DEVELOPMENT AND PERFORMANCE ASSESSMENT OF NANOCOMPOSITE MATERIALS FOR DENTAL APPLICATION

Ph.D. Thesis

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CERTIFICATE

This is to certify that the thesis entitled "**Development and Performance Assessment of Nanocomposite Materials for Dental Application**", submitted by **Mr. Shiv Ranjan Kumar** (ID No: 2012RME9549) in partial fulfilment of the requirements for the award of **Doctor of Philosophy** in Mechanical Engineering Department to the Malaviya National Institute of Technology, Jaipur is an authentic record of research work carried out by him under my supervision and guidance. To the best of our knowledge, the work incorporated in this thesis has not been submitted elsewhere for the award of any degree.

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Abstract

Teeth are one of the most important organs of human body. It is not only associated with chewing and mastication purpose but also play important roles in speech and facial aesthetics. Teeth can be damaged at various stages of life due to any of the possible reason such as physiological causes (two body or three body abrasion due to direct or indirect contact), pathological causes (disease related like Bruxism, Xerostomia), preventive causes (tooth brushing) or polishing causes (cleaning) etc. In order to restore damaged and worn teeth or to replace missing teeth, the extensive developments have been carried out since the beginning of dental practice by the dental material scientist. Composite resins have been preferred to the other available dental material because of their better esthetic look and physical, mechanical and tribological properties. Despite of development and advancement in the field of monomer/ filler technology, coupling system, light curing methods, there is strong need to increase service life of dental material by improving their performance regarding aesthetic properties, polymerization shrinkage, mechanical and tribological properties etc. The wear of dental material cannot be avoided whether it is natural teeth or artificial dental material. However, increase in dental wear may lead to formation of gap between the opposition teeth during contact creating the disturbance in mastication or chewing of food particle. Teeth also play a very important role in the lives of animals.

In this thesis, the effect of conventional nanofillers such as nanoalumina, nanosilica, nanozirconia and environment waste i.e. gypsum micro filler on the physical, chemical, mechanical and wear behavior of filled dental composite materials have been investigated. The different sets of formulation have been designed and then fabricated. The simple conventional techniques have been used for the fabrication of unfilled and particulate filled dental composites. The main focus of this study was prediction of wear analysis of the proposed fabricated dental unfilled and filled composites. Therefore, before studying the tribology analysis the basic experimental analysis were also equally important; such as physical, chemical, mechanical and thermo-mechanical analysis to predict the feasibility of the proposed dental composites. The physical and chemical

characterizations have been carried out to analyze void content, water sorption, solubility, depth of cure, degree of conversion and polymerization shrinkage etc. The mechanical properties such as micro-hardness, compressive strength and flexural properties have been also analyzed experimentally. The thermo-mechanical characterizations such as storage modulus, loss modulus, Tan delta, thermal degradation, glass transition temperature, crystallization and melting temperature were studied by using Dynamic mechanical analyzer (DMA) and Simultaneous Thermal Analyzer (STA) respectively. Dynamic mechanical analyzer (DMA) was used to measure the thermo-mechanical properties such as storage modulus (E'), loss modulus (E") and damping factor (Tan δ) of the fabricated dental composites over a temperature range of 30-350°C at 1Hz frequency to assess their suitability as restorative material in dentistry application.

The wear behavior of dental materials has been assessed with the help of Dental wear simulator (ASTM F732, Ducom, Bangalore) under food slurry and citric acid medium and for each composition the wear test performed up to 20000 cycles. Initially steady state experimental wear test was performed with respect to chewing load, profile speed and chamber temperature in both food slurry and citric acid medium. After that Taguchi design of experiment (L_{16}) technique was applied to get the optimal parameter settings and the order of significant parameters in order to get minimum wear rate of the dental composites.

The findings of all the physical, chemical and mechanical tests indicate that all the tests results have been found to be well within the ISO 4049 standard. The addition of nanofillers and micro-filler contents lead to increase in the density and void content of the dental composites. The addition of nanofillers and micro-filler contents lead to increase in the depth of cure and decrease in polymerization shrinkage of dental composite. The magnitude of mechanical properties indicates appreciably high in all dental composites which may be attributed to the presence of hard and brittle phase inorganic oxide nanoalumina, nanosilica, nanozirconia and micro sized gypsum filler because of higher degree of exfoliation and higher adhesion at the particle-matrix interface leads to higher load transfer. The Storage modulus and glass transition temperature increase with the increase in nanofillers and micro filler content.

The findings of the wear test indicate that silane treatment of fillers and the increase in filler content are two major factors influencing the wear rate of dental composite. In this regard, composite at the highest filler content demonstrated the strongest wear resistance. Finally, Analysis of variance (ANOVA) technique was applied and the results indicate that the rate of wear is greatly influenced by the filler content and the applied chewing load. The surface characterization of composite has been studied by using Scanning Electron Microscopy (SEM). Finally, Gray relational analysis (GRA) method was applied to rank the dental composites by using performance defining attributes (PDAs) including hardness, compressive strength, flexural strength, volumetric wear rate due to variation in normal load, profile speed and chamber temperature. The volumetric wear rate of dental composite without silane treated filler was quite high and decreased significantly when silane treated nanofillers and micro fillers were incorporated in the composites. The mean volumetric wear rate of experimental dental composite in citric acid is more than in food slurry medium. The silanized nanozirconia filled dental composited indicated the least wear rate in both the acidic and food slurry medium. Hence it may be used for dental application.

The sequence of ranking as per GRA method follows the order NZDC-3 (Rank 1) > NADC-3 (Rank 2) > NSDC-3 (Rank 3) > MGDC-3 (Rank 4) > NZDC-2 (Rank 5) > NSDC-2 (Rank 6) > NSDC-0 (Rank 7) > NADC-2 (Rank 8) > NADC-1(Rank 9) > MGDC-2 (Rank 10) > NSDC-1(Rank 11) > NZDC-1(Rank 12) > MGDC-1(Rank 13) > NADC-0 (Rank 14) > MGDC-0 (Rank 15) > NZDC-0 (Rank 16). Therefore, by ranking the dental composites 3wt. % nanozirconia filled dental composite (NZDC-3) shows optimal overall performance as compared to all other unfilled and particulate filled dental composites.

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List of Abbreviations

RBC : Resin based composite
BisGMA : Bisphenol-A glycidyl methacrylate
TEGDMA : Tri-ethylene glycol dimethacrylate
EBMAB : Ethyl 4 dimethyl amino benzoate
CQ : Camphorquinone
MPS : Mithacryloxy propyltrimethoxy silane
Hv : Vickers Hardness
CST : Compression strength test
FS : Flexural strength
FM : Flexural Modulus
NADC : Nanoalumina filled dental composite
NSDC : Nanosilica filled dental composite
NZDC : Nanozirconia filled dental composite
MGDC : Micro- sized gypsum filled dental composite
FTIR : Fourier Transform Infrared Spectroscopy
TEM : Transmission Electron Microscope
TGA : Thermo-Gravimetric Analysis
DSC : Differential Scanning Calorimetry
DMA : Dynamic Mechanical Analysis
SEM : Scanning Electron Microscopy
AFM : Atomic Force Microscopy
E' : Storage Modulus
E" : Loss Modulus
Tanδ : Loss Tangent Factor
ST : Silane Treated/Silanized
GRA : Gray Relational Analysis
PDA : Performance Defining Attribute

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Chapter 1

Introduction

Chapter 1

INTRODUCTION

In recent years, there has been increasing emphasis on biomedical applications to work on their material formulations. However, the term "biomaterials" have different interpretations both in materials science and clinical medicine. Whereas, biomaterials can be categorized in terms of their structural, chemical and biological characteristics, for example, in metal and alloys, ceramics and polymers with a varied degree of bioactivity. The polymeric biomaterial offers many advantages over metal or ceramic materials like ease of manufacturability to produce various shapes (latex, film, sheet, fibers, etc.), ease of secondary processability and ease of stronger bonding with the native tissue, reasonable cost and availability with desired mechanical, physical, optical, tribological properties respectively. Synthetic polymeric biomaterials have been widely used in dental materials, implants, dressings, medical disposable equipments, prosthetic materials, extracorporeal devices, encapsulates, polymeric drug delivery systems, tissue engineered products etc. In dentistry, polymeric biomaterials have been used as a restorative material, implant material, pits and fissure sealant, etc.

1.1 History of dental material

The era of dentistry is supposed to be started about 3000 B.C when dental materials were used in the form of gold bands and wires [1]. Some of inscriptions on tombstones of Egypt indicated that in Egypt, dentists were considered as medical specialists, but they were unknown about restorative dentistry. However, in long back some teeth found in Egyptian mummies were either transplanted human teeth or made of ivory. At the same time, gold foil had also been employed for dental restorative purposes. In the year 1750, the dentists of Prussia used a foil made up of silver mixed with mercury i.e. dental amalgam as reported by Taveau [2]. However, many of dentists had criticized the poor quality of the early amalgam restorations. Again, in the year 1885, Logan patented new material porcelain fused to a platinum metal [3]. Since 1910, pure metal like titanium and base metal alloys like Co-Ni, Co-Cr and Co-Ni-Cr metal alloys were used in the production of inlays, onlays, crowns, denture, etc. In the 1930s, development of poly methylmethacrylate (PMMA) for as a denture base material was the great invention in the field of dental material [4]. Various dental composites have been fabricated till date with the help of PMMA. In 1960, modern dental polymers were developed by Bowen, who invented a base monomer Bisphenol A glycidyl di-methacrylate (BisGMA) [5]. Now a day, polymeric materials are widely used in dentistry as denture material, composite filling materials, adhesive materials, cement, pits and fissure sealants, etc. However, all the polymeric materials in dentistry are not ideal for their clinical use. For example, a common clinical problem is fractures of prosthesis or fractures of composite restorations [6]. Therefore, it is essential to find new materials and develop techniques in dentistry.

1.2 Classification of dental material

Nowadays four groups of dental materials are available in dentistry such as metals, ceramics, polymers and alloy of dental composites. In metal alloy composite, Titanium, Nickel, Cobalt, etc. are used as the base metal. In dental amalgam, silver, tin and copper are being used for dental restoration application. In dental ceramics, Feldspathic porcelain, glass ceramics are silicate-based ceramics whereas aluminum oxide and zirconium oxide are oxide based ceramics. Since 1970, visible-light-cured polymeric dental composites have been used extensively in dentistry due to their aesthetic characteristics. Dental composite consists of a polymeric matrix, reinforcing fillers, stabilizers, initiators and activators that contribute with the light polymerization of the organic matrix to form cross-linked polymer networks. Additionally, silane coupling agents are involved in bonding the fillers to the polymer matrix. Inorganic fillers are added to provide physical, mechanical and optical properties to the dental composite.

Another classification of dental material can be preventive materials, restorative materials or auxiliary materials. Preventive materials such as pit and fissure sealants, sealing agents are used in preventing leakage, cracks, etc. Restorative materials such as primers, bonding agents, liners, cement bases, amalgams, resin based composites (RBC), hybrid ionomers, cast metals, metal ceramics, ceramics respectively. Dental materials can also be classified as direct restorative materials or indirect restorative materials. The direct restorative materials are used to fabricate restorations or prosthetic devices directly on the teeth or tissues intra-orally. The indirect restorative materials are formed indirectly on casts or other replicas of the teeth and other tissues extra orally. Hence, an ideal dental material should be biocompatible, should make stronger bond to tooth or bone structures, should match the natural appearance of natural tooth and exhibit other mechanical / wear properties similar to those of natural tooth.

1.3 Compositions of dental materials

The major compositions of dental composites include a polymer matrix, inorganic fiber or particulate filler, a filler-matrix coupling agent for proper adhesion between filler and resin matrix and minor additives including polymerization initiators, polymerization accelerator, stabilizers, and coloring pigments. Recent research was based on the improvement in the characterization of dental material by the discovery of organic monomers, modifications in the formulation of resin matrix and filler technology, advancement in light curing devices and the development of efficient photo initiators. Despite these achievements, the service life of dental composite is very less as compared to metal and alloy dental composites and dental ceramic material. Hence, researchers for the development of dental materials are more focused to improve the performance of current composites regarding their aesthetic properties, polymerization shrinkage, mechanical and tribological properties.

Recent improvements have been achieved mainly through the development of organic monomers, modifications in formulation and filler technology, advances in light curing equipment and the introduction of efficient photo-polymerization technique. Incorporating inorganic fillers to the resin based dental composites result into increased in mechanical properties (such as stiffness and hardness), but decreased in coefficient of thermal expansion [7], decreased in polymerization shrinkage and increased in flexural modulus [8] respectively. The development of shrinkage stress is considered to be a main cause for post-operative sensitivity and marginal leakages associated with composite restorations.

Hence, intensive research has been conducted to develop an understanding of wear resistance of tooth enamel or dental materials under different loading condition, different formulation, ambient conditions such as dry condition, citric acid solution etc. Most studies have been focused on providing comparative ranking of various dental materials using wear test machines simulating the oral conditions, whilst only a few in vitro studies have been carried out on their wear mechanisms. Future in vitro wear testing should be aimed at an understanding of the fundamental underlying wear mechanisms involved, which will lead to a better understanding of in vivo failure patterns. In this regard, researchers have designed and formulated simulation models for the analysis of effects of filler contents, filler size and resin properties on the mechanical and tribological behavior of dental composites [9].

The evolution of nanotechnology has resulted into a significant improvement in the development of advanced dental materials. With the help of nanotechnology, the dental materials with smoother surfaces, higher translucency, polishability, better physical properties and wear resistance are produced. Their properties are comparable and even better with micro filled composite and other hybrid composite. In this research, the use of micro- sized gypsum as filler material in resin based dental composites is novel. The incorporation of gypsum in the dental composite was based on the fact that as a source of calcium, gypsum can be used to re-mineralize the tooth tissue.

1.4 Filler Technology in Dentistry

Incorporating inorganic fillers to the resin based composite results into increased in mechanical properties such as stiffness, compressive strength and hardness, but the decreased in coefficient of thermal expansion [10], decreased in polymerization shrinkage [11] and increased in flexural modulus [12] respectively. The development of polymerization shrinkage stress is considered to be the main cause for post-operative sensitivity issue and marginal leakage related to composite restorations. A mathematical analysis indicated the relative importance of the different material properties of dental composites lead to shrinkage stress. In the ranking, the most important one is polymerization shrinkage, followed by Young’s modulus and then viscosity [13]. Intensive research has also been conducted to develop an understanding of wear resistance of tooth enamel and dental materials under different loading condition, different formulation, ambient conditions such as dry condition, citric acid solution. Most studies have been focused on providing a comparative ranking of various dental materials by using wear test machines which simulating the oral conditions [14]. However, only a few in vitro studies have also been performed on their wear mechanisms. Future in vitro wear testing should be performed to understand the fundamental of wear mechanisms involved, which will lead to a better understanding of in vivo failure patterns. Some researchers have designed and formulated 3D finite element simulation model for the analysis of effects of filler contents, filler size and resin properties on the mechanical and wear behavior of dental composites [15, 16].

The introduction of nanotechnology in the material science has led to various developments in the field of dentistry. As a development of nanotechnology, the addition of nanofillers leads to the formation of a smoother surface with better mechanical properties, less wear and higher translucency compared to micro-filled composites. Hence, nanofillers are being added to improve physical, mechanical and tribological properties of dental composite materials.

In Rajasthan, India, one of the critical concerns is how to utilize stone waste such as marble slurry/gypsum slurry produced during machining and cutting of stones. The slurry dumped on land can affect the productivity of land, decreased porosity, water absorption, water percolation. When dried, these fine particles cause severe air pollution. Hence in this concern, research has been carried out to utilize stone slurry like marble and gypsum and to obtain pure gypsum from the slurry. Gypsum is also recognized as a source of calcium and is being used in food items. Hence, in this research, pure gypsum has been used as one of filler in the dental composite material. ***The main purpose of this thesis is to develop a new resin based composite having less polymerization shrinkage with better physical, mechanical, chemical, thermal and tribological properties and investigate their performances in simulated food slurry condition. The use of micro- sized gypsum as filler material in resin based dental composites is novel. Finally, the outcomes of the research work would comprehensively lead us to the understanding of practical optimization of performance parameters and its correlation to the compositional attributes, which would guide the research community for developing new generation composite material for the realistic design of functionally advanced dental material for restoration and implant applications.***

1.5 Thesis Outline

The reminder of the thesis is organized as follows:

Chapter 2: Includes literature review designed to provide a summary of the basic knowledge available involving the issues of present research interest. It presents the research works on physical, mechanical, thermal, tribological behavior of various types of resin based dental composites by various investigators.

Chapter 3: Includes a description of raw materials and test procedures. It presents details of fabrication and characterization of the composites under investigation and also an explanation of the Taguchi experimental design.

Chapter 4: Presents the physical and chemical characterizations of dental composites

Chapter 5: Presents the mechanical and thermo-mechanical analysis of dental composites.

