their experiment used deuterated chloroform and THF for solvation of silorane monomers. Deuterated chloroform was specifically used for dissolving silorane before NMR analysis).For the preparation of nano HA and FA, appropriate amount of calcium nitrate tetrahydrate, sodium fluoride and

phosphoric pentoxide were required. While for FA synthesis ammonium fluoride was added as the source of fluoride ions. These products were dissolved in absolute ethanol. Then solution was mixed at a particular molar ratio. (Ca: P: F = 3:5:1) Then the steps of gelation, aging, drying, sintering and crushing were followed for preparation of nano HA and FA. The prepared product obtained nominal composition in terms of Ca/P ratio of 1.66 or 1.67.

Question arises about how much the amount of HA and FA wt % should be incorporated in silorane system. Gu et al suggested GICs containing 4 wt % HA particles exhibited enhanced mechanical properties. Moshaverinia et al reported that 5 wt % of either HA or FA modified GICs showed improve bonding strength and mechanical properties. While in case of PMMA, (polymethylmethacrylate) a self curing acrylic polymer with no adhesive properties, addition of up to 15 wt% have been observed to increase the tensile and compressive strengths but for improving fracture toughness it requires addition of up to 40 wt %. Tihan et al suggested that a percent more than 15 HA is not a benefit for mechanical properties of the composites. In the recent study conducted by A.S.Khan et al showed that if the concentration of nHA is increased to 20wt %, the bond strength of bioactive restorative polyurethane based composite improves as well.

Therefore in this experiment we used the different concentrations of nHA and nFA. Suggested concentrations were 20, 30, 40 and 50 wt%.

As we mention earlier that experiment to be carried out in artificial salivary medium. Therefore we have explained the method required for preparation. Other testing methods are also discussed below:

3.4.1 BIOACTIVITY TEST:

It is also acknowledged that human body environment is very aggressive, for that explanation every new biomaterial should be assessed to confirm the influence of the human body environment on its

properties. In the prevalent chemical and physical conditions of the human body, the newly placed biomaterial can drop their strength and may corrode or degrade.

Depending on application like placement of an osteoconductive material, the degradation through physiological fluids can be undesirable. Keeping this in mind a bioactivity test for evaluation of our modified material should be done in contact with simulated body fluid (SBF) with an ion concentration almost equal to that of human blood plasma and at pH of around 7.4. (Gluszko and Fray 2004)

SBF is a salt mixture with an ion concentration almost identical to that of human body fluids. It will be prepared by dissolving salts (NaCl, NaHCO$_3$, MgCl$_2$.6H$_2$O, CaCl$_2$, Na$_2$SO$_4$, KCl, and PO$^-_4$) into water, buffered by tris-hydroxymethyl aminomethane and hydrochloric acid (HCl) at pH 7.4 at room temperature. (Gluszko and Fray 2004)

3.4.2 SIMULATED BODY FLUID FORMATION:

Kokubo et al 1990 proposed a method for the formation of serum body fluid which was followed in this experiment. The formed simulated body fluid was like the extracellular fluid of the human body. This fluid was used for the testing the bioactivity of the materials which would suggest their behaviour in the human body. (Kokubo et al. 1990)

Initially for the formation of SBF (Simulated body fluid), all the glassware like the beakers, bottles and flasks were cleaned properly with diluted Hydrochloric acid solution, sterilized and washed with ultra pure water thoroughly. (Kokubo et al. 1990) Thereafter the glass wares were immersed in the diluted hydrochloric acid solution for 4 hours and then washed thoroughly with tap water. The utensils were then immersed in the sterilizing liquid for the overnight and were washed with ultra pure water the next morning. The glass wares were then covered with a foil paper and then placed in the dried oven at around 45°C. (Kokubo et al. 1990)

750 ml of ultra clean water was taken in a polyethylene beaker of 1000 ml. This beaker was kept on the magnetic stirrer at 36.5°C. Care was taken ensuring the clean environment to avoid dust particles getting into the solution. Thereafter 7.996 gm of Sodium Chloride NaCl (Sigma Aldrich) was added to the solution. Then 0.350 gm of Sodium bicarbonate $NaHCO_3$ (Sigma Aldrich) was added followed by 0.224 gm of Potassium Chloride KCl (Sigma Aldrich). Subsequently 0.228 gm of Potassium hydrogen phosphate $K_2HPO_4.3H_2O$ (Sigma Aldrich) was added followed by 0.305 gm of Magnesium Chloride $MgCl_2.6H_2O$ (Sigma Aldrich). After that 87.3 ml of hydrochloric acid was diluted to 1000 ml and 40 cm^3 was added into the solution. Immediately after that 0.278 gm of Calcium Chloride $CaCl_2$ (Sigma Aldrich) was added which was then followed by the addition of 0.071 gm of Sodium Sulphate Na_2SO_4 (Sigma Aldrich). After this the pH meter (Hanna) was dipped into the solution and checked. The pH was maintained at 7.4 by periodic addition of Tris-hydroxymethyl aminomethane $(CH_2OH)_3 CNH_2$. All this process was done with continuous stirring and maintaining the temperature at 36.5°C. The Ultra pure water was added to the beaker till it became 1000 ml and then it was transferred into the polyethylene flask, which was maintained at the room temperature of 20°C and ultra pure water was added, to maintain the level of 1000 ml. Finally the solution was kept in a refrigerator at 5-10°C. (Kokubo et al. 1990)

In short for chemical characterization silorane was dissolved in the THF, Hydroxyapatite and Fluoroapatite has been added into Silorane in 5, 10, 40, 50 and 60% ratio by weight. Initially Silorane was dissolved completely in the THF, obtained hydroxyapatite and fluoroapatite powder was then added in the dissolved solution by weight in required ratios. Resultant material is then placed in the petri dishes and left overnight for the evaporation of THF. The obtained material is then analysed for chemical characterization by FTIR and Raman Spectroscopy.

3.5 RAMAN AND FTIR SPECTROSCOPY:

Nicolet Amelga XR dispersive Raman spectrophotometer has been used for Raman spectra. Samples were placed on a glass slide making a thin film and were obtained in the range of 4000 – 400 cm-1, averaging 128 scans at the exposure time of 1 second, 785nm laser and the objective lens was 10x.

FTIR spectra were obtained by using a Nicolet 8700 FTIR spectrometer (Thermo Electron Corporation, UK) in combination with a photo acoustic sampling (PAS) cell. Samples were placed in the sample holder in powder form and the sampling chamber was cleaned with dry helium. Spectra were obtained in the range of 4000 – 400 cm-1 (mid infrared region) averaging 128 scans.

3.6 MECHANICAL TESTING:

For this research 4 different types of mechanical testing were to be done:
- Compressive strength
- Flexural Strength
- Flexural fatigue
- Fracture toughness

Compressive Strength:
Modified Silorane:

The specimen of size of 25 mm x 5 mm x 3 mm which were obtained from the Teflon mould were taken out from the SBF (simulated body fluid) bottle after 5 days and placed on the base of the Hounsfield universal testing machine. Load was moved down with a cross head speed of 1 mm per minute. The load was applied at the centre of the specimen and the load was increased until the specimen broke. This load was noted and recorded for the comparative studies with the original silorane and filtek supreme composite.

The same method was followed for the other two test days of 8 days and 11 days.

After the completion of test the compressive strength of the specimen was calculated from the formula of the compressive strength which is (Ihtesham et al. 2008):

$$CS = 4P/\pi t^2$$

CS: is the compressive strength

P: is the load applied in newton

T: thickness of the specimen

For these experiments the each batch (different percentages of HA and FAs) of the material had 5 samples each. Thus 5 values were taken and the average was taken to be the final compressive strength.

Commercial Silorane:

Commercially available silorane and commercially available Filtek Supreme XT were taken separately on mixing papers. 2 gm of each of the material were taken and place on it. After that 2 drops of THF (Tetra hydro furan) were placed on it and they were mixed with the spatula until they were doughy like. The doughy like material was taken and place in the Teflon moulds. They were then light cured in increments and then were left for a while. After 30 minutes the material were freed from the mould and placed in their respective bottles of 5 days, 8 days and 11 days containing simulated body fluids (SBF).

On the 5th day the materials were taken out and placed on the base of the Hounsfield universal testing machine and the force was measured until the specimen fractured. These values were noted down and compared with the other modified silorane which was the basis of this research.

The same process was followed for the 8th days test and 11th days test and the values were noted down.