Chapter 6: Includes the wear characterization of dental composites.

Chapter 7: It presents a detailed study on the effect of fillers on the wear behavior of dental and at the end optimized all the above results i.e. physical, mechanical and wear results by GRA method.

Chapter 8: Provides summary of the findings of this research work, out lines specific conclusions drawn from the experimental and analytical efforts and suggests ideas and directions for future scope.

The next chapter briefly presents/discuss the literature review of various research papers on physical, mechanical, thermo-mechanical, tribological analysis of a series of experimental dental material. The specific objectives of this work are clearly outlined in the next chapter.

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Chapter 2

Literature Review

Chapter 2

LITERATURE REVIEW

This review seeks to describe, summarize, evaluate, clarify and/or integrate the content of primary and previous reports on physical, mechanical, chemical and tribological behavior of various dental composite materials for the dental restoration and implant applications. Intensive researches have still being carried out to develop an understanding of Dental Tribology for successful design and selection of new artificial dental materials. Researchers have already shown interest for development of new dental composites and study their bio-tribology mechanism under different oral environment such as food slurry and acidic medium. The Major goals designed for dental material selection are (i) to recreate function and (ii) to get aesthetic properties. Other important considerations are mechanical properties, thermal properties, tribological properties, corrosion resistance, reasonable cost, availability and biocompatibility respectively.

The topics embraced in this literature review are:

2.1 Study on effect of oral environment on wear of natural human teeth and artificial teeth material

2.2 Influence of resinous constituents on the performance of friction materials

2.3 Influence of filler constituents on the performance of dental materials

2.4 Study of mechanical and thermal behavior of dental material

2.5 Study of tribological behavior of dental materials under food slurry and acidic medium

2.6 Implementation of Design of Experiments (DOE) and optimization techniques.

2.1. Study on effect of oral environment on wear of natural human teeth and existing artificial dental material: The literature study revealed that oral environment and bio-mechanistic aspect significantly affects the real time interfacial tribology, thereby effects on the wear aspects of dental materials. The oral environment plays a major role in the wear of both human teeth and artificial dental material. At the beginning, Gwinnett et al. [17] studied the structure, composition and function of oral environment and reported that the hardest part of human body is tooth enamel which is composed of 92–96 % mineral substances, 1–2 % organic materials and 3–4 % water by weight, whereas in the mouth of organisms there is a very important watery substance called Saliva, secreted by the salivary glands. Saliva works as a lubricating agent for enamel and soft tissues in the mouth. It also helps to reduce wear and friction between the teeth, simultaneously helps in the digestion of food particles by maintaining oral hygiene. Saliva also controls the oral environment by providing cooling effect during chewing. However, improper formation of saliva may affect the frequency of dental caries, gum disease, oral infections and other oral problems inside the human body. In similar concern, the role of saliva and effect of different types of food on the wear rate of dental material were studied by Lamkin et al. [18]. They reported that the various salivary proteins like acidic proline-rich proteins (PRP), statherins, histatins, and cystatins have affinity for mineral surfaces especially of calcium phosphate to protect the integrity of the enamel surfaces. As a lubricant, Saliva coats the oral mucosa and protects it from trauma during eating, swallowing and speaking. As persons suffering from xerostomia i.e. little saliva or having lack of water or soreness of the mouth, the food particle sticks inside mouth. Hanning et al. [19] concluded that salivary pellicle protect the enamel from short-term erosion of organic acids and can form within three minutes. However, dietary acids such as citric acid are not inhibited from dissolution of the enamel. Now a day consumption of acidic drinks and fruit juices is continuously increasing among most of the adult population. During in situ and in vitro study about the dental erosion by fruit juice, Hooper et al. [20] noticed that there is need of more research for the global issue related to the exposure of fluoride to protect the natural teeth against dental erosion by acidic medium despite using fluoride containing toothpaste.

Cheng et al. [21] reported that excessive intake of soft drinks could be responsible for complex dental consequences including dental erosion and caries. Their study was mostly based up on a case study of a 25 year old patient suffering from the erosive wear on the front teeth during the past 3 years. The patient had a history of drinking cola for 7 years and had a poor oral hygiene. The patient brushed tooth and gargled with water every morning. The patient liked holding the drink in the mouth for few seconds and tasting before swallowing. There were nothing unusual in his diet, medical history and family history of major dental issue. The patient doesn’t have any symptoms of any dental problem such as Gastroesophageal reflux (GERD), xerostomia, and bruxism. Finally, it was observed that during early stage of dental erosion, dental surface was smooth but in advanced stages enamel surface became rough. After further erosion, concavities, lesions with varying depth and width started developing.

Lewis et al. [22] reported that the mouth environment of a person who likes acidic diet could be acidic with a pH of 3 and the pH values of acidic diet range from 1 to 6 and they further concluded as the pH decreased, wear rate increased. Zero et al. [23] observed the severity of the condition depends upon diet of person i.e. whether it is acidic or not and up to what extent and time of exposure of teeth to the erosive agent, mineralization of dental tissue, and available saliva composition. Piangprach et al. [24] found that the saliva plays the essential function of maintaining the oral health. Hence, the low salivary flow causes oral imbalance related to dental wear, digestion, faculty of speech, etc. Furthermore, Lowcontentof saliva is less effective to neutralize dietary acids in the mouth contributing to erosive lesions in some individuals [25, 26]. Jarvinen et al. [27] determined that patients with a salivary flow rate of less than 1 ml/ min were at a five timesmore risk of having dental erosive wear issue than those with higher flow rates.

Therefore, the major role of saliva is to protect tooth surfaces against acid attack by providing a matrix for remineralization because it supplies calcium and phosphate ions to remineralized enamel [28,29]. Most of the mineral substances in enamel are hydroxyapatite i.e. $[\mathrm{Ca_3(PO_4)_2}]_3 \cdot \mathrm{Ca(OH)_2}$. Hence, demineralization will occur on the surface of enamel due to dissolution of hydroxyapatite in an acidic oral environment. Holum [30] defined the concept of remineralization and demineralization. Demineralization of the enamel is the immediate cause of tooth decay. Both phosphate and hydroxide ions within the hydroxyapatite structure neutralize H+ ions resulting in dissolution of the enamel as per Eq. (2.1).

$$[\mathrm{Ca_3(PO_4)_2}]_3 \cdot \mathrm{Ca(OH)_2} + 8\mathrm{H^+} \rightarrow 10\,\mathrm{Ca}^{2+} + 6\mathrm{HPO_4^{2-}} + 2\mathrm{H_2O} \qquad (2.1)$$

Hydroxyapatite, when brought into contact with fluoride ions (in toothpastes, or treated drinking water) reacts to form fluoroapatite and is called remineralization as per Eq. (2.2).

$$[\mathrm{Ca_3(PO_4)_2}]_3 \cdot \mathrm{Ca(OH)_2} + 2\mathrm{F^-} \rightarrow [\mathrm{Ca_3(PO_4)_2}]_3 \cdot \mathrm{Ca\,F_2} + 2\mathrm{OH^-} \qquad (2.2)$$

Mineral loss of the natural or artificial dental material due to a chemical process of dissolution of acidic food item is called “erosion” in the dental tribology, but the same term erosion has different meaning in engineering tribology [31, 32]. Dental erosive wear caused by acidic dissolution observed clinically was the combination of different phenomena of dental wear. One phenomena of the dental wear is the wear of surface of tooth by demineralization due to direct contact with acidic diet. Other phenomena are the abrasion during food mastication, and tooth brushing [33] etc. For the dental patient with evident palatal erosion, the mean wear rate was reported to be 6μm/month which was observed as 10 times to the normal person [34]. It has already been concluded that once acidity in the mouth increases, wear on the tooth surface will occur whether the load is applied or not [35-38]. From the available literature, it was reported that the investigation of dental erosive wear mainly focused on the direct loss of mouth tissues due to demineralization by acidic drinks or juice and the erosive wear of natural teeth or artificial dental material were increased with increase in acidity. The dental erosive wear was independent of other oral environment, loading condition and chewing speed [39-41]. However, research work on the friction and wear behavior of dental material in acidic environment is rare. Most people usually like acidic diet and take food with acidic drink simultaneously. The surfaces of dental material, therefore, are usually subjected to simultaneous chemical and physico-mechanical actions in the mouth. The wear rate of dental material in an acidic environment was more than that under other environmental condition [42]. Mulic et al. [43] studied dental erosive wear on 220 adults in which 77 men and 143 women with an age ranging from 18 to 32 years (mean 21 years, SD 4) divided into following two groups (Table 2.1).

Table 2.1 Dental erosive wear case study [43]

Group Name	Member		Remark
1) Exercise group	Total no of participant in the range of age group 18-32 = 104 (36 men, 68 women) mean is 25 years, SD is 4 yrs)	No. of participant in the range of age group 18-25 years n = 63; (17 men, 46 women); mean age 22 years	This group people are worked out twice or more per week at the fitness center. All participants are non smoker and free of any medications.
		No. of participant in the range of age group 26-32 years = 41; (19 men, 22 women); mean age 29 years)	
2) Comparison group	116 individuals (41 men, 75 women); age 18 years	This group people visited dental clinic for regular dental treatment. But they have not taken any regular physical exercise during the last five years.	

Following are the result observed by them:

- In the exercise group, around 64% participants were suffered from dental erosive wear.
- In the young people of age group 26-32 years, the dental erosion case was registered for 76% of participant. In the age group 18-25 year olds, the prevalence was 57% ($p < 0.01$), whereas in the comparison group, 20% of the 18-year-olds had dental erosive wear ($p < 0.01$).
- More men (78% of men participants) had erosive lesions than women (57% of women participants), but less significance of this difference was seen ($p = 0.064$). However, a dentine lesions in men was more significant ($p = 0.047$).
- The maximum dental erosive wear was occurred on the upper central incisors around 33%, followed by first molar which was around 27%.
- The majority of the lesions occurred in enamel. First molars indicated the highest occurrence of lesions with dentine involvement around 12%.

2.2 Influence of resinous constituents on the performance of friction materials

The literature study reveals that contributions of resin constituents are significant in enhancing various aspects of dental materials. The primary components of the resin matrix are resin monomers, an initiator or catalyst system, accelerator, inhibitor etc., for polymerization. Suh [44] reported that the first BisGMA based dental material developed in the 1960s is still being used by the dental manufacturer and dental material scientist. BisGMA is a bulky monomer with two methacrylate groups at each end. The monomer is prepared by reaction between bisphenol-A and glycidyl methacrylate. Free radical polymerization is used to converts double bond of carbons of the methacrylate groups at each site of number of monomer to a linear polymer by cross-linking phenomena. Peutzfeld [45] concluded that BisGMA is quite viscous in nature. Hence, to mix more filler uniformly, it must be thinned by using shorter and more flexible dimethacrylate monomers such as triethylene glycol dimethacrylate (TEGDMA). In the year 1970, another diacrylate monomer known as urethane dimethacrylate (UDMA) was developed for dental use. UDMA was used as a base monomer alone or along with other diacrylate monomers.

Manhart et al. [46] reported that many monomers have been used as a dental material including BisGMA and urethane dimethacrylate but none of them have proven to be clinically superior to these two monomers. In 1998, as an alternative of BisGMA, the first RBC (Resin

Based Composite) was introduced based on the ormocer chemistry (Definate, Degussa, Germany). Hickel et al. [47] developed multifunctional urethane and thioether(meth)acrylate alkoxy silanes as sol-gel precursors for the synthesis of inorganic-organic copolymer ormocer composites. Ormocers (organically modified ceramics) is a three-dimensional cross linked inorganic-organic copolymers and this material exhibits better mechanical and wear properties. Combe et al. [48] compared the polymerization using chemical activation and light activation. They found that benzoyl peroxide or sulfuric acid may be used as the polymerization initiator for chemically activation polymerization and a tertiary amine i.e. Dihydroxyethylparatoludine (DHEPT) as activator. Once both the catalysts are mixed with resin based composite (RBC), the initiator and activator contact and polymerization process begins. In the 1980s, visible light-cured (VLC) resin-based dental composites were introduced as a dental restorative material. These resin systems are widely used for many dental applications. Visible light-cured RBCs polymerizes with visible light energy which allows flexible setting time. The advantages of VLC resin based dental composites include fewer voids, greater strength, greater fracture toughness, better color stability, better shade selection, and more degree of conversion than chemically activated RBC. Visible light-cured RBC polymerizes by free radical polymerization in the presence of a photoinitiator and accelerator system. The photo initiator absorbs light energy (photons) emitted from the curing light and initiates polymerization. Photo initiators such as camphoroquinone along withan amine accelerator/catalyst (e.g., dimethylamino ethylmethacrylate DMAEM) areactivated by visible light. The activated Camphorquinone system initiates the polymerization of the dimethacrylate resin monomers. The color stability of VLC RBC is more than that of chemically activated RBC because of presence of less concentration of amine accelerators in VLC RBC than chemically cured RBC [49-51]. The commonly used photoinitiator in the field of dentistry is Camphorquinone (CQ) which has major absorption of visible light wavelengths in the range of 460-480 nm (blue). Sometimes, a combination of photoinitiators and accelerator are also used, each having its ownspecific wavelength for maximum reactivity. Stansbury [52] found that the highest absorption wavelength is 468 nm, which is within the limit of spectral output of the LED light curing units.

Albers [53] reported that since different composite resins have different photo initiators, the light wavelength range absorbed by the photo initiator for maximum polymerization should focus on the composite resin. The percentage ratio of unsaturated bond (C=C) converted to saturated bond (C-C) indicates the extent of polymerization. Ferracane et al. [54] fabricated dental composites with a higher degree of conversion and reported that more conversion led to greater mechanical and wear properties, better color stability and more biocompatible. They also proposed that to get maximum conversion, the spectral emission wavelength of the light-curing unit must conform to the minimum spectral photo-initiation requirements. The minimum spectral photo-initiation requirement will be the maximum value of absorption wavelength of all the photo initiator used in the fabrication. During polymerization, the distance between the monomers decreases as the double bond is converted into single bond. However, for presently available RBCs, this shrinkage ranges from 2%-3% per volume [55-57]. Polymerization shrinkage of the composite resin transfers shrinkage stress to the cavity walls. Shrinkage of the RBC can result into formation of marginal gap, micro leakage, staining, postoperative sensitivity, and caries dental issues.

As RBC polymerizes, a stress was developed by the surrounding tooth called polymerization shrinkage stress which varies with rate of modulus development. High modulus composites with rapid conversion rates transfer polymerization stress more rapidly to the adjacent tooth structure than lower modulus composite with slow conversion rates. Ferracane et al. [58] used visible light cure unit to cure the resin matrix filled with ceramic filler. It provided better mechanical properties and less polymerization shrinkage, water sorption, radiopacity, and the coefficient of thermal expansion.

2.3 Influence of filler constituents on the performance of dental materials

The literature study reveals that various inorganic filler particles vary in type, particle size and distribution, concentration, are the major factors contributing the performance of a dental composite. The addition of inorganic fillers into the base monomer resulted into increased in mechanical properties such as stiffness, hardness, compressive strength, flexural modulus but a decrease in mechanical property like flexural strength [59, 60]. On the other hand, the increased in filler loading and decreased in filler size improves wear resistance as well as aesthetics of dental composite [61-63]. In a recent work, Tamura et al. [64] investigated the effects of different shapes, surface textures, structures and content of nanoalumina filler particles on the wear and mechanical properties on simulated occlusal wear and toothbrush wear. They found that incorporation of nanofiller increased both the hardness and wear resistance of the dental composites and they also produced better polished surface than micro-filler.

In another work, Julian et al. [65] studied the effect of filler content and particle size on the shrinkage stress of resin composites. They reported that shrinkage stress strongly depends upon the size of the dispersed phase particles. Therefore, composites filled with spherical filler particles exhibit lower polymerization shrinkage stress as compared to those with irregular filler particles. Korichi et al. [66] examined the effect of opaque fillers and monomer ratios on the strain due to shrinkage and depth of cure of dental composite based on BisGMA based monomer. It was reported that the degree of conversion and the shrinkage strain decreased linearly with the increasing of opaque filler contents. The Degree of conversion and the final polymerization shrinkage were decreased with the increase in BisGMA content in the organic matrix due to high molecular weight and high viscosity of the resin material. A linear correlation between the shrinkage strain and degree of conversion of the investigated composites has been obtained. Fujita et al. [67] studied the influence of different particle sizes of spherical silica filler on the Knoop hardness and cured depth of visible light cured resin composite. It was observed that increasing the filler size up to four times resulted into formation of dental composite with shallower cured depth and lower Knoop hardness ratio. It was concluded that in order to get more polymerization conversion, the relative index difference between the resin and filler must be reduced below the wavelength of 468 nm, which is used to activate the CQ photo-initiator. Zhang et al. [68] examined the importance of size and shape of filler particle for the improvement of wear performance of dental composites. They suggested that small filler particles may lead to the formation of high wear resistance, as well as high degree of conversion. The tests were performed for each of the monomodal, bimodal or trimodal spherically shaped filler composites with particle size 100 nm particles. It was proposed that for the irregularly shaped material, the trimodal system proved to be better wear resistance with less number of unreacted monomer.

Feng et al. [69] investigated surface adhesion phenomena between resin matrix and filler material under the developed polymerization contraction stress (PCS). By the use of three different measuring techniques and model composites, they proved that during polymerization the monomer comes closer to each other due to polymerization contraction stress. This is the consequence of the resin being separated from the filler particles and formation of weak adhesion in the composite. Effective silane treatments of fillers will reduce the gap formation by providing the better adhesion properties between filler and resin. Lim et al. [70] determined and simulated the effect of influence of filler particle size and color parameters of experimental dental composites. Color of eleven experimental resin composites filled with two different sized Glass fillers of size (0.77 µm, 0.50µm) in 10–70wt% was measured by a spectrophotometer. Finally, they concluded that the pigment should be added to mimic the color of resin composites to that of natural tooth. Beside the strength, hardness, shrinkage and wear resistance, Translucency and opalescence of resin composites should also be considered as a criterion for designing the formulation of dental composites.

Venhoven et al. [63] reported that the size of filler particles and presence of chemical coupling between filler and resin plays major role for the mechanical coherence of dental composites. In the range of the conventional monomer (BisGMA, TEGDMA, UDMA, HEMA etc), they observed that chemical coupling between low particle size of glass filler and resin led to better mechanical coherence and wear resistance during an in vitro erosive wear test in erosive medium. Finally, they obtained a critical value of the filler particle size (1.3-1.5pm) for which the food fibres are not able to erode the surface so the wear resistance in the erosive medium will be increased.

Kasraei et al. [71] conducted a case study to observe the bonding strength between resin-dentin mixed with nanofiller particles. They had collected Fifty-four human intact premolar teeth and made 6 groups of nine each.The occlusal surfaces were ground and polished with silicon carbide papers. An experimental adhesive system based on acetone was mixed with fumed nanosilica filler contents that varying from 0 to 10wt.% and then the experimental adhesive agents were applied to dentin surface. The specimens were thermo cycled for 500 cycles and kept for two week in distilled water and then the micro tensile bond strength of the specimens was measured. One way ANOVA and DunnettT3 tests were applied to analyze the data. Finally, they concluded that filler content seems to be one of the important factors influencing the bond strength of dental adhesives. Maximum resin dentin bond strength was obtained with 1wt.% silanized nanosilica filled experimental adhesive system. Incorporation of silanized nanosilica up to 1wt.% the experimental adhesive system increased the resin-dentin microtensile bonding strength. Therefore, the increased in levels of nanofiller may be caused with the decrease in the resin-dentin bonds.

Goncalves et al. [72] formulated twenty compositions by varying resins BisGMA and TEGDMA mixture in the ratio of 3:7, 4:6, 5:5, 6:4 and 7:3 and barium glass filler of content 40-70wt.% in the step of 10wt. %. They analyzed the effect of variation of different content of monomer and fillers on curing depth, degree of conversion, polymerization shrinkage, polymerization stress, reaction rate, elastic modulus and loss tangent of all experimental dental composites. The finding of result indicated that the resin matrix had stronger influence on polymerization stress, degree of conversion and reaction rate, whereas filler content had stronger influence on shrinkage, modulus and loss tangent. Polymerization shrinkage and polymerization conversion rate were significantly related to polymerization stress. The main challenge faced by researcher in the development of dental material is to get formulations with low shrinkage without sacrificing degree of conversion. It was also suggested that the polymerization stress can be reduced by modifying the resin composition without reducing filler content. Karmaker et al. [73] investigated the influence of silane treatment of fillers on physical and mechanical properties such as viscosity, flexural strength, and hydrolytic degradation of experimental dental composite. The result indicated that with increased in the concentration of silane led to decrease in viscosities of the experimental composite resins. The flexural strengths of composites filled with silane treated were found more than that of composites with untreated fillers. Hence, it can be concluded that the silane treatment of filler improved the flexural strength. However, no significant difference was reported for the flexural strength of composite filled with fillers of different silane concentration. Hence, degree of strength enhancement was independent of concentration of silane added. On the other side, the resistance to hydrolytic degradation increased with silane concentration and was the highest at 1.1% silane.

Lisia et al. [74] formulated a resin composite containing a novel mono-modal inorganic filler submicron sized Ba–Si–Al glass particles and compared with experimental composite containing micro filler. Two different formulations were obtained using conventional dimethacrylate co-monomer, incorporating mass fractions of 75% micron and 78% submicron sized filler. Both experimental composites were characterized in terms of radiopacity, degree of conversion, filler resin morphology, hardness, flexural properties, fracture, surface roughness before and after simulated tooth brushing abrasion and compressive creep. Both the composites were similar in radiopacity, flexural strength, work-of-fracture, and creep. It was revealed that the submicron composite was harder but had lower flexural modulus and lower degree of conversion. Despite the submicron composite had higher gloss, no significant differences in roughness was reported before brushing. As brushing increases the roughness and decreases the gloss on both materials, but the submicron sized filler based composite retained higher gloss after brushing. The mono modal submicron glass filler system demonstrated more aesthetic properties hence have potential for use in dental application.

Nagarajan et al. [75] fabricated dental ceramic composite filled with 76 wt.% silica glass and 16wt.% nanoalumina filler particles in a polymeric resin matrix. Wear tests were conducted on a pin-on-disk tribometer with water as a lubricant to simulate the oral condition. It was found that when the load was increased from 1 to 5 N, the volumetric wear rate of dental composite increased slightly but when load was further increased to 10 N, the volumetric wear rate was increased by one order of magnitude. On further increasing in load from 10N to 20N, the volumetric wear rate was found to be independent of load. Worn surfaces were examined using SEM and TEM which revealed that a surface film had formed on the wear tracks at all loads and each film contained a mixture of alumina crystallites and glass particles. They proposed that three mechanisms occurred at the sliding contact firstly tribochemical reactions and film formation, secondly dissolution of the reacted products and finally mechanical removal of the film by micro fracture. They defined load vs. wear relation on the basis of those mechanism. Wear at lower load is due to a tribochemical mechanism, i.e., formation and dissolution of the reaction products. Wear at higher load is due to simultaneous action of tribological, chemical processes and mechanical detachment of the surface film. Finally, they concluded that the optimization of the wear behavior of this composite may require a change in the chemistry as well as the size distribution of the filler particles.

Shajiiff et al. [76] studied the effect of the filler content and monomer concentration in a microfilled composite made of conventional monomer BisGMA and TEGDMA monomers and silica filler with concentrations of 20 and 40% by weight. It was observed that between 0 and 8 days incubation with enzyme, more Bis-HPPP and TEGMA were generated at lower filler content material (20 wt. %) than the higher filler content material (40 wt. %), while the reverse effect was observed between 8 and 16 days. The data indicated that biodegradation product release profiles are dependent on the filler/resin ratios, and suggest that this parameter should be taken into consideration while assessing product release for biocompatibility issues of dental composite systems. The physical presence of filler appears to influence the release profile of products. The higher filler content composite underwent a significant surface disintegration following chemical degradation of the resin phase.

Alsharif et al. [12] evaluated the effect of nanoalumina fillers on the mechanical properties of resin based dental composites. The dental composites were prepared by adding different weight percentage (40, 50, and 60 wt.%) of silane-treated nanoalumina filler. The mechanical characterizations such as Vickers hardness and flexural modulus of the dental composites mixed with nanoalumina filler were found to be superior compared to the dental composite without silanated fillers. However, the flexural strength values of dental composites were slightly decreased as the filler loading increased. The increased in silanated filler led to decrease in the correlation between filler particles and resin matrix.

Callaghan et al. [77] evaluated the effect of varying different weight percentages (2%, 5.1%, 5.7%, and 7.6 wt.%) of glass fiber content on the wear characteristics of fiber-reinforced dental composites. Friction and wear tests were performed on Pin on disc Tribometer with the disc of similar fiber reinforced composite material with 5.1 wt.% fiber and fiber length of 3 mm. They observed that the wear volume of fiber reinforced composite was proportional to the sliding distance up to the transition period. After the transition period, the volumetric wear rate of the fiber reinforced composite depends mainly on the fiber volume fraction. Fiber reinforced composite with lower finer content 2% and 7.6% exhibited highest wear rates. This was attributed to insufficient fiber reinforcement and clustering of fibers resulting in fiber plucking of the resin matrix. Increase in fiber reinforcement up to (5.1% and 5.7 wt.%) exhibited the lowest steady-state wear rate for all loading condition. In comparison to particulate filled composite, 5.7 wt.% fiber reinforced composite performed better under wear conditions on the applied load and the sliding distance. After the transition period, the coefficient of friction depends mainly on the fiber volume fraction. The wear rate in dental composites with longer fibers was less than that of shorter fiber of same content. It can be concluded that the Fiber reinforced composites with longer fibers provide better strengthening mechanisms with respect to fiber reinforced composite with shorter fiber.

2.4 Study of mechanical and thermal behavior of dental material: This literature study describes various experimental results of mechanical and thermal properties of dental materials. Foroutan et al. [78] compared the mechanical properties of dental restorative samples having monomer system (60% BisGMA and 40% TEGDMA) and nano and micro-sized Al_2O_3 filler particles. Various mechanical properties such as flexural strength (FS), diametral tensile strength (DST), and hardness tests (H_V) were estimated. Finally, the results indicated that on adding 10 wt. % of nanoalumina filler in the resin matrix, the flexural strength increased by more than hundred percent and the diametral tensile strength by around eighty percent. FE-SEM images of worn surfaces indicated a brittle type of fracture in both the nano and micro filled based dental composite. The improvement in mechanical properties of nanofiller based dental composites were attributed to better filler/polymer interaction. It was concluded that a more efficient dispersion nanoparticle may lead to even more improved composite dental restorative materials in terms of mechanical properties. Wang et al. [79] discussed various mechanical testing required to assess the performance of dental materials. The tests discussed by him are tensile testing, compression testing, diametral compression test, flexural strength, hardness test, and resistance to fatigue etc with their characteristics and parameters.

Al-Haik et al. [80] investigated mechanical properties of natural teeth enamel, natural teeth dentine, glass ionomer cement, nanocomposite and silver amalgam fillers using a nanoindentation technique. It was revealed that the human enamel has the highest hardness and modulus for all tested materials However, traditional silver amalgam have shown better mechanical and wear performance than the nanocomposite. The glass ionomer indicated least wear resistance properties among the four tested materials. This conclusion was also supported by the fact that among the three filler the glass ionomer exhibited lowest hardness.

Khvostenkoa et al. [81] developed Bioactive glass (BAG) reinforced dental composite and reported that Bioactive glass exhibits antimicrobial properties and reminerlize the tooth tissue by releasing ion, and therefore it can be a considered as an additive for dental restorative materials. All dental composite containing Bioactive glass (BAG) was observed to be better mechanical properties than a tested commercial material Heliomolar. The analysis was done using two-way ANOVA and Tukey’s multiple comparison tests ($p \leq 0.05$). Some of mechanical properties of BAG filled dental composite were also found to be better than or comparable to published values for two other commercial composites, Filtek Z250and Filtek Supreme Plus.

El-Safty et al. [82] investigatedten dental resin-composites having three flowable, three bulk-fills and four conventionalusing nanoindentations test to determine the hardness and elastic modulus. They observed that the hardness of composite varied in the range of 0.73 GPa to 1.60 GPa whereas the elastic modulus from 14.44 GPa to 24.07 GPa. Finally, they concluded that there was a positive correlation for elastic properties and nanohardness with filler content for a specific resin matrix. Hence, for a series of BisGMA/TEGDMA system, the elastic modulus and nanohardness of the resin-composites increased significantly with increasing filler loading. It was further observed that the elastic modulus and nanohardnesses for two bulk-fill and flowable composite were found lower than those for conventional nano-hybrid composites which was due to the uniform dispersion of nanoparticle lead to proper and stronger binding between resin and filler.

Samuel et al. [83] investigated the use of mesoporous fillers for better interphase bonding between micromechanical filler and resin matrix. The use of such a micromechanical bonding interphase phenomena will eliminate the need of silane for proper binding. It was found that composite filled with mesoporous and nonporous fillers exhibited better mechanical properties than the composites filled with either of these fillers alone. Hence, the combined effect of mesoporous and nonporous materials will produce stronger dental materials that may resist hydrolysis as well as wear. The composites filled with a combination of mesoporous and nonporous spherical fillers were light cured. The reason behind the use of combination of fillers was to increase the filler loading by increasing high surface area. The mechanical properties of these composites filled with a combination of with mesoporous and nonporous fillers were also comparable to (semi-porous and nonporous fillers based composite Solitaire TM. Atai et al. [84] formulated a new resin based monomer alternative to BisGMA called BTDMA. The developed material was compared with commonly used BisGMA monomer for their Physical and mechanical properties. Polymerizations were done in the presence of Camphorquinone and DMAEMA initiator system, and revealed the same degree of conversion as BisGMA based composite. FTIR spectroscopy was used to measure Degree of conversion of the light-cured and heat-cured composites. It was observed that the mechanical properties of proposed composite are comparable with the properties of the BisGMA based composite however, its water sorption is higher. Finally, it was concluded that BTDMA indicated a promising material with good mechanical properties comparable with the BisGMA based composites, but the drawback was its water sorption which was higher due to the presence of the carboxylic acid groups in its structure. Michalek et al. [85] prepared and characterized dental composite filled with up to 2 vol. % of MWCNT in two composite series Al_2O_3/MWCNT and Al_2O_3/ZrO_2/MWCNT composites. The homogeneity of the composite powders was maintained by of freeze drying and granulation method. Addition of 1vol% of the MWCNT into the Al_2O_3, and Al_2O_3/ZrO_2 matrices resulted into increase of fracture toughness by 8% and 35% compared to the monolithic alumina reference. Incorporation of 2 vol% of the MWCNT increased the electrical conductivity from 10^{-12} S/m to $2.7x10^{-1}$ S/m in pure alumina Al_2O_3 matrix based composite. Thomaidis et al. [86] investigated the correlation of mechanical properties of four modern dental composites including a micro hybrid (Filtek Z-250), a nanofill (Filtek Ultimate), a nanohybrid (Majesty Posterior) and an ormocer (Admira). The analyses of results were done using ANOVA, Tukey post hoc test and Pearson correlation. A strong correlation was found only between hardness and Flexural Modulus.

Arcis et al. [87] developed and studied the mechanical properties of 14 composite made of matrix made up of BisDMA, TEDGMA, Bis-GMA, HEMA and reinforcing filler (micron or nanosized hydroxyapatite). Fillers were treated with a coupling agent such as citric, malic, acrylic, methacrylic acid. It was observed that addition of 50-60 % of hydroxyapatite filler particle led to increase in both of Young’s Modulus and surface hardness; however, the flexural strength decreased. Micro sized hydroxyapatite reinforced dental composite indicated better mechanical properties than nanohydroxyapatite reinforced dental composite.

Mormann et al. [88] estimated the two-body wear and tooth brushing wear rate of various artificial and natural teeth. Other parameters such as gloss and roughness measurements and Martens hardness were also determined. Nine aesthetic CAD/CAM materials and one direct resin-based nanocomposite were tested and compared with the human enamel as control sample. Two-body wear test was performed in a computer-controlled chewing simulator against human enamel as antagonist disc. 3D-surface analyzer was used to measure quantitative analysis of wear. Before and after abrasive tooth brushing of machine-polished specimens, gloss and roughness measurements were taken with the help of gloss meter and an inductive surface profilometer. Marten’s hardness of all specimens was also measured. One-way ANOVA (analysis of variance) was used to find the statistical significance of parameters. Among all the used dental material, zirconia ceramics did not show any material wear but a low wear of the enamel antagonist. Other experimental material such as CAD/CAM-silicate and-lithium disilicate ceramics, hybrid ceramics and nanocomposite indicated similar wear behavior as that of human enamel. Conventional polymer indicated highest material loss against the antagonist disk in two body wear phenomena. Gloss retention was highest for zirconium dioxide ceramics followed by silicate ceramics, hybrid ceramics and nanocomposites. Conventional polymers indicated least gloss retention. Martens hardness was also observed to be different for each of materials such as ceramics, between ceramics and composites, and between resin composites and acrylic block materials as well.