CHAPTER 4

RESULTS

RESULTS

4.1 HYDROXYAPATITE AND FLUOROAPATITE
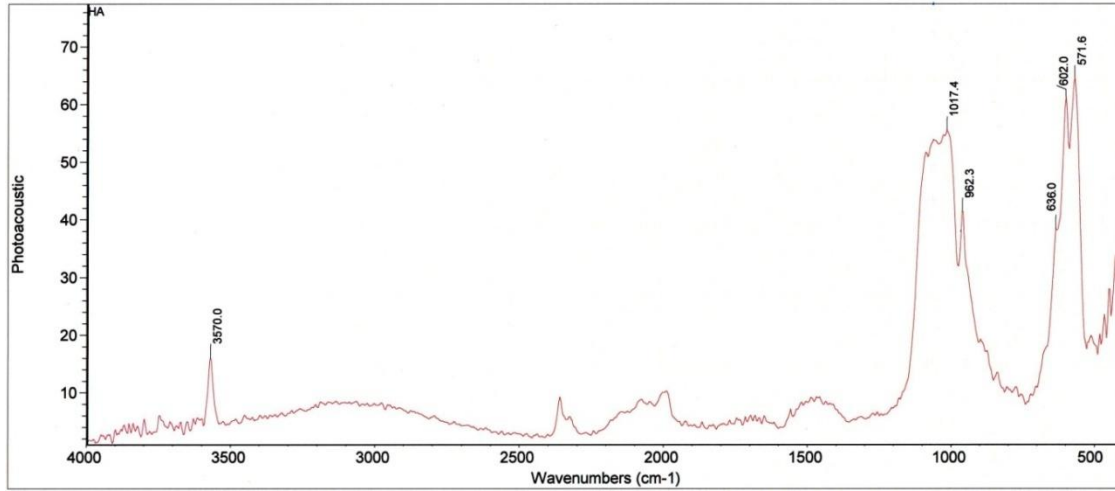
Figure 4.1: FTIR Spectrum of Hydroxyapatite

Initially the synthesized hydroxyapatite and fluoroapatite powders have been examined using the FTIR to characterize the purity of the obtained HA and FA samples. The characteristic peaks of hydroxyl, carbonate and phosphate groups were present in the spectrum. Hydroxyl band is observed at 3570 and 636 cm^{-1}, showing the stretching and liberation mode respectively. Carbonate band is

Figure 4.2: FTIR Spectrum of Fluoroapatite

being observed in 1420 cm^{-1} and phosphate bands can be seen at 1017, 962, 602 and 571 cm^{-1}. The band at 602 and 571 cm^{-1} are due to phosphate bending vibrations and the bands at 1017 and 962 cm^{-1} are phosphate stretching vibration bands. The bands pres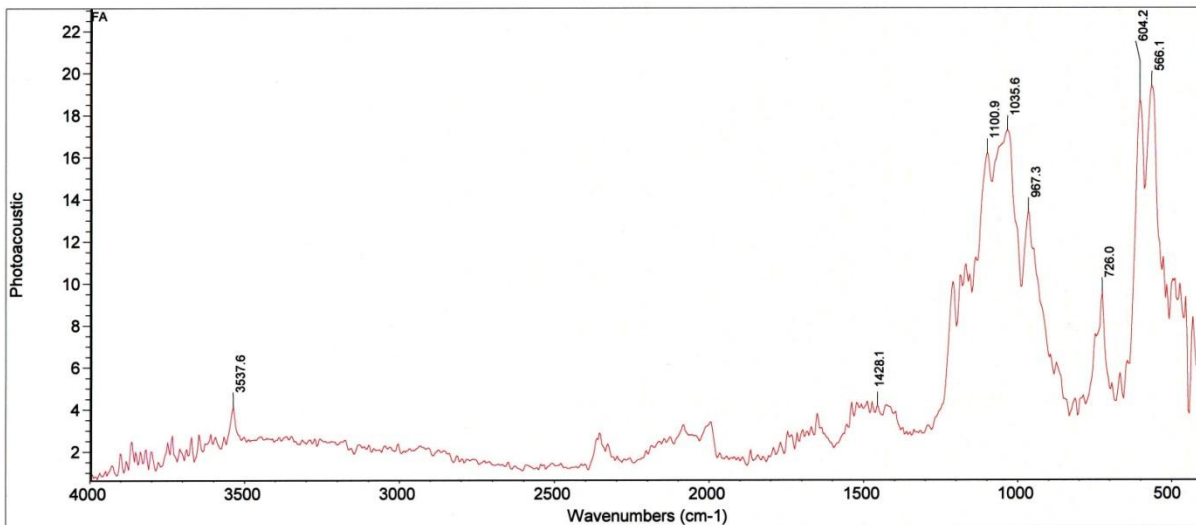ent in the region of 1500 – 1400 cm^{-1} are the carbonate bands, which suggest the presence of carbonate functional group. They can originate from the CO_2 present in the air and can enter in the hydroxyapatite structure. The sample of FA shows the clear reduction in the hydroxyl peak and disappearance of phosphate peak at 636 cm^{-1}, which is the confirmation of FA formulation. The broader phosphate peak in the region of 950 – 1100 cm^{-1} shows the degree of crystallinity which is increased due to the process of sintering. (Rehman, Moshaverinia et al. 2008; Salehi and Fathi 2010) In Raman spectrum of Hydroxyapatite phosphate group can be seen at 963 cm^{-1}, which is used for quantitative analysis. Peaks at 1077 and 1044 are the ν_3 and at 963 cm^{-1} is ν_1 of P – O. The presence of peak at 603 cm^{-1} indicates the ν_4 of the O – P – O. (Kontoyannis, Bouropoulos et al. 1997; Rehman, Khan et al. 2008)
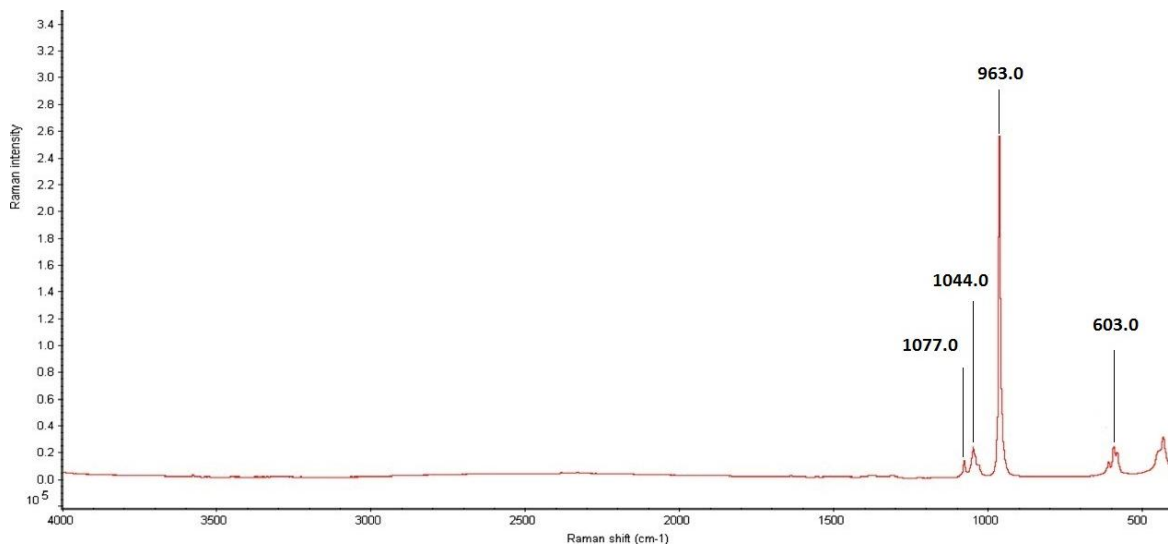
Figure 4.3: Raman Spectrum of Hydroxyapatite

Figure 4.4 on next page shows the Raman spectrum of fluoroapatite, in which the peaks at 1046 and 967 cm^{-1} shows the ν3 and ν1 stretch of phosphate respectively. The peaks at 591 and 437 cm^{-1} indicates the ν4 and ν2 bends respectively. (Williams and Knittle 1996)
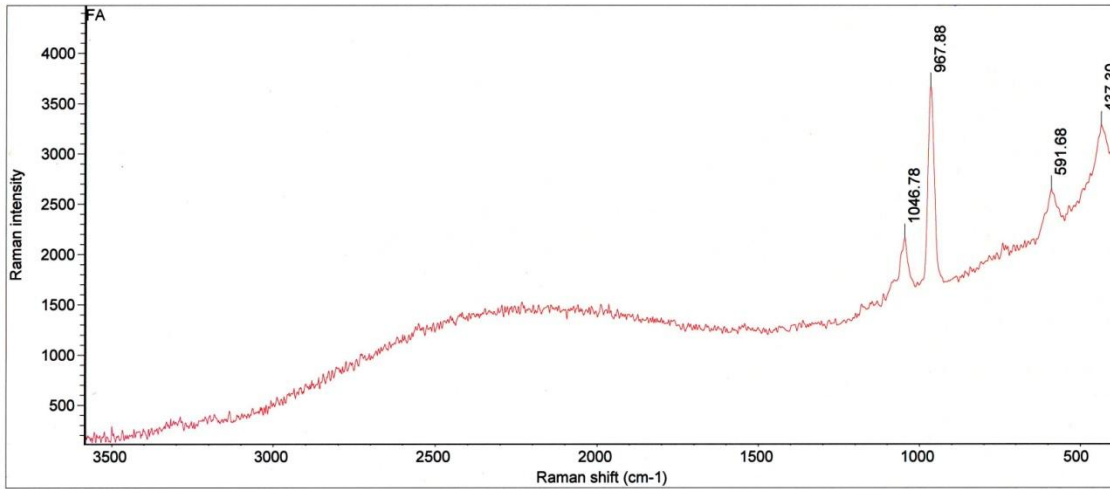
Figure 4.4: Raman Spectrum of Fluoroapatite

4.2 SILORANE
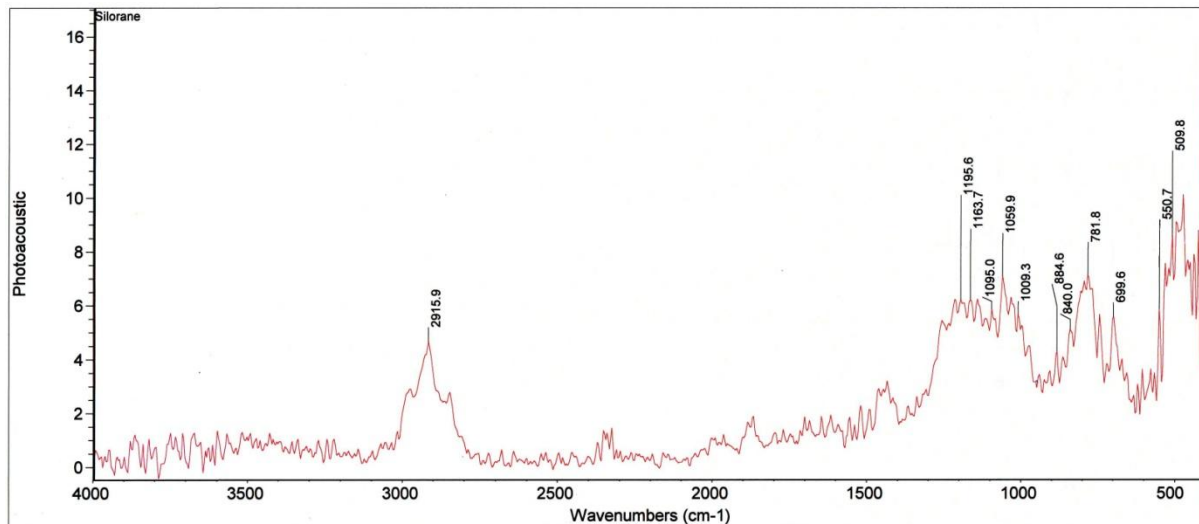
Figure 4.5: FTIR of Silorane

Figure 4.5 shows the FTIR spectrum of Silorane. The fine structure in 884 – 886 cm^{-1} region shows some primary reference bands in the spectrum of Silorane and shows the absorption of primary oxirane bands. (Chappelow, Pinzino et al. 2007) The peak at 2915 cm^{-1} indicated the presence of CH group. Different Siloxane bands can be seen in the region of 770 – 3000 cm^{-1}. Peaks at 781, 848,

1059, 1095, 1195, 1259 and 2915 cm^{-1} indicates the ν SiCH$_3$, (SiOSi, CO) and CH$_3$ respectively. (Britcher, Kehoe et al. 1995)
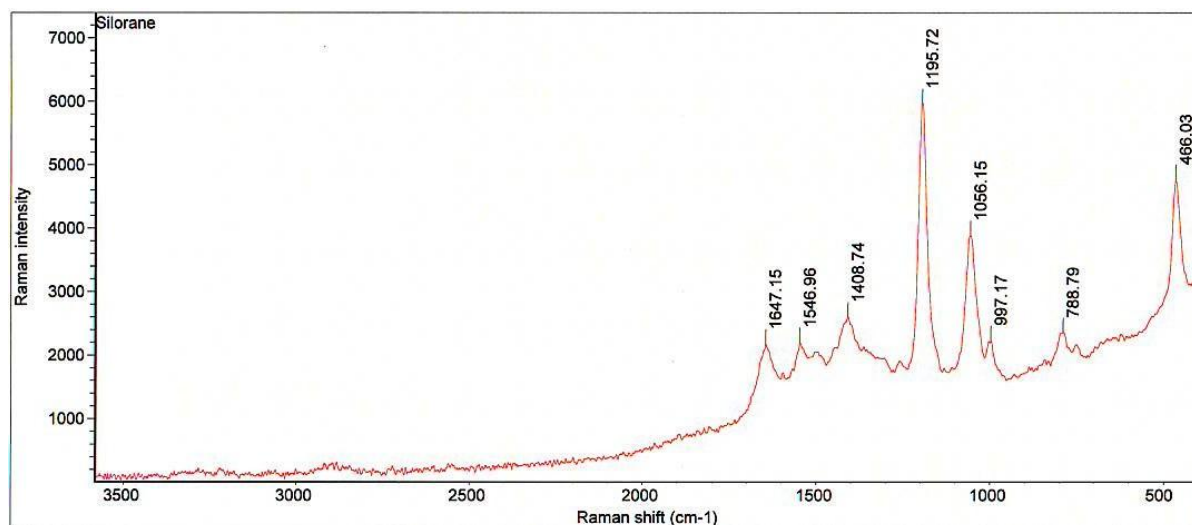
Figure 4.6: Raman Spectrum of Silorane

Figure 4.6 shows the Raman spectrum of Silorane confirming the presence of ν phase of Siloxane. Strongest infrared absorption of siloxane is a sharp bend occurring at 1056 cm^{-1}. The peak at 1640 cm^{-1} shows the presence of C = C group. The peak at 1195 and 466 cm^{-1} indicates the presence of O-Si-O. (Gnyba, Keranen et al. 2002; Navarra 2008)

4.3 SOLVATION OF SILORANE:

Solvation of Silorane was done in Acetone, DMF and THF. After the evaporation of the solvents, samples were analysed by FTIR spectroscopy. FTIR spectrum of Silorane dissolved in THF shows the close resemblance to the Silorane spectrum, showing no chemical changes. Rest of the experiment was performed using THF as a solvent.
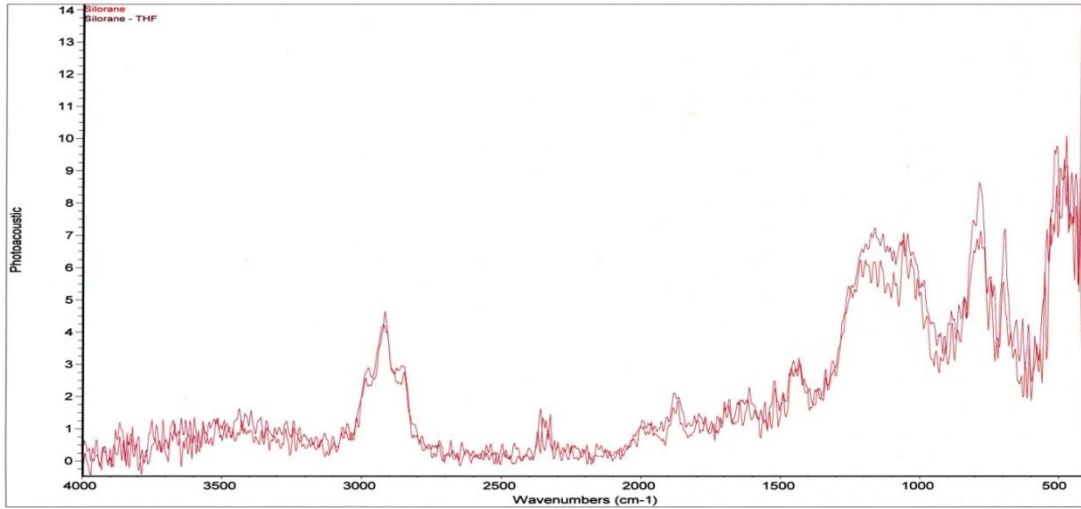
Figure 4.7: FTIR spectrum of Silorane compared with Silorane after solvation in THF

4.4 SILORANE INCORPORATED WITH HYDROXYAPATITE:

4.4.1 FTIR SPECTROSCOPY

Hydroxyapatite was incorporated in Silorane in the ratio of 5, 10 40, 50 and 60% by weight. FTIR

spectrum of Silorane incorporated with different percentages is shown in figure. The spectrum in figure
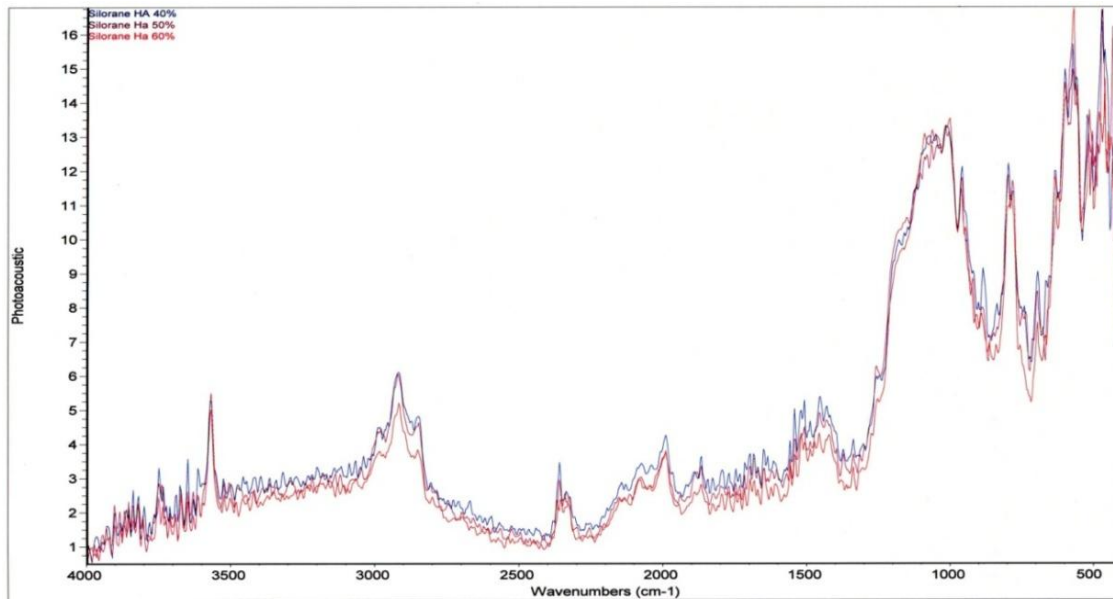
Figure 4.8: FTIR spectrum of Hydroxyapatite incorporated Silorane by 40, 50 and 60% by wt