Okadaa et al. [89] investigated the effect of length of storage of some branded dental composite in saliva liquid on their surface hardness. The materials were immersed in human parotid saliva. Vickers hardness number (H_V) was measured after 1, 7, 20 and 40 days of storage in saliva. It is found that calcium and phosphorus ions of saliva were liberated and diffused into the hydrogel matrix of dental composite and strengthened the surface. Frauscher et al. [90] investigated the relationship between depth of cure (DOC) and mechanical properties of resin based dental composite by varying the monomer composition. Depth of cure was determined as the depth at which the 80% of surface hardness value was reached. One and multiple-way ANOVA, Tukey HSD post-hoc test ($\alpha = 00.05$) and partial eta-squared statistic were applied to analyze the result. It was revealed that depth of cure increased with increasing curing time. Time of curing and material properties showed the strongest effect on DOC.

2.5 Study of tribological behavior of dental materials under food slurry and acidic medium

The literature study describes various developments in the field of dental tribology in the last decade. Apart from saliva, the other major parameter associated with tribological behavior of human teeth and artificial dental oral environment includes and food particles and chewing load during mastication. Mass [91] investigated microscopic wear features on the occlusal surfaces of teeth during three body Abrasion by food particles by carrying out compression tests. It was observed that smaller sized filler particle led to less wear as compared to larger sized filler particle and it was suggested that wear could be independent of load. However, Eisenburger and Addy [92] reported that the load influenced the wear of enamel surface in acidic and neutral condition by attrition both in acidic and neutral conditions. Although such studies focused on the effects of food particles and normal load on wear of human teeth and artificial material in terms of mass loss or specific wear rate rather than investigating the mechanical of dental wear in detail.

Imfeld [93] identified six different kinds of non-carious issue including abrasion, attrition, erosion, abfraction, resorption and demastication (Table 2.2). In general, the terms dental abrasion, attrition, erosion and abfraction have been frequently used in dentistry. However, the definition and classification of dental wear are different from engineering tribology. For example in dental tribology, erosion is the surface loss due to chemical erosion i.e. corrosion which has different meaning of erosion in engineering tribology. Similarly, there is no term attrition in engineering tribology. In fact, “attrition” merely refers a two-body contact, such as tooth to tooth or tooth to denture contact.

Table 2.2 Classifications and definitions of tooth surface loss

S.N	Types of tooth surface lesions	Definition
1	Abrasion	third body wear, tooth surface wear by third body or food particle during the mastication
2	Attrition	Hard tissue loss during two body wear between tooth to tooth contact
3	Erosion	Hard tissue loss of tooth surface by acidic reaction without bacterial involvement
4	Resorption	biological degradation and assimilation of substances previously produced by the body
5	Abfraction	wedge-shape defect at the gum line
6	Demastication	During mastication, the wearing awayof human tooth or dental material by the bolus

Hence, as per definition by Imfeld, the term “erosion” used in tooth loss is similar to the term “corrosion” used in tribology [94]. In the similar context, in 2004, Grippo et al. [38] suggested that the term “erosion” should be removed from the field of dentistry and should be replaced with the term “corrosion” to denote chemical dissolution of teeth and dental material. Whereas another term abfraction is the loss of material under repeated or cyclic loading or higher bite force. Hence abfraction might potentiate tooth wear by abrasion and/or erosion. On the contrary, the term “adhesion,” which is widely used in the field of tribology, is not encountered in the dental literature. The explanation might be that dental tissue, particularly dental enamel, is similar to ceramic materials; perhaps adhesive wear would not occur at the tooth surface during the masticatory process.

Sajewicz [95] investigated and compared the wear resistance of enamel and four commercial dental materials: Arkon, Ecusit, Ful-Fil, and Filtek. It was found that Filtek demonstrated the highest wear resistance as compared to the other materials, and enamel showed the highest wear resistance when it was coupled with Ecusit, which means that Ecusit is the least destructive of all the materials tested with respect to tooth enamel. Finally he concluded that the energetic approach (the specific wear energy) can be useful for the assessment of the influence of different factors, such as environmental factors, counter body material, load, sliding speed and so on, on the tribological behavior of different materials (not only enamel or dental materials). Dental composites are key materials for dental restorations due to their aesthetics, chemical inertness, biocompatibility, and convenient clinical manipulation. They are used to restore the function, integrity, and morphology of missing tooth structure. Generally, dental composites are divided into two types: direct dental restorative composites and indirect dental restorative composites.

Nagarajan et al. [14] fabricated dental ceramic composite filled with 76 wt% silica glass and 16 nanoalumina filler particles in a polymeric resin matrix. Wear tests were conducted on a pin-on-disk Tribometer with water as a lubricant to simulate the oral condition. It was found that when the load was increased from 1 to 5 N, the volumetric wear rate of dental composite increased slightly but when load was further increased to 10N; the volumetric wear rate was increased by one order of magnitude. On further increasing the load from 10N to 20N, the wear rate was found to be independent of load. Worn surfaces were examined using SEM and TEM exposed that a surface film had formed on the wear tracks at all loads and each film contained a mixture of small γ- Al_2 O_3crystallites and glass particles. They proposed that three mechanisms occurred at the sliding contact firstly tribochemical reactions and film formation, secondly dissolution of ingredients and finally mechanical removal of the film by micro fracture. They defined load vs. wear relation on the basis of those mechanism. Wear at lower load is due to a tribochemical mechanism, i.e., formation and dissolution of the reaction products. Wear at higher load is due to simultaneous effect of both the phenomena of tribochemical processes and mechanical detachment of the surface film. Finally they concluded that the optimization of the wear behavior of this composite may require a change in the chemistry as well as the size distribution of the filler particles.

Ferracane et al. [96] developed dental material for posterior restorations. They reported that the wear resistance of dental material has been substantially improved by changes in formulation and is the strategy followed by many researchers to solve dental material issue. However, only few literatures are available to support this conclusion for large restorations. They concluded that wear may still be a significant mode of failure for person suffering from bruxing, clenching habits and chewing Tobacco habit. In this regard, research should develop in vitro method for predicting this multifactorial phenomenon. In light of the collective evidence, same conclusion is made by Soderholm and Richards [97]. In the most of restoration, concerns are no longer considered to be major but for posterior and large restoration, the wear resistance of dental composite restoratives is still be a concern in direct occlusal contact, or for those patients suffering from bruxism, clenching behavior and Tobacco habit. Wear study remains as important concerns in such cases for dental researchers. There are many questions to address when performing in vitro wear evaluations, and to date, little has actually been accomplished to standardize test methods or data reporting. Critical questions include the following:

- What type(s) of wear needs to be simulated using wear simulating device (i.e. abrasive, attritive, erosive, adhesive, abfraction), and what quantity should be reported (i.e. wear depth, area, volume, specific wear rate etc.)?
- What types of wear simulator device should be used (reciprocating, sliding etc)?
- What assurances should the user required to provide in order to give the audience confidence in the results produced by the simulation/measuring device (i.e. accuracy, precision, performance of standards, etc.)

Sajewicz et al. [98] developed a new tribometer which simulates oral kinematic conditions and determines the effect of different loading produced during masticatory process. Tribological behaviors such as two body and three body wear of dental materials and hard tooth tissues were performed. The finding of results indicated that the tribometer was able to simulate the oral behavior during mastication. The Tribometer may be employed in the dentistry as well as in the engineering field. Friction and Wear behavior of dental enamel occurring during two- and three-body wear tests were observed. The essential influence of the loading pattern on the wear rate and friction kinetic was shown. Simultaneously, similar surface texture for all groups of the tests was found. The EDS analysis allowed to find the transfer of the material from the steel counter sample to the enamel surface.

Wang et al. [99] evaluated volumetric wear of dental material by considering dental restorative material specimen as the pin. For the abrasive counter face, a diamond grinding wheel was used. The volumetric wear rate was estimated from the change of length and cross sectional area of specimen. They found that a glass bead filled BisGMA/TEDGMA resin indicated increase in relative wear rate with volume fraction and decrease in average particle diameter of glass bead.

Arsecularatne et al. [100] evaluated wear behavior of an enamel cusp sliding on a flat enamel specimen during in vitro reciprocating wear tests under distilled water condition. They analyzed wear performance of their experimental dental material for two wear models developed for ceramics such as tensile crack model and contact severity model. It was finally observed that contact severity model was shown to be more suitable for enamel. Its application to enamel revealed a marked influence of coefficient of friction on the enamel wear rate. Moreover, depending on the coefficient of friction, enamel wear can be severe under forces generated during normal operation of teeth.

Scherge et al. [101] reported that wear rate of dental material is a complex phenomenon. It depends on the dental material or tooth material, the type of toothbrush (speed and profile) and the brushing slurry concentration. Relative dentin abrasivity (RDA) method is used to measure Tooth wear in abrasion experiments using a toothbrush. It was observed that RDA provides simulated wear process by finding wear rate of brush versus tooth in micro-tribological setup. This setup allowed to correlate friction and wear behavior to topography and structure of the tooth and will enable the evaluation of cleaning processes microscopically in the future. In addition, results of this work were in agreement with the literature results of RDA experiments.

Romalho et al. [102] evaluated the effects of temperature variation on the mechanical and wear properties of three commercial posterior restorative composite materials, Synergy, Surefil and Alert. They observed that one composite Surefil was the least sensitive to temperature variation, while another composite Synergy indicated best resistance to wear with respect to temperature variation. It is noticeable that the performance of the dental composites in an oral environment could be significantly affected by temperature, especially concerning tribological performance; namely abrasion, resistance and fracture.

Study on erosive behavior of teeth in different media as well as on different depth of polymerization is investigated by Zheng et al. [103]. The in vitro erosion behavior of human tooth enamel was performed at different depth in the medium of citric acid solution with pH 3.20. The time of erosion was kept at 3 min. The wear characterization of eroded surfaces was examined using Nanoscratch Tester. It was concluded that the erosion resistance of human enamel strongly depended on its location along axial direction of tooth. The wear rate was characterized mainly by decreased hardness and slight substance loss in the outer enamel. For the interior enamel, a honeycomb like structure appeared on the eroded surface as a result of severe dissolution of enamel, and significant substance loss occurred. They further investigated the in vitro erosion behavior of human tooth enamel in citric acid solution of pH 3.2 [104]. Microscopic examinations showed that no obvious substance loss occurred on the enamel surface at the early stage of erosion, and the erosive lesion was characterized mainly by partial demineralization and decreased hardness.

In recent research, Guo et al. [105] incorporated different weight percentage (2.5% or 5.0%) of zirconia–silica (ZS) or zirconia–yttria–silica (ZYS) ceramic nanofibers in resin material and studied their mechanical properties including energy at break of the dental composites. They reported that reinforcement of nanofibers in resin based composites improved the flexural strength, modulus and energy at break characteristics respectively.

2.6. Implementation of Design of Experiments (DOE) and optimization techniques: The literature and material scientist suggest that the dental composite materials must be composed of multi-ingredients broadly classified under the monomer, fillers, coupling agent, polymerization initiators, pigment, and optical modifier. Selection of appropriate ingredients, formulation designing, understanding prevailing dental tribology and developing formulation based on the experimental results are the real challenge faced by scholars and industries. There are three main problems in the development of dental material viz. how to select the raw material, how to find interaction among the components and how to optimize the formulation. Sometimes researchers make use of optimization tools to predict the behavior of such materials and analyze the experimental result. Some of the literatures targeting these problems are reported here. Khvostenkoa et al. [81] applied two-way ANOVA and Tukey's multiple comparison test ($p \leq 0.05$) for analyzing the experimental result for the dental composite filled with bioactive glass (BAG). Thomaidis et al. [86] characterized four modern dental resin composites. Their mechanical properties were tested, their properties were statistically analyzed by ANOVA, Tukey post hoc test ($a = 0.05$) and Pearson correlation. Beigi et al. [106] studied and evaluated crosslink density of ternary thiolene- methacrylate and mechanical properties such as fracture toughness, flexural and dynamic mechanical properties, and systems. They compared the result with corresponding conventional methacrylate system. ANOVA and Tukey HSD tests (significance level = 0.05) were used to compare the data. Arcis et al. [87] measured and analyzed mechanical properties of several composite made of matrix (BisDMA+ TEDGMA +BisGMA + HEMA) and a reinforcing filler (micro or nanoparticle of hydroxyapatite). Surface was modified by using a coupling agent (citric, malic, acrylic, methacrylic acid). Five specimen of 14 different composite were prepared for each mechanical test like flexural strength, Young Modulus, Vickers hardness. Few computations are done like mean value, standard deviation, ANOVA, Newman Keul Multiplication test. Tamura et al. [64] applied ANOVA to investigate the level of significance of different parameters such as (size, shapes, surface textures, structures and contents of filler) on the wear and mechanical properties of dental composite using two-way ANOVA. Kasraei et al. [71] did a case study to evaluate the influence of adding nanofiller particles in dentin bonding agent on resin-dentin bond strength.

Design and development of dental composite materials involving optimization of interdependent properties has become very complex and complicated. The proposed materials should have good mechanical properties and should also possess low wear rate under varying load, speed and temperature conditions. The selection of an optimal dental composition from many alternatives on the basis of different attributes is a Multiple Attributes Decision-Making (MADM) problem. In the past, several researchers used different MADM approaches such as: TOPSIS (Technique for Order Preference by Similarity to Ideal Solution), VIKOR (Vise

Kriterijumska Optimizacija Kompromisno Resenje), AHP (Analytical Hierarchy Process), ELECTRE (Elimination and Choice Translating Reality), GRA (Grey Relation Approach) and PSI (Preference Selection Index)to various areas such as science, engineering, management etc. [107-112]. GRA is an outranking technique for a finite set of alternatives to be ranked and selected among performance defining attributes which are often conflicting. It is also a simple ranking method in conception and application compared with the other methods for multi-attribute analysis and has been successfully applied in several fields [113, 114].

2.7 The Knowledge Gap in Earlier Investigations

The literature review on resin based composite dental material reveals the following research gap, through which the objectives of the present research work can be set.

The review of literatures presented above and summarized reveals following research gaps that need to be paid attention:

1. The research on filler ingredients e.g. comparative analysis of variation in different fillers, its type, size on the wear performance of dental materials are lacking in literatures.
2. The study related to silane treatment of filler and their effect of wear characterization is rare.
3. Research and Development to find an alternative for BisGMA have been considered as a challenge in the field of dentistry and any investigation in this regard would be beneficial in the development of dental materials.
4. The study of effect of the filler loading and monomer concentrations on the properties such as hardness, glass transition temperature (Tg) and polymerization shrinkage, and shrinkage-stress is still untouched by the researcher.
5. The main challenge faced by the researcher in the field of dental material is to fabricate the dental composite with low shrinkage without reducing degree of conversion. Since reducing shrinkage at the loss of degree of conversion is not the wise idea. Hence, balancing low shrinkage and maintaining high conversion is the best way to find the best formulation.
6. Literatures based on utilization of gypsum in the biomedical or especially in dentistry are scarcely available.

7. Studies carried out worldwide on wear behavior of composites have largely been experimental and use of statistical techniques in analyzing wear characteristics is rare.
8. Taguchi method, in spite of being a simple, efficient and systematic approach to optimize designs for performance, quality and cost, is used only in a limited number of applications worldwide. Its implementation in parametric appraisal of wear processes has hardly been reported.

2.8 Proposed objectives in my research work

The objectives of this work are outlined as follows

- Fabrication of new class of particulate filled and unfilled bionanocomposite by light curing techniques for dental restoration application under low shrinkage without sacrificing degree of conversion.
- Characterization of physical (such as void content, water sorption, solubility) and chemical properties (such as depth of cure, degree of conversion, polymerization shrinkage) of the proposed unfilled and particulate filled dental materials.
- Characterization of mechanical and thermo-mechanical properties such as hardness, compressive strength, flexural strength, thermo-gravimetric analysis and dynamic mechanical analysis are done
- Study the abrasive wear characteristics and coefficient-of-friction analysis of the dental composites under food slurry and acidic mediums by using L_{16} Taguchi orthogonal array design approach.
- Finally, Gray Relational Analysis optimization techniques was implemented by taking into consideration of the physical, chemical, mechanical and wear characteristics of the unfilled and particulate filled dental composites in order to get the optimal composition for dental restorative application.

Chapter Summary

This chapter has provided

- An exhaustive review of research works on various aspects of fiber and particulate reinforced polymer composites reported by various investigators.
- The knowledge gap in earlier investigations.
- The objectives of the present work.

The next chapter describes the materials and methods used for the processing of the composites, the experimental planning, Taguchi method, the physical and mechanical characterization, thermal and thermo-mechanical properties.

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Chapter 3

Materials and Methodology

Chapter 3

MATERIALS AND METHODS

This chapter briefly presents/discuss, properties and specifications of the selected ingredients/materials, design of different sets of friction composite formulations for the research work, the standard fabrication procedure, the processing conditions adopted as per ASTM, ISO or Industrial standard and the different characterization performed in order to justify commercial viability of the product.

3.1 Materials selection, their properties and specifications

The research gaps presented and discussed in the chapter-2 motivate us to explore research for the development of dental material for better properties in terms of physical, mechanical, chemical and tribological characterization than the existing materials. For the same purpose, following materials are chosen as listed in Table 3.1.