4.8 and 4.9 clearly indicates the presence of hydroxyapatite in the structure of Silorane. The sample shows broader CH_3 bands with a higher intensity. All the samples show the presence of OH bands. Bands of Phosphate group of HA and Silorane appears in the same spectral region as presented in Figure 4.7.
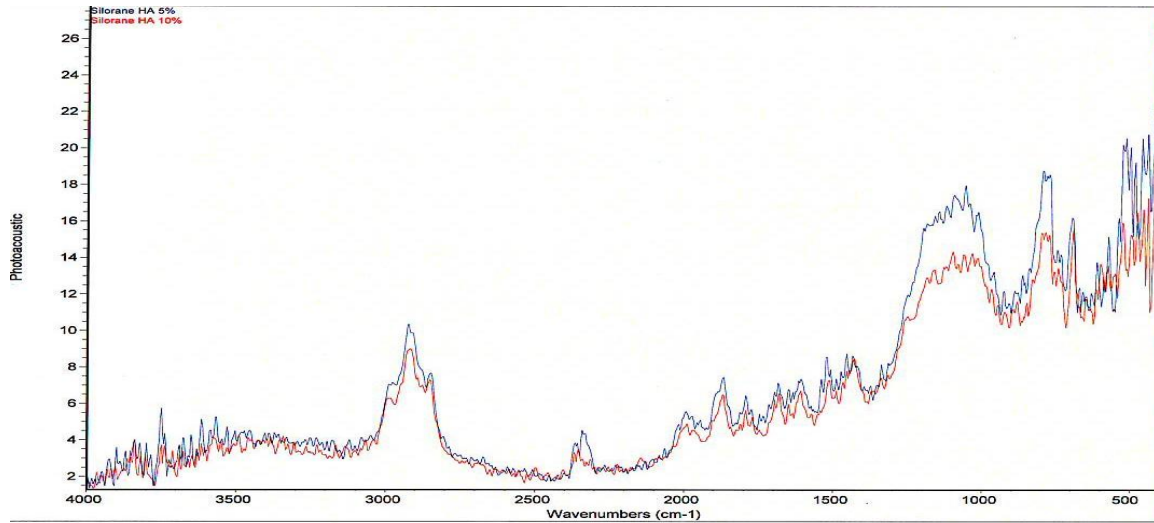
Figure 4.9: FTIR spectrum of Hydroxyapatite incorporated in Silorane by 5 and 10% wt ratio

4.4.2 RAMAN SPECTROSCOPY
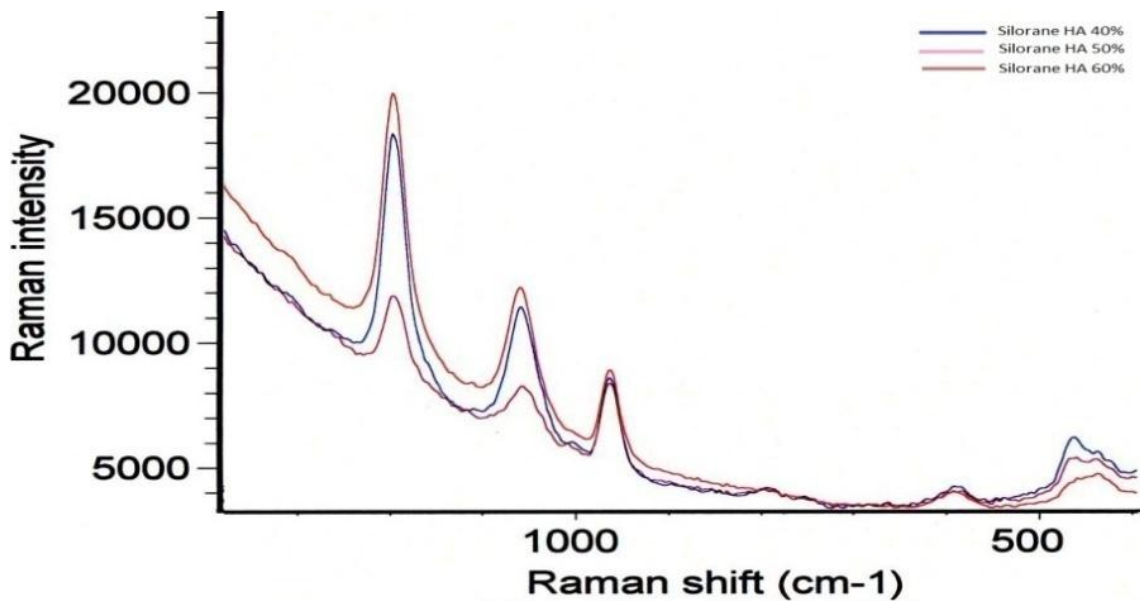
Figure 4.10: Raman Spectrum of Silorane incorporated with HA, 40 50 and 60% by wt
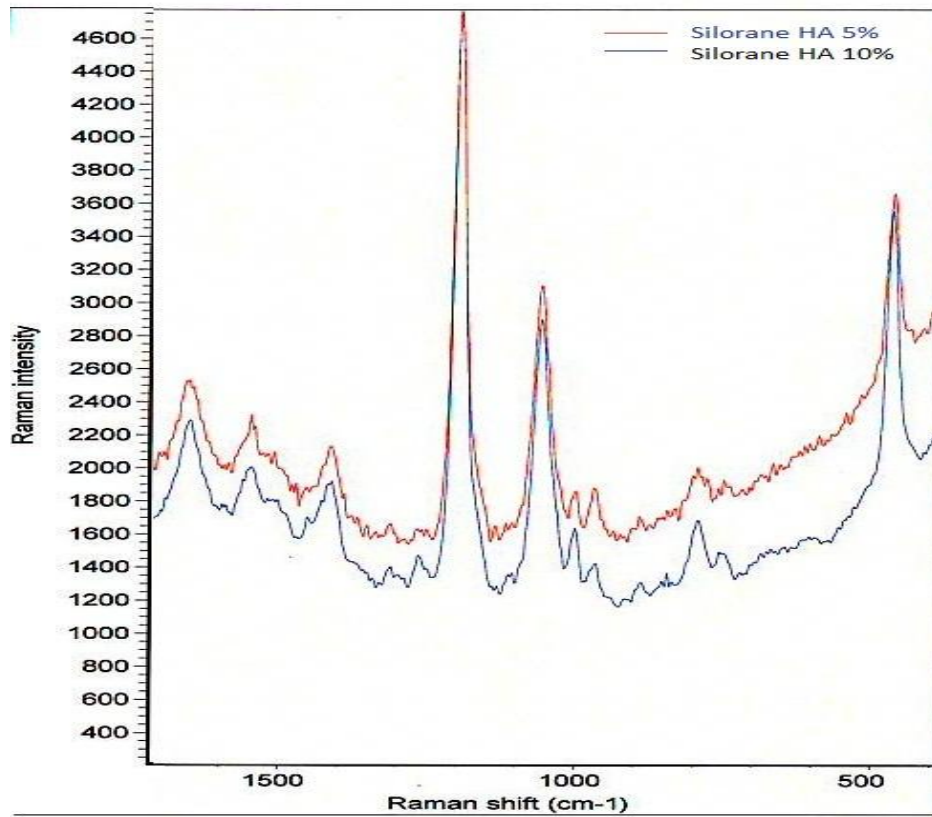
Figure4.11: Raman Spectrum of Silorane incorporated with HA 5 and 10%

Figure 4.10 and 4.11 shows the presence of O-Si-O at around 1200 cm^{-1} and the peak of phosphate group of hydroxyapatite can be seen at 963 cm^{-1} but with lower intensity.

4.5 SILORANE INCORPORATED WITH FLUOROAPATITE

4.5.1 FTIR SPECTROSCOPY
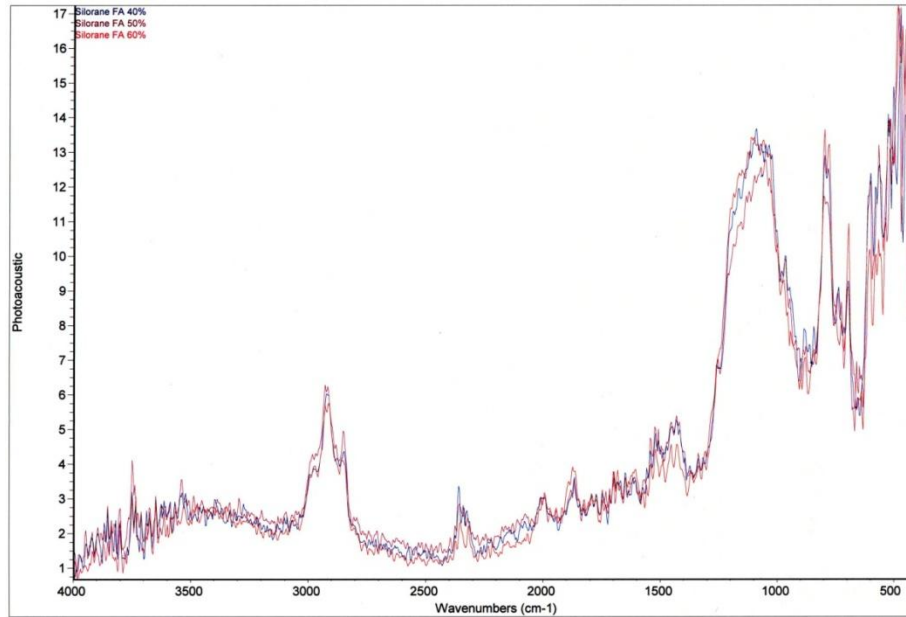
Figure 4.12: FTIR Spectrum of Fluoroapatite incorporated Silorane40, 50 and 60% by wt
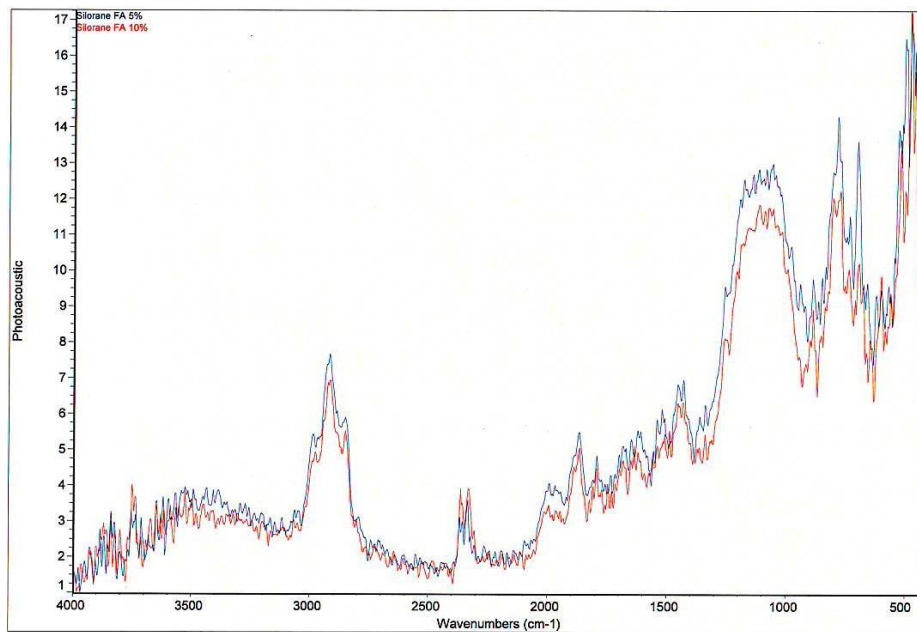
Figure 4.13: FTIR Spectrum of Fluoroapatite incorporated Silorane5 and 10%

Figure 4.12 and 4.13 shows the FTIR spectrum of Silorane incorporated with 5, 10, 40, 50 and 60% Fluoroapatite. There is no OH peak as it was in hydroxyapatite. The CH_3 peak at 2915 cm^{-1} is well defined. The phosphate and O-Si-O peak appears in the same region of around 1000 – 1200 cm^{-1}.

4.5.2 RAMAN SPECTROSCOPY
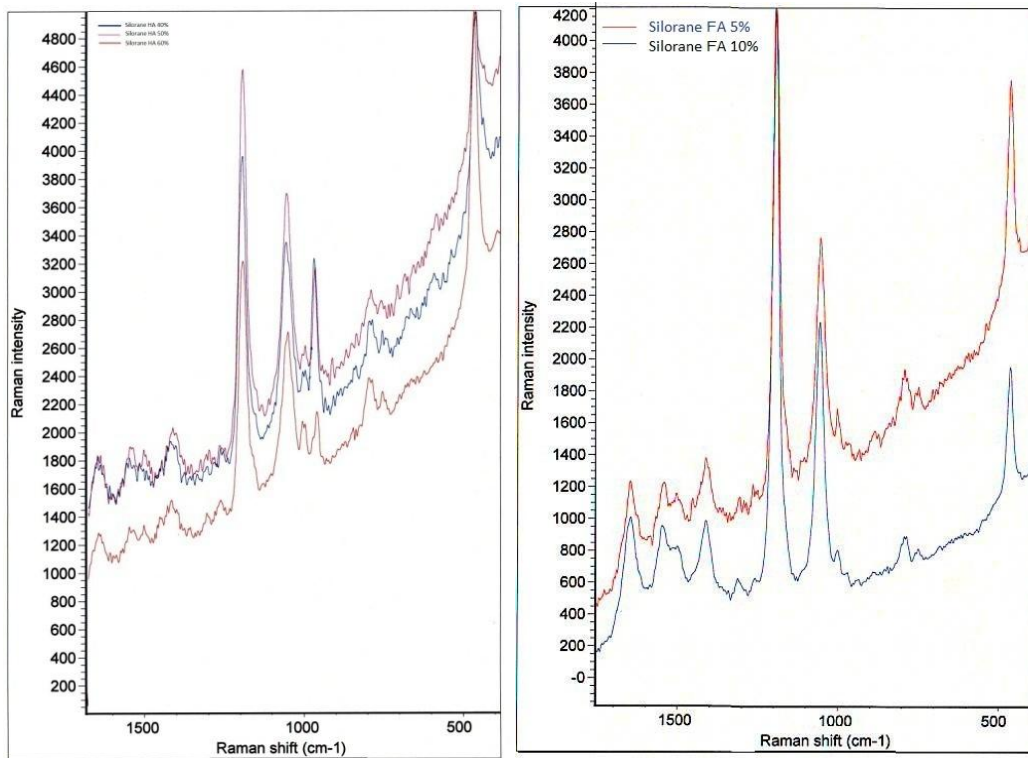
Figure 4.14: Raman Spectrum of Fluoroapatite incorporated Silorane. 5, 10, 40, 50 and 60% by wt

Figure 4.14 indicates the Raman spectrum of Silorane incorporated with Fluoroapatite by 5, 10, 40, 50 and 60% by wt. The peaks around 1200 and 466 cm^{-1} indicates the O-Si-O stretching. The peak at 963 cm^{-1} shows the phosphate band with low intensity. (Gnyba, Keranen et al. 2002; Navarra 2008)
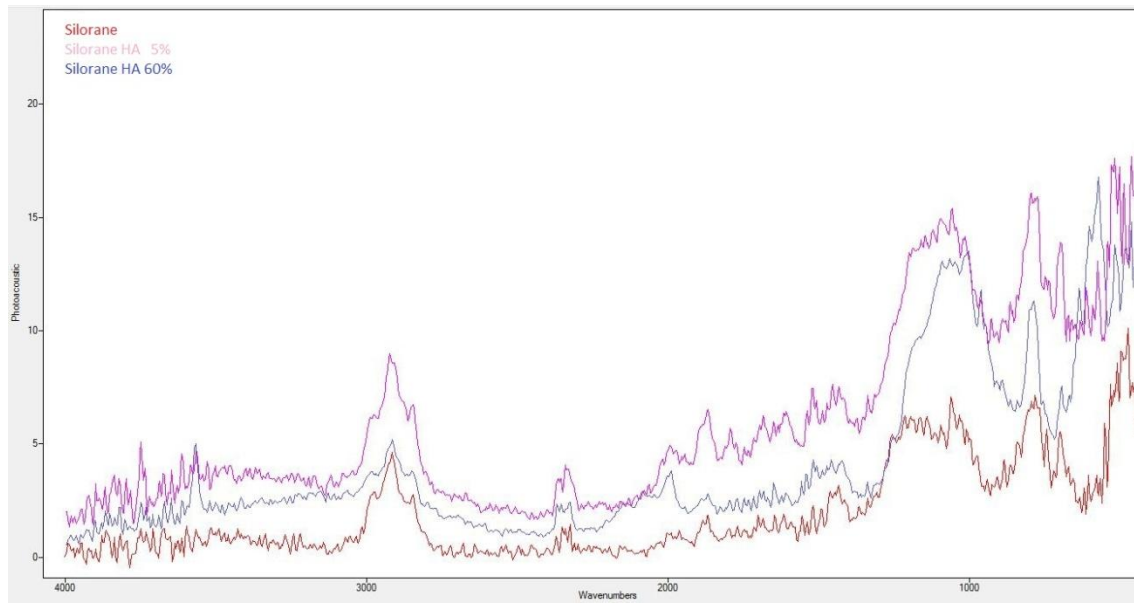
Figure 4.15: FTIR Spectrum showing Silorane incorporated with 5 and 60% Hydroxyapatite

4.6) COMPRESSIVE STRENGTH:

The compressive strength of the 6 different specimens was obtained by placing the specimen in the Hounsfield universal testing machine. The values obtained initially were in Newton and then converted into mega Pascals accordingly. The compressive strength of the specimens was measured by the formula given here below:

$$CS= 4P/\pi t^2$$

Where

CS= compressive strength

P= load in Newton

t= thickness of the specimen

All the charts are marked with error bars as per requirement. Error bars represent the variability of data and are marked to indicate the error in the findings. They generally give idea of how accurate the results are.

Different types of error bars are present and can be used to give different interpretations. In this study, we have applied error bar with standard error, which is inferential type. It measures how variable the mean will be. We achieved narrower inferential error values which gives more precise estimate of true value.

4.7) 5TH DAY TEST OF THE SAMPLES:

The specimens, which were subjected to force to obtain the compressive forces on the 5thday were taken out from the bottle in which they were stored within the SBF (Simulated body fluid). On the initial day five specimens of each samples were immersed into the simulated body fluid solution, A number of specimens were created which include Filtek Silorane, Filtek Supreme XT, 5 % incorporated Hydroxyapatite powder in Silorane, 5% incorporated Fluoroapatite powder in Silorane, 10 % incorporated Hydroxyapatite powder in Silorane and 10 % incorporated powder in Silorane. But out of all the five specimens only three samples of Filtek Silorane could be tested, 4 samples of Filtek Supreme XT could be tested, 3 samples of 5 % HA in silorane, 4 samples for 5 % FA in silorane, 5 specimens for 10 % HA in silorane and 10 % FA were uniform all over and good enough for compressive strength. Either there were air bubbles in the samples or there was not a proper thickness in the specimens.