Table 3.1 List of materials used in the research work

S.N	Type of ingredient	Name of element	Supplier
1.	Resin	Bis-GMA	EsstechInc, Essington, PA, USA
2.		TEGDMA	TCI, Tokyo, Japan
3.		Camphorquinone (CQ)	Spectrochem, Mumbai, India
4.		Ethyl 4-dimethylamino benzoate (EDMAB)	Sigma Aldrich, Bangalore, India
5.	Filler	Alumina particle size 60nm	Nanotech Technology Pvt ltd, Bangalore, India
6.		Zirconia particle size 60nm	Nanotech Technology Pvt ltd, Bangalore, India
7.		Silica particle size 60nm	Nanotech Technology Pvt ltd, Bangalore, India
8.		Gypsum powder	Metro Trading Corporation, Jaipur, India
9.	Binding agent	Mithacryloxypropyltrimethoxy silane	TCI, Tokyo, Japan

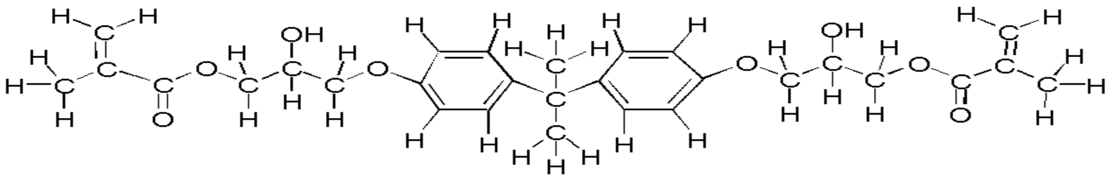
The detailed properties and specification of the selected materials are presented below:

3.1.1BisphenolA-Glycidyl Methacrylate (BisGMA)

Methyl methacrylate was introduced to dentistry during the 1930s. Earlier, it was used for only denture base material. Heat curing was used to harden the base materials. During the 1940s, German researchers introduced cold-curing process to cure the methacrylatesmonomer. The introduction of this curing process provided provision of curing the plastic restorations directly into the oral cavity. However, methyl methacrylates exhibited a major problem with more polymerization shrinkage as much as 21vol. % (7% linearly).

Table 3.2 General specifications of the BisGMA (supplier's data)

S.No	Property		Specifications
1.	Appearance	:	Clear,viscousyellowtoambercolor.
2.	Odor	:	Penetrating,mustyodor
3.	Odorthreshold	:	ND
4.	Physicalstate	:	Liquid
5.	PH	:	6.8to7.2
6.	Flashpoint:	:	>240°F,>115°C(Seta flash)
7.	Evaporationrate	:	NA
8.	Flammability(solid,gas)	:	NA
9.	Flammablelimit,airvol%		
	lower	:	NE
	upper	:	NE
10.	Vaporpressure	:	ND
11.	Vapordensity(air=1)	:	ND
12.	Specificgravity(h2o=1)	:	1.15 @4°C,39.2°F
13.	Solubility(water)	:	Negligible
14.	Partitioncoefficient:water/oil	:	ND
15.	Auto ignitiontemperature	:	NE
16.	Decompositiontemperature	:	ND
17.	Percentvolatilew/w%	:	Negligible



bisGMA

Figure 3.1 The chemical structure of BisGMA

Later pre-polymerizedmethyl methacrylate beads were mixed with the monomer to reduce the polymerization shrinkage to around 3.5 % linearly. However, such shrinkage was still too excessive and created clinical issue to the restoration. Dr. Raphael Bowen solved the problem of excessive shrinkage by replacing the epoxy groups with methacrylate groups. He produced a dimethacrylate that was called bisGMA or "Bowen's resin". In vitro, this material behaved well, but when tried clinically, the material did not cure. The base monomer BisGMA has advantageof its higher molecular weight and low polymerization shrinkage. However, the stiff central backbone structure and the pending OH groups (Figure 3.1) made this monomer also quite viscous. Therefore, high viscosity of resin resists in mixing more filler particles in the monomer. On the other side, the major advantage of having high viscosity is that the material retains its shape fast and prevents sedimentation of fillers particles. The general specifications of the BisGMA are listed in Table 3.2.

3.1.2 Triethylene Glycol Dimethacrylate (TEDGMA)

Triethylene Glycol Dimethacrylate is a hydrophilic difunctionalmethacrylic monomer having three –CH_2OH- group providing high crosslink density, low shrinkage, flexibility and impact strength(Figure 3.2).It is employed as alow viscosity reactive diluent as well as cross linking agent for various applications such as dental polymers, anaerobic adhesives, sealants, UV-cured coatings, photopolymers for solder masks and circuit boards, and fuel-resistant metal parts, wood impregnation resins, glass coatings, ion exchange resins, cosmetic resins, and contact lenses. TEGDMA can be used to improve the following properties to polymers such as adhesion, weather resistance, flexibility, impact resistance, hydrophilicity, heat resistance, wear resistance etc. However, in dentistry, the major purpose of using Triethylene Glycol Dimethacrylate is to reduce the viscosity of BisGMA i.e. as diluents so that more filler particles can be incorporated. Triethylene Glycol Dimethacrylateforms copolymers with acrylic acid and its salts, amides and esters, and with methacrylates, etc.Triethylene Glycol Dimethacrylate readily undergoes addition reactions with a wide variety of organic and inorganic compounds. The general specifications of TEDGMA are listed in Table 3.3

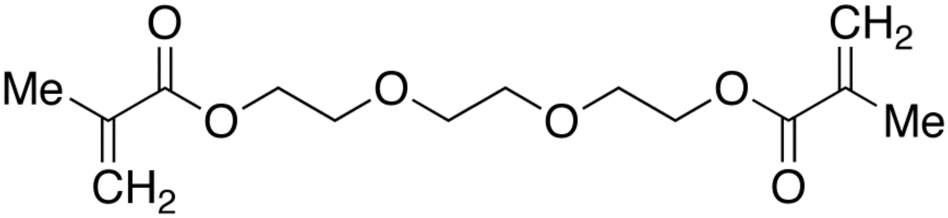


Figure 3.2 The chemical structure of TEDGMA

Table 3.3 General specifications of the TEDGMA (supplier's data):

S.No.	Property	Specifications
1.	Molecular formula, molecular mass	$C_{14}H_{22}O_6$ 286.3 kg/kmol
2.	Assay (Gas chromatography)	min. 95%
3.	Total ester, wt.	min. 99%
4.	Water content (DIN 51777)	max. 0.2%
5.	Color on dispatch (APHA, DIN 53409)	max. 100
6.	Standard stabilization (GC)	250±100 ppm MEHQ
7.	Appearance	Colorless
8.	Methacrylic acid (DIN EN ISO 2114)	max. 0.2%
9.	Physical form	clear liquid
10.	Density at 25 °C	1.092 g/cm3
11.	Boiling point	>300 °C at 1013.25 h Pa 170–172 °C at 6.67 h Pa 162 °C at 1.6 h Pa
12.	Viscosity at 20 °C	12 m Pa ·s
13.	Flash point	169 °C
14.	Index of refraction, 20 °C	1.4600
15.	Vapor pressure, 30 °C	6.67 h Pa
16.	Surface tension	36.5 dynes/cm
17.	Functionality, theoretical	2
18.	Water solubility, wt. at 20 °C	2.6%
19.	Freezing point	–52 °C

3.1.3 Camphorquinone

Camphorquinone (CQ) is a visible-light-sensitive photo initiator responsible for initiating free-radical polymerization. It has adiketone structure as shown in Figure 3.3. Camphorquinone absorbs blue visible light energy in the region of 400 to 500 nm with a peak at 468nm. Camphorquinone absorbed all the photons associated within this frequency range to excite them from their ground state to short-lived, activated triplet state.

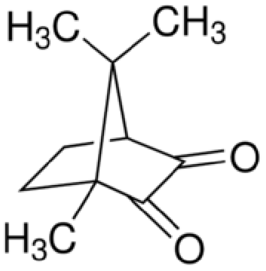


Figure 3.3 The chemical structure of Camphorquinone

These excited triplets initiates polymerization by forming alkyl free radical with an amine co-initiator. The general specification of the Camphorquinone is listed in Table 3.4.

Table 3.4 General specifications of the Camphorquinone (supplier's data)

S.No	Property		Specifications
1.	Appearance Form :	**:**	Crystalline
2.	Colour :	**:**	Yellow
3.	Melting point/freezing Point	**:**	Melting point/range: 197-203 °C-lit.
4.	Incompatible materials	**:**	Strong oxidizing agents

3.1.4 Ethyl 4-dimethylaminobenzoate (EDMAB)

A polymerization accelerator called co-initiator (mostly amines) is also needed to complete photo polymerization process. One of the most common amine is ethyl 4-(dimethylamino) benzoate (EDAB) as shown in Figure 3.4. The quantity of polymerization accelerator is preferably in the range of about 0.10 to 2.00 wt. % of resin matrix. The quantity of polymerization accelerator also depends up on quantity of photo initiator. The quantity of amine should be four times the quantity of Camphorquinone. Other tertiary amines may be used such as, for example, tri-ethanol amine, 4-(dimethylamino) -phenethyl alcohol, Dimethyl Amino Ethyl Methacrylate. The general specifications of EDMAB are listed in Table **3.5.**

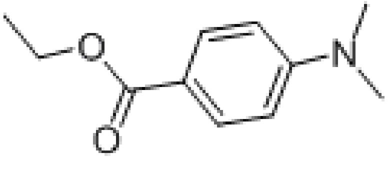


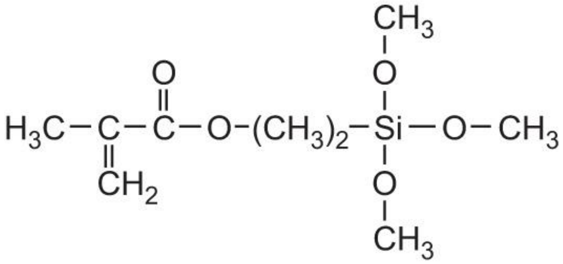
Figure 3.4 The chemical structure of EDMAB

3.1.5 Mithacryloxypropyltrimethoxysilane: The major purpose of a silane is to bind the filler to the resin. The most commonly used silane is Mithacryloxypropyltrimethoxysilane(MPS) having three methacryloxy (-OCH_3) group on the silicon as shown in Figure **3.5**. The silane treatment of filler results into formation of siloxane group (Si-O-Si). The interfacial strength between the resin and filler is increased resulting to improve physical, mechanical and wear properties of composite materials.. The general specifications of EDMAB are listed in Table **3.6.**

Table 3.5 General specifications of the EDMAB (supplier's data):

S.No	Properties	:	Specification
1	mp	:	63-66°C(lit.)
2	bp	:	190-191°C
3	density	:	1.06
4	Fp	:	190-191°C/
5	Water Solubility	:	Insoluble
6	BRN	:	2210233
7	Stability:	:	Stable. Incompatible with reducing agents, oxidizing agents, bases, acids.

The silane agent does this by preventing hydrolytic breakdown along the filler/matrix interface which may result in cracking of the resin and by allowing stress transfer between the filler and matrix (Figure 3.5).



$$H_3C-\underset{\underset{CH_2}{\|}}{C}-\overset{\overset{O}{\|}}{C}-O-(CH_3)_2-\overset{\overset{CH_3}{|}}{\overset{O}{|}}{\underset{\underset{CH_3}{|}}{\underset{O}{|}}{Si}}-O-CH_3$$

Figure 3.5 The chemical structure of Mithacryloxy propyl trimethoxysilane

Table 3.6 General specifications of the Mithacryloxy propyl trimethoxysilane (supplier's data):

S.No	Properties	:	Specification
1	Experimental Boiling Point	:	95-100 °C / 3 mm (284.9796-292.3254 °C / 760 mmHg)
2	Experimental Flash Point	:	123 °C
3	Experimental Gravity	:	1.059 g/mL
4	Experimental Refraction Index	:	1.429

3.1.6 Filler material

3.1.6.1 Silica Nanofiller [52, 60, 65, 70, 71]

A silicon dioxide nanoparticle, also known as silica nanoparticle or nanosilica, exhibits the properties of better stability, low toxicity and ability to be functionalized with a range of molecules and polymers. According to structure, nanosilicacan be of two types for examples P-type and S-type. The P-type nanosilica possesses numerous nanoporeswith a pore volume of 0.61 ml/g. The S-type particles have smaller surface area than P- type whereas P-type nanosilica particles reflect higher ultraviolet light as compared to the S-type. Silicon belongs to Block P, Period 3 while oxygen belongs to Block P, Period 2 of the periodic table. Table 3.7 provides the chemical properties of silicon dioxide.

Table 3.7 Chemical properties of silicon dioxide (supplier's data):

Chemical Composition			
Chemical symbol	SiO_2		
CAS No	7631-86-9		
Group	Silicon 14	**Element**	**Content (%)**
	Oxygen 16	Silicon	46.83
		Oxygen	53.33
Electronic configuration	Silicon [Ne] $3s^2$ $3p^2$		
	Oxygen [He] $2s^2$ $2p^4$		

Physical Properties

Silicon dioxide nanoparticles appear in the form of a white powder. The physical properties of nanosilica are presented in Table 3.8.

Table 3.8 Physical properties of these nanoparticles (supplier's data):

Properties	**Metric**	**Imperial**
Density	2.4 g/cm^3	0.086 lb/in^3
Molar Mass	59.96 g/mol	-

Thermal Properties

The thermal properties of silicon dioxide nanoparticles are given in the Table 3.9.

Table 3.9 Thermal properties of silicon dioxide nanoparticles (supplier's data):

Properties	**Metric**	**Imperial**
Melting Point	1600°C	2912°F
Boling Point	2230°C	4046°F

Applications

The major applications of silica nanoparticles include:

- As an additive for rubber and plastics
- As a strengthening filler for concrete and other construction composites
- As a stable, non-toxic platform for biomedical applications such as drug delivery, artificial joint materials.

3.1.6.2 AluminaNanofiller [51, 53, 70, 72, 82]: An aluminum oxide nanoparticle, also known as alumina nanoparticle or nanoalumina, exhibits the properties of improving electrical conductivity, toughness and ductility, and hardness and strength etc. compared to virgin material. The application of nanoalumina is increasing day by day.

In periodic table, Aluminum is placed at Block P, Period 3, while oxygen is placed at Block P, Period 2.Nanoalumina particles are spherical and appear as white powder.

Chemical Properties

The chemical properties of aluminum oxide nanoparticles are outlined in the following Table 3.10

Table 3.10 Chemical properties of aluminum oxide nanoparticles(supplier's data):

Chemical Data			
Chemical symbol	Al_2O_3		
CAS No.	1344-28-1		
Group	Aluminum 13	**Element**	**Content (%)**
		Aluminum	52.92
	Oxygen 16	Oxygen	47.04
Electronic configuration	Aluminum [Ne] $3s^2 3p^1$		
	Oxygen [He] $2s^2 2p^4$		

Physical Properties

The physical properties of aluminum oxide nanoparticles are given in the following Table 3.11.

Table 3.11 Physical properties of aluminum oxide nanoparticles(supplier's data):

Properties	Metric	Imperial
Density	3.9 g/cm^3	0.140 lb/in^3
Molar mass	101.96 g/mol	-

Thermal Properties

The thermal properties of aluminum oxide nanoparticles are provided in the Table 3.12below.

Table 3.12 Thermal properties of aluminum oxide nanoparticles(supplier's data):

Properties	Metric
Melting point	2040°C
Boiling point	2977°C

Applications

The major applications of nanoalumina include integrate circuit base boards, Transparent ceramics, high-pressure sodium lamps, and EP-ROM window, YAG laser crystals, cosmetic fillers, Single crystal, ruby, sapphire, sapphire, and yttrium aluminum garnets, High-strength aluminum oxide ceramic and C substrates, Packaging materials, cutting tools, high purity crucible, winding axle, and furnace tubes, Polishing materials, glass products, metal products, semiconductor materials, Plastic, tape, and grinding belts, Paint, rubber, plastic wear-resistant reinforcement, and advanced waterproof materials, Catalyst, catalyst carrier, analytical reagents, Vapor deposition materials, special glass, fluorescent materials, composite materials and resins etc. In the liquid form, nanoalumina particles are used for the applications such as Plastics, rubber, ceramics, refractory products, to improve ceramics density, smoothness, fracture toughness, creep resistance, thermal fatigue resistance, and polymer products wear resistance

3.1.6.3 ZirconiaNanofiller [82, 84]: A zirconium oxide nanoparticles, also known as Zirconia nanoparticle or nanozirconia exhibits the properties of improving aesthetic look, hardness and strength, to reduce shrinkage etc. compared to virgin material. nanozirconia(ZrO_2) are available in the form of nanodots, nanofluids and nanocrystals. They are often doped with yttrium oxide, calcia or magnesia. In periodic table, zirconium isplaced at Block D and Period

5 and oxygen is placed at Block P and Period 2. nanozirconia appears in white powder form. The chemical, physical and thermal properties of nanozirconiaare presented in Table 3.13, Table 3.14 and Table 3.15.