The compressive strength of the Filtek Silorane on day 5 was 375 MPa. The compressive strength of filtek supreme XT was more than silorane 380 MPa as the figure below shows. The 5 % nano Hydroxyapatite crystals incorporated silorane and nano fluoroapatite crystals silorane were found to be equal to that of filtek supreme XT of 380 MPa. But a change was observed in the 10 % nano hydroxyapatite silorane and nano fluoroapatite silorane, and the value was higher at 390 MPa as shown in the figure on next page.

Table 4.1: Compressive strengths of specimens after 5 days
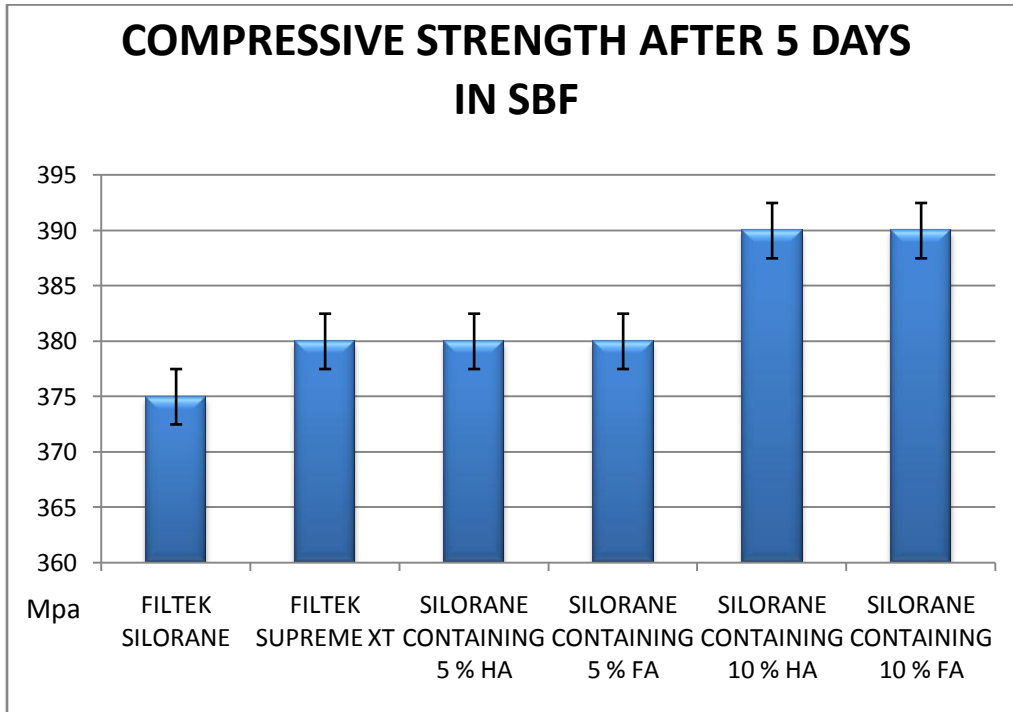
Table 4.2: Compressive strength of specimens on day 5

SAMPLE NAMES	COMPRESSIVE STRENGTH
FILTEK SILORANE	375 MPa
FILTEK SUPREME XT	380 MPa
5 % HA INCORPORATED SILORANE	380 MPa
5 % FA INCORPORATED SILORANE	380 MPa
10 % HA INCORPORATED SILORANE	390 MPa
10 % FA INCORPORATED SILORANE	390 MPa

4.8) 8TH DAY TEST OF THE SAMPLES:

Five specimens of each of the sample of Filtek Silorane, Filtek Supreme XT, 5 % incorporated HA and FA in silorane and 10 % incorporated HA and FA in silorane were made. Some problems also occurred during the sample formation due to which only 4 samples of Filtek Silorane, 3 samples of

Filtek Supreme XT, 5 samples of 5 % HA in silorane, 3 sample of 5 % FA in silorane, 4 samples of 10 % HA in silorane and 3 samples of 10 % FA in silorane could be mechanically tested due to problems in the uniformity of the samples.

As shown in the figure below, the compressive strength of Filtek Silorane increases to 385 MPa after immersion in the SBF for 8 days. Increase in the compressive strength of Filtek Supreme XT was also observed which had reached to 390 MPa. The compressive strength of 5 % nano HA in silorane and nano FA in silorane had increased and were equal to that of Filtek Supreme XT which was equal to 390 MPa. Finally, the compressive strength of 10 % HA in silorane and FA in silorane had increased to 400 MPa as shown in the figure below.

Table 4.3: Compressive strengths of specimens after 8 days
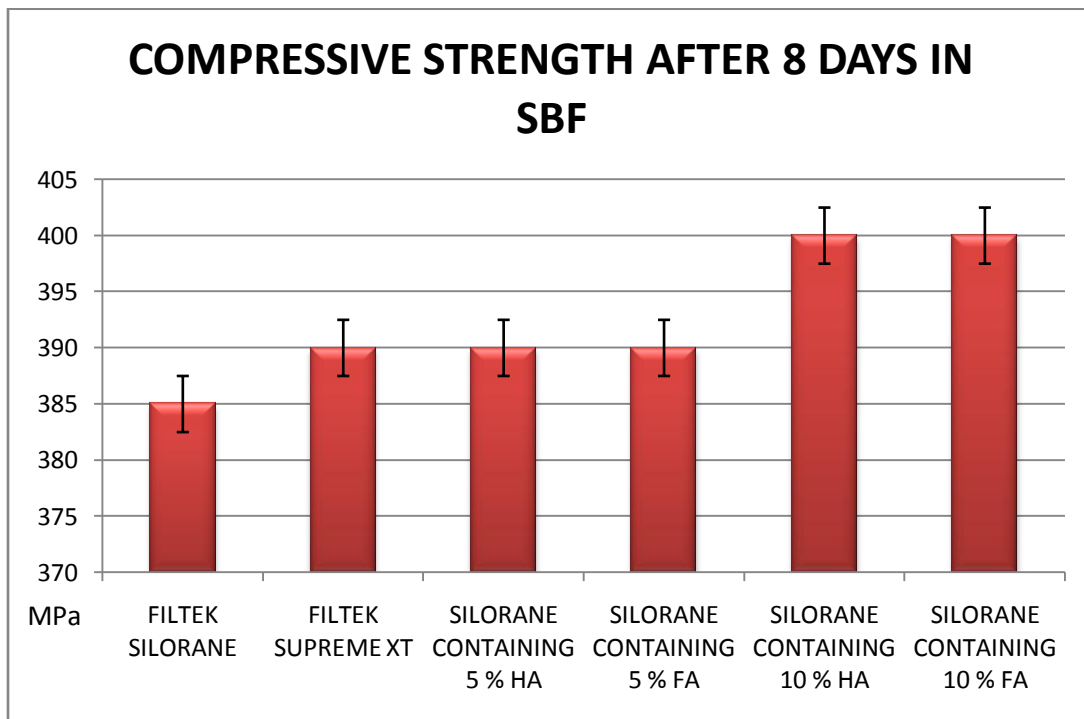
Table 4.4: Compressive strengths of specimens on day 8

SAMPLE NAMES	COMPRESSIVE STRENGTH
FILTEK SILORANE	385 MPa
FILTEK SUPREME XT	390 MPa
5 % HA INCORPORATED SILORANE	390 MPa
5 % FA INCORPORATED SILORANE	390 MPa
10 % HA INCORPORATED SILORANE	400 MPa
10 % FA INCORPORATED SILORANE	400 MPa

4.9) 11TH DAY TEST OF THE SAMPLES:

5 Specimens of each of the material Filtek Silorane, Filtek Supreme, 5 % nano HA incorporated silorane, 5 % nano FA incorporated silorane, 10 % nano HA incorporated Silorane and 10 % FA incorporated Silorane were formed. There were some problems associated with the samples due to which only 4 samples from Filtek Silorane were uniform enough that compressive strength testing could be done. 5 samples of Filtek Supreme XT were good enough for the mechanical testing. 4 samples of 5 % HA incorporated silorane and 3 samples of 5 % FA incorporated silorane were in a proper condition that compressive strength testing could be done on them. Also, 5 samples from 10 % HA incorporated in silorane and 2 samples of 10 % FA incorporated silorane were with good margins and uniformity that the mechanical testing could be done properly on the specimens.

The compressive strength of Filtek Silorane was calculated to be 395 MPa on the 11th day of being immersed in the SBF. The compressive strength of Filtek Supreme had reached 400 MPa on the 11thday of immersion into SBF. 5 % HA in silorane and 5 % FA in silorane had also some improvement in the compressive strength and it was found to be 400 MPa as shown in the figure

below. The compressive strength of 10 % in silorane HA and 10 % FA in silorane was the most of

the selected samples which was at 410 MPa again as shown in the figure below.

Table 4.5: Compressive strengths of specimens after 11 days

COMPRESSIVE STRENGTH AFTER 11 DAYS IN SBF
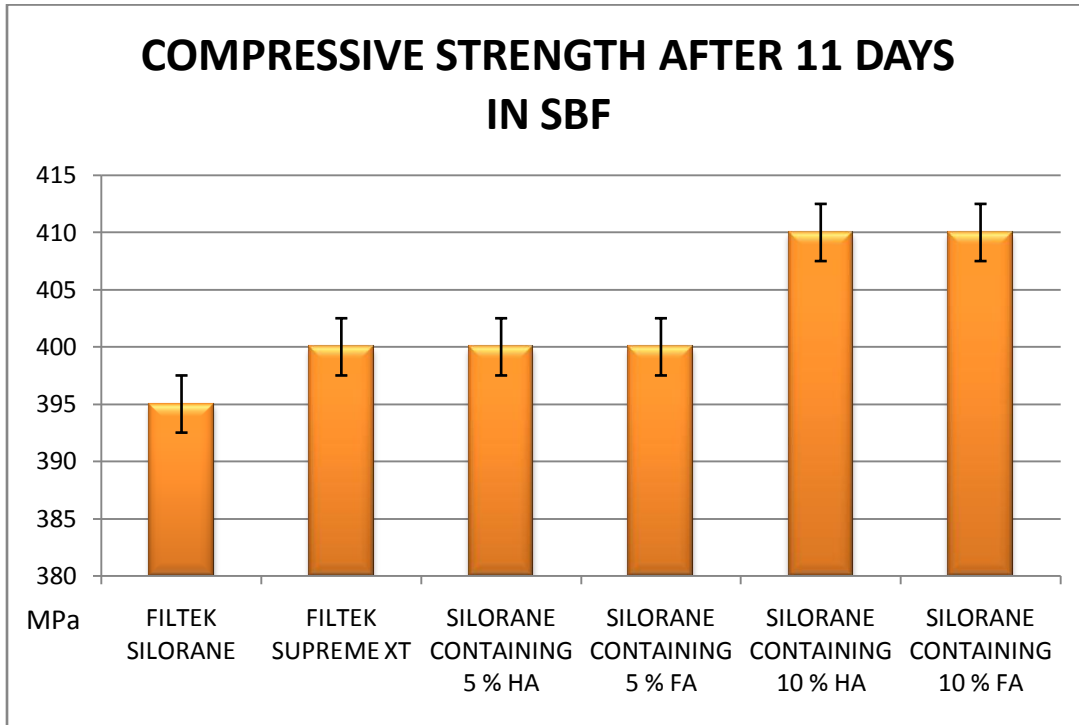
Table 4.6: Compressive strengths of specimens on day 11

SAMPLE NAMES	COMPRESSIVE STRENGTH
FILTEK SILORANE	395 MPa
FILTEK SUPREME XT	400 MPa
5 % HA INCORPORATED SILORANE	400 MPa
5 % FA INCORPORATED SILORANE	400 MPa
10 % HA INCORPORATED SILORANE	410 MPa
10 % FA INCORPORATED SILORANE	410 MPa

4.10) BIOACTIVITY TESTING:

Final testing was carried out on the 11 days immersed samples in the simulated body fluid. They were observed for the formation of apatite layer on the surface to assess their bioactivity.

There was evidence of formation of thin apatite layer on the surface after 11 days of immersion in SBF with regular replenishment of the SBF solution, which renders the material bioactive.

CHAPTER 5

DISCUSSION

5.1 DISCUSSION:

In the present study initially Hydroxyapatite and Fluoroapatite were prepared by sol gel method. Sol gel method is considered to be a reliable and simple method for the formation of nano sized Hydroxyapatite and Fluoroapatite. The obtained powders were then analyzed by FTIR to understand the chemical structure of both the apatites. Spectrums confirm the presence of hydroxyl, phosphate and carbonate group in the obtained samples. Spectrums used by Rehman et al (2008) were used as references, to confirm that the obtained powders of HA and FA were pure. Furthermore, comparison of mechanical properties of a commercially available composite based material with commercially available silorane based materials and FA and HA incorporated silorane materials were done. All the tests in this study were conducted by immersing the specimens in simulated body fluid for their respective amount of days which were 5 days, 8 days and 11 days.

5.2 SOLVATION OF SILORANE

Solubility is the ability of a material to dissolve in a liquid solvent to form a solution. The dissolved amount illustrates the percentage of material solubility in a solvent. The process is vital to incorporate multiple solid materials into each other. Different solvents were used to analyse the solubility of Silorane and was dissolved in Acetone, DMF and THF. It was found soluble in all the mentioned solvents. Silorane dissolved in DMF had to be heated up to 80°C for evaporation. Acetone and THF were evaporated at room temperature when left over night. The resultant samples were then analyzed by the FTIR for the chemical changes took place in Silorane during solvation. The peaks which were obtained on the spectra indicated that the resultant material of Silorane was not distorted and it was in the original condition and there was no distortion from the novel condition. In short, no solvent brought any significant change in the chemical structure; Silorane dissolved in THF shows the closest spectrum to the commercial available Silorane. THF was

selected as a solvent for the experiment based on its quick evaporation rate and Silorane's stability in the liquid.

5.3 INCORPORATION OF HA/FA IN SILORANE

Silorane was dissolved in THF and different amount of Hydroxyapatite and Fluoroapatite powder were incorporated in the solution. Initially 40, 50 and 60% of HA and FA were incorporated and analyzed chemically by FTIR and Raman Spectroscopy. The resultant spectrum were showing large amount of hydroxyapatite in Silorane. Thus, it was decided to incorporate 5 and 10% of HA and FA in Silorane. The hypothesis can be explained as, hydroxyapatite and fluoroapatite were being added as filler in Silorane. The Silorane used was commercial grade and is available in the form of solid paste which was set to use by dental practitioners. It shows that the material already have a filler content and by incorporating 40, 50 and 60% the filler content in the material was being disturbed. FTIR and Raman Spectra even showed a large amount of HA and FA in them. That is why smaller amount of HA and FA were added i.e. 5 and 10% and chemically characterized by FTIR and Raman Spectroscopy.

5.4 INCORPORATION OF HYDROXYAPATITE

Figure 4.8 and 4.10 shows the FTIR and Raman spectrum of 40, 50 and 60% of Hydroxyapatite incorporated in Silorane. Both the spectra show the presence of Hydroxyapatite in Silorane. In FTIR spectrum, the presence of hydroxyl group can be seen clearly. The $SiOCH_3$ group can be seen in the region of 2915 cm^{-1} but the bands seem a little distorted. Phosphate and O-Si-O are present in the same region of 550 – 1200 cm^{-1}. In Raman spectrum (Figure 14) there is a prominent O-Si-O peak at around 1200 cm^{-1} and phosphate peak can be seen at 963 cm^{-1}. In Raman and FTIR spectra of 40, 50 and 60% hydroxyapatite incorporated in Silorane, all the samples shows almost similar chemical properties with a little difference in intensities. The object of the experiment was the invention of a

bioactive restorative material. The material obtained after the incorporation of hydroxyapatite should be bioactive, as well as the material should not lose its chemical, physical and mechanical properties. The resultant material contains a significant amount of filler contents which will increase the bioactivity but on the other hand physical and mechanical properties may be compromised due to increase in ratio of filler contents which were up to 60%. For the reason, the samples of 5 and 10% hydroxyapatite incorporated Silorane were obtained and chemically characterized by Raman and FTIR. The resultant spectra show traces of hydroxyapatite in Silorane with low intensity hydroxyl peak and well defined peak of $SiO.CH_3$ at 2915 cm^{-1}. Figure below shows the comparison of the FTIR spectrum of Silorane and Silorane incorporated with 5 and 60% hydroxyapatite. The spectrum clearly shows the sample of Silorane incorporated with 60% hydroxyapatite shows presence of hydroxyapatite compromising the O-Si-O structure in 2915 and around 1000 – 1100 cm^{-1} region.
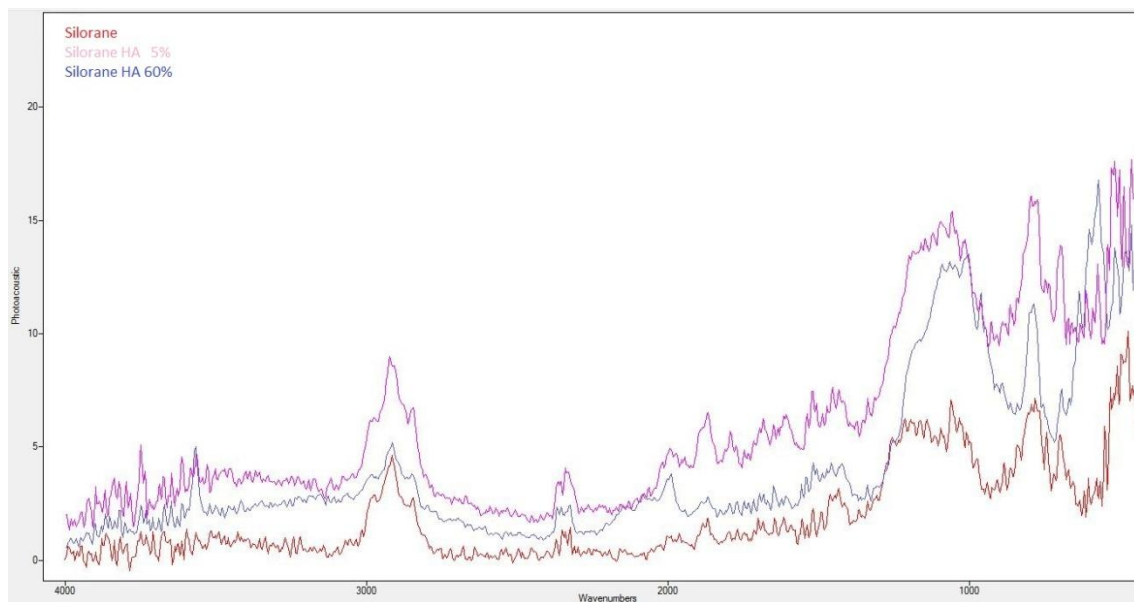
Figure 5.1: FTIR Spectrum showing Silorane incorporated with 5 and 60% Hydroxyapatite