Table 3.13 Chemical properties of zirconium oxide nanoparticles(supplier's data):

Chemical Data			
Chemical symbol	ZrO_2		
CAS No	1314-23-4		
Group	Zirconium 4	**Element**	**Content (%)**
		Zirconium	74.03
	Oxygen 16	Oxygen	24.34
Electronic configuration	Zirconium [Kr] $4d^2$ $5s^2$ Oxygen [He] $2s^2$ $2p^4$		

Table 3.14 Physical properties Zirconium oxide nanoparticles(supplier's data):

Properties	**Metric**
Density	5680 kg/m^3
Molar Mass	231.891 g/mol

Thermal Properties

Table 3.15 Thermal properties of zirconium oxide nanoparticles(supplier's data):

Properties	**Metric**
Melting Point	2715°C
Boiling Point	4300°C

Applications

The major applications of nanozirconia are in ceramics for making ceramic pigments, porce lain glaze, etc. , in making artificial jewellery, in making abrasive, insulating and fire-retarding materials, optical storage, light shutters and stereo television glasses.

3.1.6.4 Gypsum Powder

Gypsum is made artificially or obtained from the natural sources such as stone waste. It has two molecules of water for each molecules of calcium sulfate Being a non-toxic material and source of calcium, gypsum has recently been introduced as a filler material in the biomedical engineering application. Non toxic mineral gypsum has been recognized as very helpful to human, animal,plant life and the environment. Gypsum is used as a soil additive, to create surgical and orthopedic casts, as a color additive for drugs and cosmetics, a primary ingredient in tooth paste, as a food additive. Its major applications as a food additive includes as an ingredient in canned vegetables, flour, white bread, ice cream, blue cheese, and other foods . Gypsum A non-toxic mineral, gypsum can be helpful to humans, animals, plant life, and the environment (Table 3.16).

Table 3.16 Physical and chemical properties of Gypsum(supplier's data):

Appearance (Color)	:	White Appearance
(Form)	:	Powder or Chunks
Complexiometric	:	EDTA 28.5 - 30.3 %
% Calcium ICP Major Analysis Confirms	:	Confirmed
Calcium Component Trace Metal Analysis		
Purity	:	< 100.0 ppm
Meets Requirements	:	>=99.99% Based On Trace Metals Analysis

3.2 Fabrication of Dental Composite

Preparation of the dental resin composite:

1. The resinous matrix (50 wt% BisGMA + 49 wt% diluents monomer, TEGDMA) are mixed in a container and kept under sonication for 2 h to obtain a homogeneous mixture.
2. The Camphorquinone (0.4 wt %) is added to the resin matrix as a polymerization initiator followed by the addition of Ethyl-4-dimethylamino benzoate (EDMAB) (0.6 wt %) as an accelerator. The mixture is stirred thoroughly up to 6 h to ensure uniform distribution.
3. The container is covered with aluminum foil to reduce light initiated polymerization.
4. Filler particles undergo an ultrasonic treatment in acetone for 10 minutes prior to mixing with the resin.(i.e. The fillers are kept under continuous vacuum at 100^{o} C for 2 h additionally maintained under vacuum for 10 h in order to ensure the removal of the entrapped moisture and volatile matter followed by slow cooling under vacuum to room temperature.
5. Four different set of composites are fabricated (as per proposed formulation).
6. In initial mixing attempts it can be observed that micro-sized filler particles are easily dispersed in the resin matrix to a rather high proportion of 60 wt. %. On the other hand, maximum amount of nano-sized filleradmitted by the matrix can be up to around 30 wt. %.

Inserting larger amounts increases the viscosity of the composites beyond the handling capabilities.

3.3 Designation and detailed composition of composites

Table 3.17 Detail composition of nanoalumina filled dental composite

Sample Designation	Composition
NADC-0	Resin + Filler (0% ST-Al_2O_3+ 3% SiO_2 + 3% ZrO_2 + 3% Gypsum)
NADC-1	Resin + Filler (1% ST-Al_2O_3+ 3% SiO_2 + 3% ZrO_2 + 3% Gypsum)
NADC-2	Resin + Filler (2% ST-Al_2O_3+ 3% SiO_2 + 3% ZrO_2 + 3% Gypsum)
NADC-3	Resin + Filler (3% ST-Al_2O_3+ 3% SiO_2 + 3% ZrO_2 + 3% Gypsum)

Here NADC-0, 1, 2, 3 means filled dental composite filled with 0,1,2,3 wt.-% silane treated nanoalumina, ST-Al_2O_3 means silane treated nanoalumina filler, Resin matrix includes 50 wt.-% BisGMA, 49 wt. % TEGDMA, 0.2 wt.-% CQ and 0.8 wt.% EDMAB

Table 3.18 Detail composition of nanozirconia filled dental composite

Sample Designation	Composition
NZDC-0	Resin + Filler (3% Al_2O_3 + 3% SiO_2 + 0% ST-ZrO_2 + 3% Gypsum)
NZDC-1	Resin + Filler (3% Al_2O_3 + 3% SiO_2 + 1% ST-ZrO_2 + 3% Gypsum)
NZDC-2	Resin + Filler (3% Al_2O_3+ 3% SiO_2 + 2% ST-ZrO_2 + 3% Gypsum)
NZDC-3	Resin + Filler (3% Al_2O_3 + 3% SiO_2 + 3% ST-ZrO_2 + 3% Gypsum)

Here NZDC-0, 1, 2, 3 means filled dental composite filled with 0,1,2,3 wt.-% silane treated nanozirconia, ST- ZrO_2means silane treated nanozirconia filler, Resin matrix includes 50 wt.-% BisGMA, 49 wt. % TEGDMA, 0.2 wt.-% CQ and 0.8 wt.% EDMAB

Table 3.19 Detail composition of nanosilica filled dental composite

Sample Designation	Composition
S-0	Resin + Filler (3% Al_2O_3 + 0% ST-SiO_2 + 3% ZrO_2 + 3% Gypsum)
S-1	Resin + Filler (3% Al_2O_3 + 1% ST-SiO_2 + 3% ZrO_2 + 3% Gypsum)
S-2	Resin + Filler (3% Al_2O_3 + 2% ST-SiO_2 + 3% ZrO_2 + 3% Gypsum)
S-3	Resin + Filler (3% Al_2O_3 + 3% ST-SiO_2 + 3% ZrO_2 + 3% Gypsum)

Here NSDC-0, 1, 2, 3 means filled dental composite filled with 0,1,2,3 wt.-% silane treated nanosilica ST-SiO_2 means silane treated nanosilica filler, Resin matrix includes 50 wt.-% BisGMA, 49 wt. % TEGDMA, 0.2 wt.-% CQ and 0.8 wt.% EDMAB

Table 3.20 Detail composition of gypsum filled dental composite

Sample Designation	Composition
G-0	Resin + Filler (3%Al_2O_3 + 3%SiO_2 + 3%ZrO_2 + 0% ST-Gypsum)
G-1	Resin + Filler (3%Al_2O_3 + 3%SiO_2 + 3%ZrO_2 + 1% ST-Gypsum)
G-2	Resin + Filler (3%Al_2O_3 + 3%SiO_2 + 3%ZrO_2 + 2% ST-Gypsum)
G-3	Resin + Filler (3%Al_2O_3 + 3%SiO_2 + 3%ZrO_2 + 3% ST-Gypsum)

Here MGDC-0,1,2,3 means filled dental composite filled with 0,1,2,3 wt.-% silane treated gypsum particle, ST- Gypsum *means silane treated gypsum micron filler, Resin matrix includes 50 wt.-% BisGMA, 49 wt. % TEGDMA, 0.2 wt.-% CQ and 0.8 wt.% EDMAB.*

3.4 Physical andChemical Characterization

The dental composite is fabricated with the silane treated filler. For the filler treatment, 95wt.-% ethanol / 5wt.-% water solution is prepared and adjusted the pH 4.5–5.5 with acetic acid and then 15wt.-% filler particles relative to silaneis added to the solution. The filler particles are added to the treatment solution and stirred for approximately 1 h using a magnetic stirrer (REMI 5mlh Plus). The mixture is filtered then washed with ethanol and then the treated filler is dried in an oven at 80°C for 24 h.

3.4.1 Fourier Transformed Infra Red Spectrometer (FT-IR Analysis)

Perkin Elmer FT-IR Spectrum 2 is a compact, easy to use, powerful instrument with fully integrated, universal sampling system for measurements in the range of 4100-400 cm^{-1} for liquid (in KBr cell) and solid (in KBr pellets) samples (Figure 3.6).

Both treated and untreated filler particles are also compacted into thin pellets and characterized using Fourier transform infrared (FTIR) spectroscopy (Perkin–Elmer Spectrum One) in the transmission mode over the wave number range of 400–4000 cm^{-1} with a resolution of 4 cm^{-1} performing 8 scans using ATR (Attenuated Total Reflection) Method.

3.4.2 Transform electron microscope TEM Analysis:

The Tecnai G^2 20 S-Twin is a 200kv transmission electron microscope designed to offer high resolution imaging and analysis solution for life sciences, material science, nanotechnology and the semiconductor and data storage industries. The Tecnai G^2 supports a wide range of techniques including high resolution scanning S/TEM diffraction, chemical analysis and 3D tomography. The on axis BF/DF detectors provide the Z-contrast imaging and EELS. The high angle, annular dark field detector generates atomic resolution dark field STEM images. The equipment provides a point resolution of 0.24 nm, line resolution of 0.14 nm and STEM resolution of 1.0 nm. EDAX gives the elemental composition of material.Silane treated and untreated filler are compacted in Cu grid for Transmission Electron Microscope (Tecnai G^2 20 S-Twin, USA) characterization (Figure 3.7).

Figure 3.6 Fourier TransformInfra red Spectroscopy

3.4.3 Field Emission Scanning electron microscope (FE-SEM)

The Nova Nano FE-SEM 450 is a field-emission scanning electron microscope (FE-SEM), which attains ultra-high imaging resolution without the specimen size restrictions of a conventional in-lens FE-SEM due to the advanced design of the electron optics. The NanoSEM 450's field-emission source allows the user to achieve high imaging resolution at a range of kV, at both low (high-resolution imaging) and high (microanalytical imaging) currents. Secondary electron (SE) imaging can be undertaken in both field-free and immersion mode for comprehensive low-to-high resolution imaging of a variety of samples. The Nova Nano FESEM 450 provides set of integrated tools, including a 16-bit on-board digital pattern generator and dedicated patterning software, a high-speed electrostatic beam blanker and gas-injection systems for direct electron beam writing of nanostructures.

Figure 3.7 Transmission Electron Microscope

The Nova NanoSEM 650’s stage is powered by piezo-motors for producing finer, predictable and repeatable XY movements over a range of 150 mm. To study surface morphology of worn surface, the specimens after wear test are sputter-coated with platinum to a thickness of 5 nm (approx.). Worn surfaces of representative resin composites after 20,000 oscillating load cyclesare examined by FE-SEM at 5 kV acceleration voltages (Figure 3.8).

3.4.4 Void Content

The void contents of the composites are evaluated by using Eq. (3.1) given below [115].

$$\text{Void Content} = \frac{\text{theoretical density } (\rho_t) - \text{apparent density } (\rho_e)}{\text{theoretical density } (\rho_t)} \times 100 \qquad (3.1)$$

Rule of mixture is used for calculating theoretical density of nanosilica, nanoalumina, nanozirconia and gypsum filled dental composite respectively.The apparent density of the dental composites is calculated by simple water immersion techniques.

Figure 3.8 Field Emission Scanning Electron Microscopy

3.4.5 Water Sorption and solubility

Solubility and water sorption are measured according to ISO 4049 [115]. Four composite with 0, 1, 2, 3 wt. % of each of silane treated filler as per the formulation are fabricated. Composites are inserted into stainless steel mold, with 6 mm diameter and 1 mm thickness, between two glass slides. Then they are cured on each side to form disk shape specimen. After curing, the specimen is dried and stored in an oven at 37°C until a constant mass (m_1) had been achieved. Then, the disc is immersed in water for a week at room temperature so that unreacted monomers would be eliminated. Every day, weight of sample is measured and change in weight of composite is reported. After a week, the specimen is removed, dried and weighted as mass (m_2). The samples are then placed in the desiccators and dried at 37 °C until a final constant mass is obtained (m_d), and volumes of the specimens (V) are also measured. Changes in weight of sample due to water absorption have been reported. Water sorption (W_{SP}) and solubility (W_{SL}) of these materials are calculated using the Eq. (3.2) and Eq. (3.3) respectively.

$$W_{SP}\,(\mu g/mm^3) = \frac{m_2 - m_1}{V} \times 10^6 \quad (3.2)$$

$$W_{SL}\,(\mu g/mm^3) = \frac{m_1 - m_d}{V} \times 10^6 \quad (3.3)$$

3.4.6 Degree of conversion

The degree of conversion (DC %) is measured using FTIR spectroscopy. The absorbance peaks of the cured and uncured samples are obtained using 8 scans at a resolution of 4 cm^{-1}. Dental composites with different wt. % of nanosilica particles are light polymerized for 40 s using a visible light source (LED Light Curing Unit, 1200 mW/cm^2, 450–490 nm, Dentmark Mumbai). The spectrum of each sample after curing is also obtained. The Degree of Conversion of each composite is determined from the ratio of absorbance intensities of aliphatic (C-C) peak at 1638 cm^{-1} and normalized against the aromatic (C=C) peak at 1608 cm^{-1}, as per Eq. (3.4) [116]:

$$\text{Degree of conversion} = 1 - \frac{(I_{curedAliph\ \ 1638}/I_{curedArom\ \ 1608})}{(I_{uncuredAliph\ \ 1638}/I_{ucuredArom\ \ 1608})} \quad (3.4)$$

where, $I_{curedAliph\ \ 1638}$ is the absorbance peak intensity of C-C bond at 1638 cm^{-1} of the cured specimen, $I_{curedArom\ \ 1608}$ is the absorbance peak intensity of C=C bond at 1608 cm^{-1} of the cured specimen, $I_{uncuredAliph\ \ 1638}$ is the absorbance peak intensity of C-C bond at 1638 cm^{-1} of the uncured specimen and $I_{ucuredArom\ \ 1608}$ is the absorbance peak intensity of C=C bond at 1608 cm^{-1} of the uncured specimen.

3.4.7 Depth of cure

The samples are prepared by filling uncured formulation in the glass mold of size (Ø5 mm×6 mm) and cured for 20 s from one end. The uncured material is removed with a razor blade and then the cure length is measured with a micrometer accurate to 0.01 mm. The procedure is performed according to ISO 4049[117].

3.4.8 Polymerization shrinkage

Polymerization shrinkage is estimated in terms of change in volume before and after polymerization. The procedure is performed according to ASTM method D792 [118]. A weighing machine accurate to ±0.0001 g (Contech Instrument Ltd, Mumbai), a measuring cylinder and a spring balance are used for the test. Weights of cured /uncured samples in air/ water are measured. The volume polymerization shrinkage is calculated according to the following Eq. (3.5).

$$\text{PolymerizationShrinkage} = \frac{V_1 - V_2}{V_2} \times 100 \qquad (3.5)$$

where, V_1 volume before shrinkage, V_2 volume after shrinkage

3.5 Mechanical and Thermo-mechanical characterization

3.5.1 Vickers Hardness Testing

Four samples of composite filled with different wt. - % (0, 1, 2, 3 wt %) of nanosilicaare fabricated in a Glass mould (5 mm diameter and 6 mm height). Prior to testing, the cured samples are kept in the distilled water at temperature 37°C for 24 h. The test is carried out with a micro-hardness tester (Walter UHL VMHT) shown in Figure 3.9. A load of 300 g is applied for 10 s. Six indentations are made on each sample. The mean value (d) of six indentations on each sample is estimated. The H_V values are calculated accordance to the ASTM E384-11e1 standard using the Eq. (3.6).

$$\text{Hv} = 1854.4 \times \frac{F}{d^2} \qquad (3.6)$$

where, H_V is Vickers Hardness in Kg/mm^2

F is load in Kg and d is diameter in mm.

3.5.2 Compression Strength testing: cylindrical shaped specimens are prepared by filling the unpolymerized composite material in metal mould of Specimen size (height 6±0.1mm, Diameter, 4±0.1mm) (As per ASTM D695-08 [119].Six sample of same composition are tested on Universal testing machine (UTM) Instron 1195 (Figure 3.10).To ensure complete polymerization sample, the sample are irradiated for 40 sec.All specimens are stored for 24 hr in distilled water 37^oC prior to testing. The compressive strength is calculated as per Eq. (3.7)

$$\sigma_c = \frac{4P}{\pi D^2} \qquad (3.7)$$

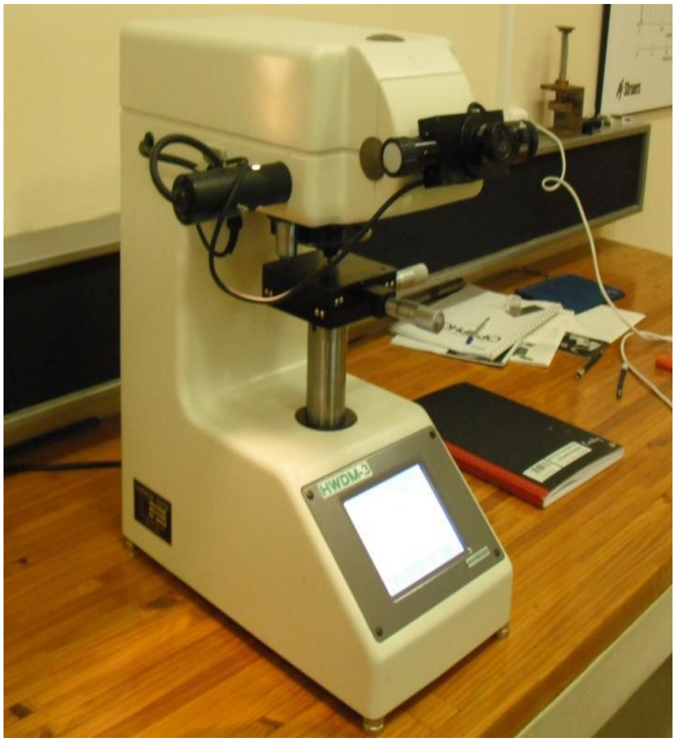


Figure 3.9 Vickers Hardness Testing Machine

3.5.3 Flexural Test

The flexural strength are measured on the rectangular specimen of dimensions (25 mm × 2 mm × 2 mm). The curing and storage condition of the test specimens are same as Vickers hardness test. The test is performed at room temperature with a three-point bending test using Universal Testing machine UTM Instron 1195, at a cross-head speed of 0.75 mm/min (Figure 3.10). The FS values are calculated according to ISO 4049 standard [116] using the Eq. (3.8)

$$\sigma_b = \frac{3Pl}{2bh^2} \qquad (3.8)$$

where, l the distance between the supports (mm); b the specimen width (mm); h the specimen thickness (mm); d the deflection (mm) at load F; and P is the maximum load (N) exerted on the specimen.

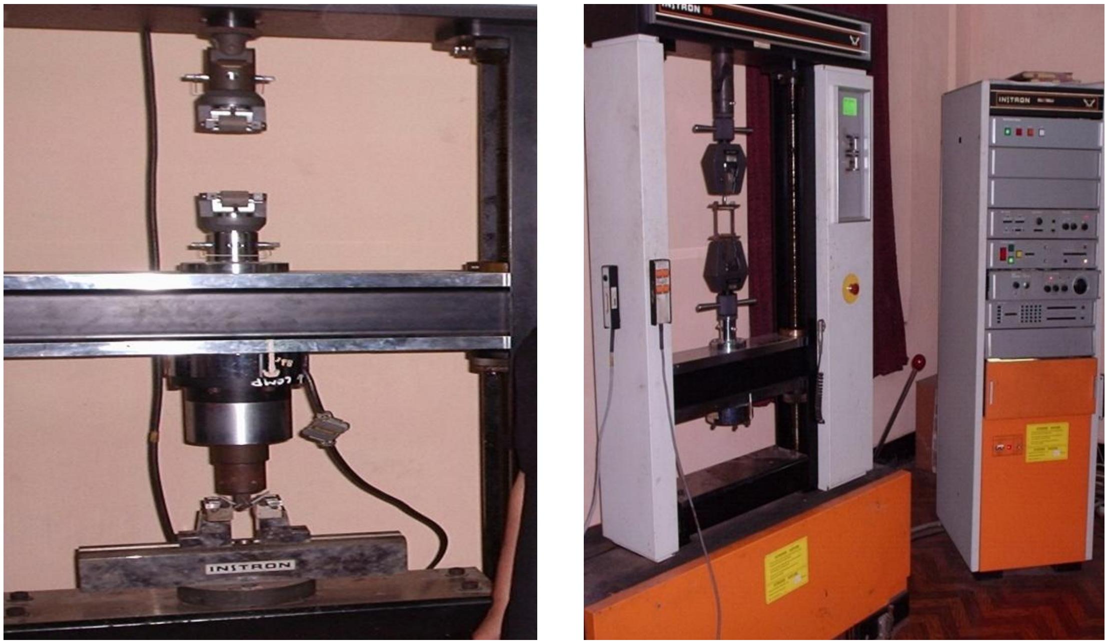


Figure 3.10 Photograph of Instron 1195 UTM machine

3.5.4 Dynamic Mechanical Analysis

Perkin Elmer DMA 8000 can be used to characterize bulk properties of materials such as Modulus; Compliance & Damping (tan delta). It measures changes of rheological behavior under dynamic conditions as a function of temperature, time, frequency, stress, atmosphere or a combination of these parameters. Uses include measurements of Stress-strain, creep recovery, thermo-mechanical and stress relaxation measurements. DMA is ideal for advance research & routine quality testing in polymers, composites, pharmaceutical & food industries.

Cylindrical specimens of dental composite filled with different wt. % (0, 1, 2, 3 wt %) of nanosilicaare fabricated in the glass mould of size Ø 5.30 × 6.2 mm^2. The samples are cured for 60 s on each side. Dynamic mechanical analysis tests (DMA) are performed in compression mode on Perkin Elmer Pyris-7 Dynamic Mechanical analyzer at a frequency of 1 Hz. The frequency of 1 Hz closely simulates mastication process in the oral cavity. Elastic (Storage) modulus (E'), loss modulus (E'') and loss tangent (Tanδ) are recorded against temperature in the range of 30–250°C at a heating rate of 2°C/min (Figure 3.11).

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Figure 3.11 Dynamic Mechanical Analyzer

3.5.5 Simultaneous Thermal Analysis

The STA 6000 features the innovative Saturn-A Sensor for high quality, simultaneous TG and DTA/DSC measurements. This advanced sensor is optimized to achieve flat DTA baselines and high sensitivity. Because both sample and reference are measured simultaneously, you can be sure of the integrity of your analysis. The corrosion-resistant, pure platinum pan holder and reference ring make the instrument suitable for a wide variety of samples and applications.

The powder samples are heated under nitrogen atmosphere from 30°C to 350°C at a heating rate of 10°C/min. Simultaneous Thermal Analysis (STA) generally refers to the simultaneous application of Thermo gravimetric (TGA) and Differential Scanning Calorimetry (DSC) to one and the same sample in a single instrument. Thermo-gravimetric analysis (TGA) has been carried out to analyze the high temperature stability and degradation behavior. DSC has been carried out to analyze glass transition, melting and crystallization phase (Figure 3.12).

Figure 3.12 Simultaneous Thermal Analyzer

3.6Wear Characterization

The Dental Wear Simulator is used for evaluating the friction and wear properties of combination of materials that are being considered for use as dental restoration and implant application. Six different types of profile motion such as profile eight, circular, elliptical, square, linear along X and Y direction can be performed to simulate mastication and other movement of teeth in human and animal. The bottom specimen movement is by servo-motor moving the X-Y stage on LM guides, the motion is controlled by PLC controller(Figure 3.13). The volumetric wear rate of each dental composite is determined with a Dental wear simulator (Ducom, Bangalore, India) as shown in Figure 3.13. Dental wear simulator is compatible to conduct tests according to ASTM F732 test procedure. Each experiment run is repeated twice and the average value is reported to get accuracy. The number of cycles for each specimen is 20000 as per standard procedure. Each specimen is removed from the testing device after being subjected to different wear cycles, and then cleaned under running water to remove all debris. The weight of each specimen is measured using an High Precision weighing machine accurate to ±0.0001 g (Contech Instrument Ltd, Mumbai, India) before and after the wear test. All measurements are performed at room temperature and the wear volume of each specimen is quantified by the following relation:

$$\Delta V = \frac{\Delta m}{\rho} \tag{3.9}$$

where, ΔV = volumetric wear loss (mm^3), Δm = mass loss (g) and ρ = density of specimen (g/cm^3), measured according to the Archimedes' principle.

For simulation of three-body wear, as a third body, an aqueous slurry of 33 mass % lightly pre-ground poppy seeds (60 s in a coffee grinder) are prepared using the procedure as per available literature [120]. Experimental design has been performed using Taguchi method. Taguchi method finds the optimum result by reducing number of experiment to be performed. In this study, Taguchi experimental method is planned for four factors and four levels.

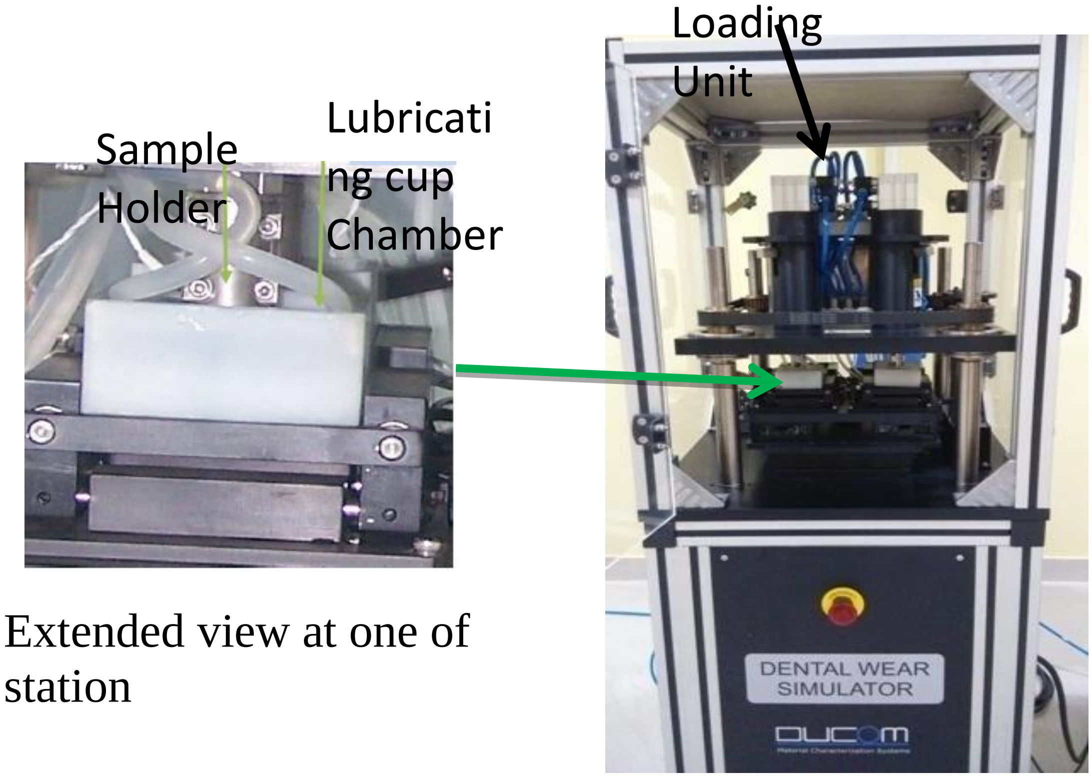

Figure 3.13 Dental Wear Simulators

3.7Process Optimization and Taguchi Method

Statistical methods are commonly used to improve the quality of a product or process. Such methods enable the user to define and study the effect of every single condition possible in an experiment, where numerous factors are involved. Dental wear phenomena in food slurry and acidic medium are abrasion process in which a number of control factors collectively determine the performance output i.e. the volumetric wear rate. Hence, in the present work a statistical technique called Taguchi method is used to optimize the process parameters leading to minimum volumetric wear rate of dental composite under study. This part of the chapter presents the Taguchi experimental design methodology in detail.

3.7.1. Taguchi Experimental Design

Taguchi technique is a powerful tool for design of high quality systems based on orthogonal array experiments that provide much-reduced variance for the experiments with an optimum setting of process control parameters. In Orthogonal array, experiments are performed in such a way where the columns for the independent variables are “orthogonal” to one another. From a scientific viewpoint, these experiments are either one or a series of tests to either confirm a hypothesis or to understand a process in further detail. Experiments from a manufacturing point of view, however, are concerned with finding the optimum product and process, which is both cost effective and of a high quality. The experimenter needs to know the factors involved, the range of these factors are varied between, the levels assigned to each factor as well as a method to calculate and quantify the response of each factor. This one factor at a time approach will provide the most favorable level for each factor but not the optimum combination of all the interacting factors involved. Thus, experimentation in this scenario can be considered as an iterative process. Although it will provide a result, such methods are not time or cost effective. But the design of experiments is a scientific approach to effectively plan and perform experiments, using statistics. In such designs, the combination of each factor at every level is studied to determine the combination that would yield the best result.

The most important stage in the design of experiment lies in the selection of the control factors. Therefore, initially a large number of factors are included so that non-significant variables can be identified at earliest opportunity. Despite of being a simple, efficient and systematic approach to optimize designs for performance, quality and cost, Taguchi method is rarely used in dental wear application. Table 3.21 indicates the factors selected for experimental analysis using Taguchi method. The array chosen in this study is L_{16} orthogonal array design which has 16 rows corresponding to the number of variables selected.

Table 3.21 Levels of variables used in three-body abrasive wear test

Control Factors	LEVEL				Unit
	I	II	III	IV	
A: Filler Content	0	1	2	3	wt.%
B: Chewing Load	40	60	80	100	N
C: Profile Speed	20	40	60	80	%
D: Chamber Temperature	5	15	25	35	°C

All experiments are performed in the track of Profile eight with profile size 100%. At 80% profile speed, the specimen covered 30 mm distance (profile size 100% in profile eight) in 2.98 sec with the speed of 10.06 mm/sec.

This method achieves the integration of design of experiments (DOE) with the parametric optimization of the process yielding the desired results. The orthogonal array (OA) requires a set of well-balanced (minimum experimental runs) experiments. Taguchi’s method uses a statistical measure of performance called signal-to-noise ratio (S/N), which is logarithmic function of desired output to serve as objective functions for optimization. The S/N ratio considers both the mean and the variability into account. It is defined as the ratio of the mean (signal) to the standard deviation (noise). The ratio depends on the quality characteristics of the product/process to be optimized. The three categories of S/N ratios are used: lower the-better (LB), higher-the-better (HB) and nominal-the best (NB). The experimental observations are transformed into a signal-to-noise (S/N) ratio. There are several S/N ratios available depending on the type of characteristics. The S/N ratio for minimum wear rate coming under smaller is better characteristic, which can be calculated as logarithmic transformation of the loss function as shown in Eq. (3.10).

Smaller is the better characteristic: $\frac{S}{N} = -log\frac{1}{n}(\sum y^2)$ (3.10)

3.8Gray Relational Analysis optimization Technique [Ref aaaa]

Multiple attributes decision making or multiple criteria decision-making (MADM/MCDM) is the approach dealing with the ranking and selection of one or more materials from a set of alternatives. The MCDM provides an emphatic structure for material selection based on the evaluation of multiple conflict criteria.As there are several PDCs, one must be satisfied to obtain an optimal solution of any decision making problems. The GRA method is intended to provide a complete ranking of the alternatives from the best to the worst. The various steps of GRA method can be expressed as:

Step I- Identification of the alternatives and PDAs: Firstly, the number of alternatives and various PDAs used in the performance evaluation of given MCDM are identified.

Step-2: A performance matrix is created after identifying the *PDAs* and alternatives of the problem. If the number of alternative is M and the number of *PDAs* are N then the performance matrix having an order of M × N is represented as Eq. (3.11):

$$P_{M\times N}=\begin{array}{c} \\ A_1 \\ A_2 \\ \vdots \\ A_M \end{array}\begin{array}{c}\begin{array}{cccc} C_1 & C_2 & \cdots & C_N \end{array}\\ \begin{bmatrix} P_{11} & P_{12} & \cdots & P_{1N} \\ P_{21} & P_{22} & \cdots & P_{2N} \\ \vdots & \vdots & \ddots & \vdots \\ P_{M1} & P_{M2} & \cdots & P_{MN} \end{bmatrix}\end{array} (3.11)$$

Where, $A_1, A_2 \cdots A_M$ are the M alternatives and $C_1, C_2 \cdots C_N$ are the N PDAs.

The element P_{ij} of the performance matrix $P_{M\times N}$ represents the actual value of the ith alternative in term of jth PDA.