While the sample with 5% hydroxyapatite shows traces of hydroxyapatite maintaining the unique chemical structure of Silorane. This can also be seen in Raman Spectrum of figure 4.10 and 4.11.
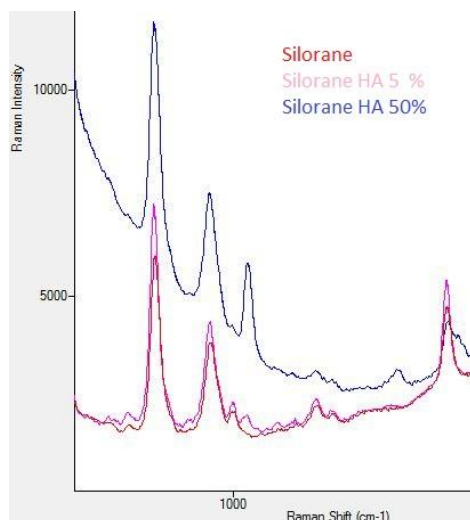
Figure 5.2: Raman Spectrum of Silorane incorporated with 5 and 50 % Hydroxyapatite

Addition of 40, 50 and 60% hydroxyapatite alter the silorane chemical structure and showed prominent presence of hydroxyapatite. While 5 and 10% of hydroxyapatite showing the presence of apatite without interfering with the existing silorane structure.

5.5 INCORPORATION OF FLUOROAPATITE

The results of incorporation of Fluoroapatite in Silorane were similar to a great extent with Silorane incorporated with hydroxyapatite. The FTIR and Raman spectrum of fluoroapatite incorporated in Silorane by 40, 50 and 60% is shown in figure 4.12 and 4.14 respectively and 5 and 10% in figure 4.13 and 4.15 respectively. 40, 50 and 60% fluoroapatite results in the modification of the chemical structure because of the increase in filler size. The spectra of 5 and 10% show the presence of fluoroapatite without modifying the chemical structure of the Silorane. Moreover fluoride ions are already present in the filler matrix of Silorane and by adding fluoroapatite it may increase the concentration of fluoride in the matrix.

5.6) MECHANICAL TESTING*:*

The mechanical testing of the dental materials is very significant in order to assess how much force a material can tolerate without getting fractured in oral cavity. As the forces in the posterior teeth can exceed up to 800 Newton, a filling materials should have good mechanical properties in order to survive in the oral environment.

The compressive strength testing of four different materials was done in this research. (Filtek Silorane, Filtek Supreme XT, 5 % and 10 % HA incorporated Silorane and 5 % and 10 % FA incorporated Silorane) These tests were conducted on three different intervals (Day 5, day 8 and day 11).

5.6.1) COMPRESSIVE STRENGTH:

Compressive strength of a material is the quantity of force a material can withstand until it fractures.

5.6.2) TEST ON THE 5TH DAY:

On the fifth day, when the compressive strength of all the six samples were measured, best compressive strength was that of the 10 % nano HA incorporated in silorane and 10 % nano FA incorporated in silorane. Their compressive strength after 5 days was 390 MPa, which was more when compared with the 5 % nano HA and FA incorporated silorane and Filtek Supreme XT. (All three of them exhibited compressive strength value of 380 MPa). The lowest compressive strength of materials was of Filtek Silorane which was at 375 MPa.

5.6.3) TEST ON THE 8TH DAY OF IMMERSION:

The next set of the experiments were carried out on the 8th day of immersing the samples in to simulated body fluid. The compressive strength test again showed that all the materials showed increased strength but the samples which had the highest amount of compressive strength were

again the 10 % nano HA and FA incorporated silorane at value of 400 MPa which were well over the limit set by the ISO. The compressive strength of 5 % nano HA and FA incorporated silorane increased along with Filtek supreme XT to 390 MPa which was more than that on 5th day. Again the material with the least amount of compressive strength was Filtek Silorane which had the compressive strength of 385 MPa. It can not be said that Silorane is a failed material because it has the least amount of compressive strength as its compressive strength increases from 5th to 8th day. Though, overall compressive strength is lower than other materials.

5.6.4) 11TH DAY TEST IN SBF:

Final experiments were carried out on the 11th day of immersion of the samples in the simulated body fluid. The compressive strength of the Filtek silorane was found to be 395 MPa, which was an increase from 8th day sample. But, again the compressive strength was less than the comparative groups. The compressive strength of 10 % nano HA and FA incorporated Silorane was observed at 410 MPa. This was followed by 5 % nano FA and HA incorporated silorane and the Filtek Supreme XT which had the value of 400 MPa.

The compressive strength of all the materials increased while they were immersed in the simulated body fluid. The Filtek Silorane and Filtek Supreme XT have the compressive strength which has already been proven by the manufacturers, but regarding the incorporated nano HA and FA silorane; there is an increase in their compressive strength which is due to the nano size HA and FA fillers. The more the fillers the more would be the strength of the material. It is also important that a proper balance of the matrix and filler should be maintained so that material does not become too brittle. Nano HA and FA are very small in size and are very closely packed together to fill up every small void which maybe present in the matrix of the composite material. Another advantage of using nano sized fillers is the ease of manipulation. The nano size of the fillers gives a proper polish to the

material and does not have to be excessively polished by the clinician. Thus, the smaller the size of the filler particles the more will be the compressive strength of the composite material as proved in this study.

There was evidence of formation of thin apatite layer on the surface after 11 days of immersion in SBF with regular replenishment of the SBF solution, which renders the material bioactive.

CHAPTER 6

CONCLUSION and FUTURE WORK

6.1 CONCLUSION:

Incorporation of the synthesized nano-HA and FA into Filtek™ Silorane resulted in the invention of a novel bioactive restorative material. The chemical structural analysis obtained by employing FTIR and Raman spectroscopic techniques indicated that there was chemical bond formation between the apatites (OH and PO) and siloxane (Si – O – Si) functional groups. As Silorane is a material, which has been introduced in the market very recently, there was no previous study available for the reference of this study. The hydroxyapatite and fluoroapatite synthesized in this study was characterized by FTIR and Raman Spectroscopy. The obtained spectra were compared with the previous studies and their chemical structure was confirmed. HA and FA were added as a filler content in Silorane, addition of more bioactive material may increase the bioactive nature of a material but it may interfere with the chemical, physical and mechanical properties of a material, reducing the mechanical properties in particular. HA and FA used in 40, 50 and 60% by wt., were interfering with the chemical structure of the Silorane by changing the filler content of the material. Hydroxyapatite used in 5 and 10% showed better results than that of 40, 50 and 60%. The samples with 5 and 10% of hydroxyapatite and fluoroapatite show the presence of apatites without altering the chemical structure of Silorane.

The incorporation of nano hydroxyapatite and nano fluoroapatite into the silorane filling material helps in making the material bioactive and also on the same time it increases the mechanical properties of the material. In this research pure nano hydroxyapatite and nano fluoroapatite powders were made via the sol-gel technique (Rehman et al. 2008) and then they were incorporated into Filtek Silorane. These were then compared with the mechanical properties of the commercially available Filtek Silorane and Filtek Supreme XT. The tests were conducted on the 5th day, 8th day and 11th day after immersion in the simulated body fluid. The compressive strength of the materials was tested. The lowest compressive strength was of the filtek silorane on all three days of the tests. It

was noted that the compressive strength was comparatively lower on the 5th day when compared with other materials but increased similarly when compared to the other materials in the due amount of tests on the compressive strength test days which were on the 8th and 11th day. The compressive strength of 5 % nano HA and FA incorporated silorane was equal to Filtek Supreme XT on all the test days. The best results obtained were of the 10 % nano HA and FA incorporated silorane which had the highest amount of compressive strength on all three test days when compared with the other samples.

6.2 FUTURE WORK:

This study has the potential to be expanded further as the present contributes in a small way towards the development of a novel bioactive restorative material. HA and FA were successfully incorporated in Silorane and characterized chemically. There are significant number of experiments, which remained to be performed on the apatite incorporated Silorane to check the resultant material's physical, mechanical and biological properties. If the resultant material show some bioactivity and other properties were not altered, it would be considered as a milestone in the field of dental restorative materials. And if the incorporation of apatites even results in the better mechanical, physical and bonding properties that would be an advantage. After that the material will go under clinical trials i.e. the newly formed dental restorative material will be used on the patients and results obtain from the clinical trials will let us know the future of this bioactive dental restorative material.

The study conducted in this research was done on the specimens which were immersed in the SBF for days 5, days 8 and days 11 respectively. The future studies should be done over a longer period of time as the composite filling materials are permanent restorations.

The experimental studies should be carried out on a longer period of time extending up to 1 year with the specimens kept in the oral environment. The loads and mechanical tests should also be done in this environment so that the behaviour of the restorative material in the human mouth can be examined.

Lastly, I would like to highlight the main problem which was faced during the experiment was non-availability of the proper mechanical testing equipments to do the required testing. The bond strength of the material and few other mentioned mechanical properties are important features which should have been studied but were not because of this limitation.

CHAPTER 7

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