Step-3: The values in the performance matrix are normalized into range of [0, 1]. The normalized values of each element in the performance matrix can be calculated as follows:

Larger the better,

$$P'_{ij}=\frac{P_{ij}-\min\{P_{ij}\}}{\max\{P_{ij}\}-\min\{P_{ij}\}}$$

Smaller the better,

$$P'_{ij}=\frac{\min\{P_{ij}\}-P_{ij}}{\max\{P_{ij}\}-\min\{P_{ij}\}} (3.12)$$

The normalized matrix constructed as:

$$P'_{M\times N}=\begin{bmatrix} P'_{11} & P'_{12} & \cdots & P'_{1N} \\ P'_{21} & P'_{22} & \cdots & P'_{2N} \\ \vdots & \vdots & \cdots & \vdots \\ P'_{M1} & P'_{M2} & \cdots & P'_{MN} \end{bmatrix} (3.13)$$

Step-4: Generate the reference sequence (X_j) from the normalized matrix by taking the largest normalized value of each criterion as Eq. (3.14)

$$X_j=\max_{i=1}^{M}\{P'_{ij}\} (3.14)$$

Step-5: Construct the difference matrix by calculating the difference between a normalized term and its reference value as Eq. (3.15)

$$\Pi_{ij}=\left|X_j-P'_{ij}\right|$$

$$\Pi = \begin{bmatrix} \Pi_{11} & \Pi_{12} & \cdots & \Pi_{1N} \\ \Pi_{21} & \Pi_{22} & \cdots & \Pi_{2N} \\ \vdots & \vdots & \cdots & \vdots \\ \Pi_{M1} & \Pi_{M2} & \cdots & \Pi_{MN} \end{bmatrix} (3.15)$$

Step-6: Grey correlation coefficient for each term is determined as Eq. (3.16)

$$\chi_{ij} = \frac{\min_{i=1}^{M} \min_{i=1}^{N} \Pi_{ij} + \zeta \max_{i=1}^{M} \max_{i=1}^{N} \Pi_{ij}}{\Pi_{ij} + \zeta \max_{i=1}^{M} \max_{i=1}^{N} \Pi_{ij}} (3.16)$$

Where $\zeta \in [0, 1]$ is known as the distinguishing coefficient and generally takes the value of 0.5 because this value generally offers good stability with moderate distinguishing effects.

Step-7: A grey correlation degree is calculated as Eq. (3.17)

$$\varpi_i = \frac{1}{N} \sum_{j=1}^{N} \left[\chi_{ij}\right] (3.17)$$

ϖ_i, is the grey correlation degree that indicates the magnitude of correlation measured between the reference sequence and the i^{th} data sequence. Therefore, using the grey correlation degrees, the dental material formulation sequence can be prioritized and the one with the highest degree of correlation will be identified as the best formulation representing the optimal solution.

Chapter summery

This chapter briefly presents/discusses following things:

1. The properties and specifications of the ingredients/materials selected along with the design of different sets of dental composite formulations.
2. The details of standard fabrication procedure and the processing conditions adopted as per Industrial standard,
3. The description of various physical and mechanical characterizations performed in order to justify commercial viability of the product.
4. A brief discussion on working of Dental Wear Simulator adopted for assessment of performance of dental material.
5. The detailed description of Dynamic Mechanical Analyzer (DMA) apparatus used to measure the temperature-dependent dynamic-mechanical characteristics like stiffness and damping properties of the investigated composites.

6. A brief discussion on performance attributes adopted for assessment of the performance of the developed composites.

The next chapter briefly presents/discuss the various physical, mechanical and thermal characteristics of the fabricated/developed friction composite materials.

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Chapter 4

Physical and Chemical characterizations of Dental composites

Chapter 4

Physical and Chemical Characterizations of dental Composites

Introduction

This chapter discusses the results based on the physical and chemical properties of dental composites according to the formulations discussed in previous chapter. The detail physical and chemical properties include spectroscopy analysis of filler, determination of void content, water sorption, solubility, polymerization shrinkage, depth of cure and degree of conversion. The interpretation of the results and the comparison among various dental composite samples are also presented. This chapter consists of four parts: part I consists of dental composite filled with silane treated nanoalumina, part II consists of dental composite filled silane treated nanozirconia, part III consists of dental composite filled nanosilica and part IV consists of dental composite filled with silane treated micro sized gypsum.

Part I

4.1 Physical and chemical characterization of nanoalumina filled dental composites

4.1.1 Fourier transform infrared analysis of nanoalumina filled dental composites

Infrared spectra of nanoalumina before and after silane treatment have been recorded in Figure 4.1. The presence of the Si-O-Si peak at 1047.03 cm^{-1} indicates that silane is successfully adsorbed on the surface of the filler. This siloxane group comes from the –Si(O(CH)$_3$)$_3$ part of Mithacryloxy propyltrimethoxy silane. These findings are in agreement with Tripp et al. [121] who studied in detail silanization of Aerosil silica in the low frequency region i.e below 1300 cm^{-1}. The reaction of cholromethylesilane with silanol group produced bands due to Si-O-Si. They assigned 1040–1100 cm^{-1} band to a siloxane network Si–O–Si which is supported on the surface. In another research, broad absorption in the 1200-950 cm^{-1} range indicates the formation of Al-O-Si and Si-O-Si bonds. These vibration modes appear at frequencies relatively close to that of Al-O-Al bonds, due to the similar mass of Al and Si atoms.

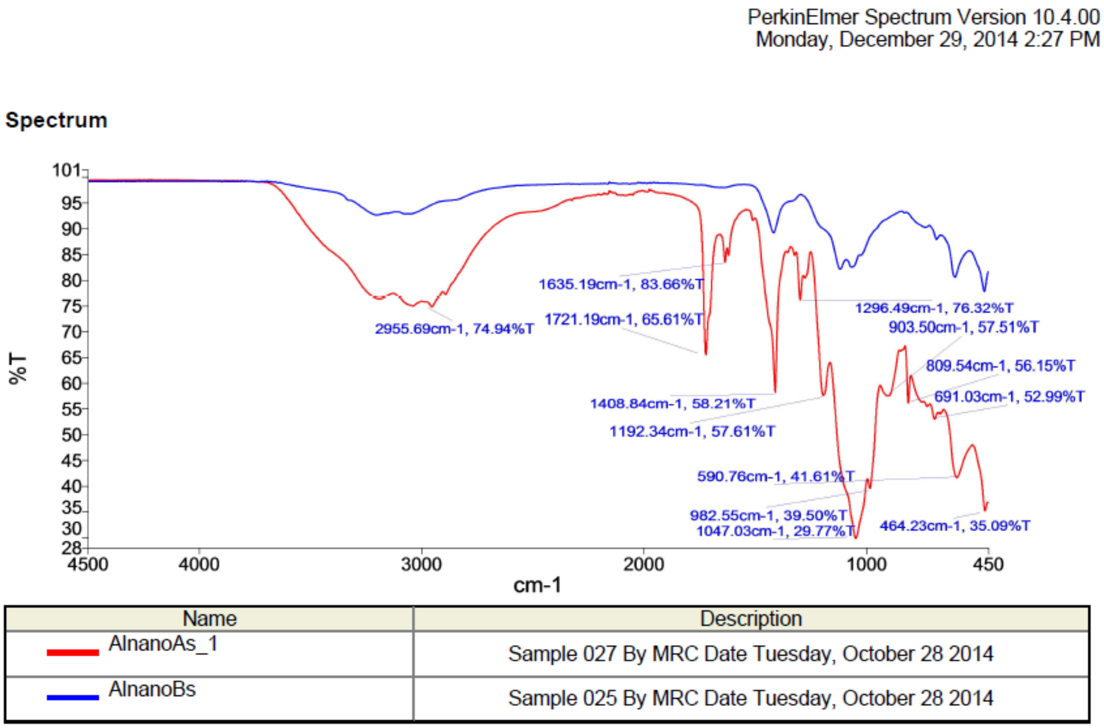


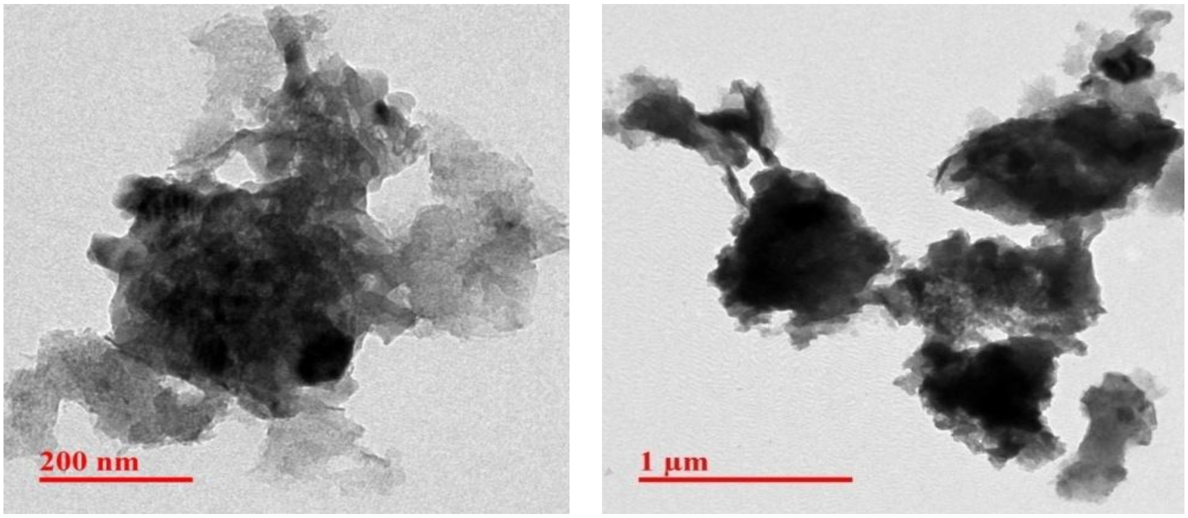
Figure 4.1 Infra Red Spectra of Nanofiller before (AlnanoBs) and after silane treatment (AlnanoAs)

The positions of the peaks in the range of 1200-950 cm^{-1} are associated to the –OH groups [122]. The appearance of the band at 1408.84 cm^{-1} indicates the C=O stretching due to acrylate group on the surface of treated filler. A strong peak due to C=O absorption at 1721 cm^{-1} indicates the presence of C=O group. The C=O group comes from carbonyl group present in Methacryloxy propyltrimethoxy silane i.e.it is attached to -C=O--H-O-Si- [123]. The appearance of peaks at 2955 cm^{-1} i.e. under alkyl stretching band (n = 2850-3000 cm^{-1}) indicates the presence of stretching of the C–H bonds [124].

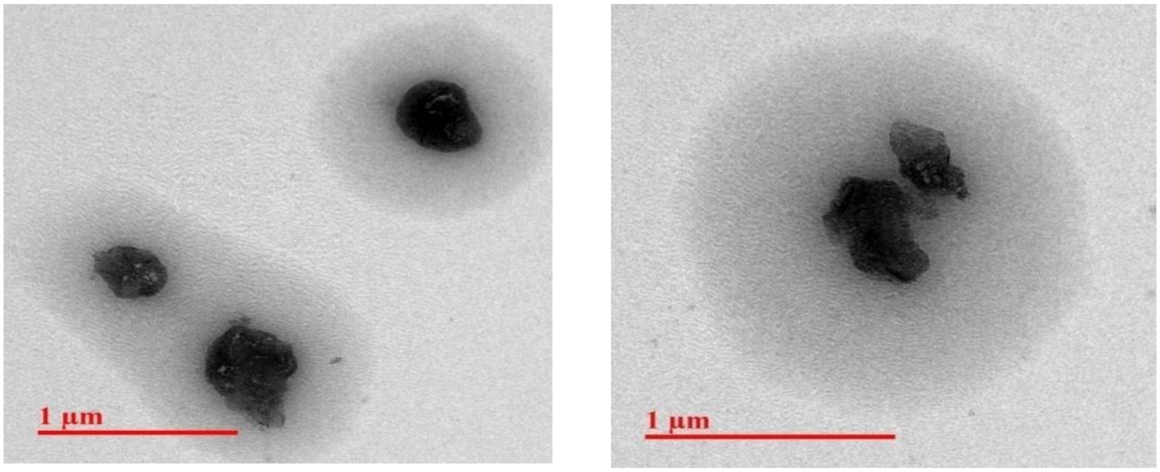
4.1.2 Transmission electron microscopy analysis of nanoalumina filled dental composites

Transmission electron microscopy analysis (TEM) has been performed to visually observe the morphology of the nano-sized substituent in the composites. Images of the nano filler before and after silane treatment under TEM are shown in Figure 4.2. Following observations are obtained:

a) Great diversity in the ultra structure is observed between fillers with and without silane treatment. For without treated nano filler, views of their ultra structures are consistent at both low and high magnification modes. For silane treated nano filler, the filler particles are covered or surrounded by silane.



(a).Before Silane treatment (b).Before Silane treatment



(a).After Silane treatment (b).After silane treatment

Figure 4.2 TEM images of nanoalumina before and after silane treatment

b) From Figure 4.2, it can be observed that the nanoalumina particles are well dispersed in the polymer matrix. This is due to the fact that as the nanoparticle size decreases to nanometer dimensions, its surface area per unit volume increases both the Van der Waals force and the accumulated hydrogen-bonding force among nanoparticles. To disperse agglomerated nanoparticles, the inter-particle forces should be reduced by coating the particle surfaces with additives that make the surfaces more compatible with the surrounding polymer.

4.1.3 Effect of void content on nanoalumina filled dental composites

The void contents of the composites are evaluated by using Eq. (4.1) given below [115].

$$\text{Void Content} = \frac{\text{theoretical density } (\rho_t) - \text{apparent density } (\rho_e)}{\text{theoretical density } (\rho_t)} \times 100 \qquad (4.1)$$

Rule of mixture is used for calculating the theoretical density of the nanoalumina filled dental composites. The theoretical density, apparent density and void contents of nanoalumina filled dental composites are presented in Table 4.1.

Table 4.1 Effect of void content on nanoalumina filled dental composites

Sl. No.	Composition	Theoretical Density (gm/cc)	Apparent Density(gm/cc)	Void Content (%)
1	NADC-0: (Composite without Alumina)	1.1814	1.1800	0.12
2	NADC-1: (Composite with 1% Alumina)	1.1903	1.1882	0.18
3	NADC-2: (Composite with 2% Alumina)	1.1993	1.1960	0.27
4	NADC-3: (Composite with 3% Alumina)	1.2084	1.1981	0.78

Note: NADC: Nanoalumina reinforced dental composite

From Table 4.1, it indicates that the void content for the dental composite with 3 wt.% of nanoalumina filled composite is much higher than other unfilled and filled dental composites.

4.1.4 Depth of cure, Polymerization Shrinkage and degree of conversion of nanoalumina filled dental composites

Figure 4.3 indicates the depth of cure for the composites filled with different wt. percentage of nanoalumina particles. The depth of cure for the dental composites with 0, 1, 2 and 3 wt. % of nanoalumina particles are 2.4, 2.8, 2.95 and 3.2 mm respectively. Hence, increase in nanoalumina filler content resulted into increased in depth of cure of dental composites. It may be due to the fact that with the increased in silane modified nanoalumina, increased the coupling between resin matrix and filler particles. The resulted uniform and precise mixture allows light transmission for deep layer. During polymerization, the monomer makes strong long polymer chain and strong coupling between filler and resin matrix. The depth of cure of dental composite is influenced by organic resin and inorganic filler materials. Some studies demonstrated that increased in filler content improves the hardness and depth of cure of dental composite composites [125, 126].

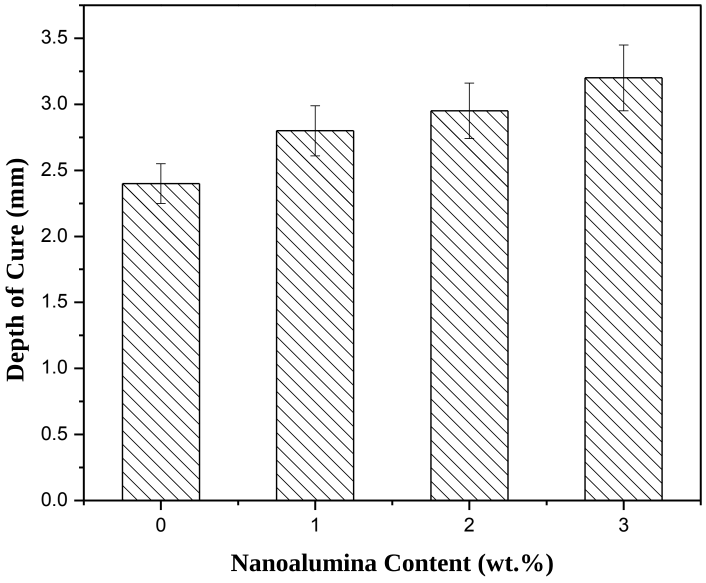


Figure 4.3 Depth of cure for different weight percentages of nanoalumina filled dental composites

Figure 4.4 indicates the polymerization shrinkage for the composite filled with different wt. % of nanoalumina particles. The polymerization shrinkages for the dental composite with 0, 1, 2 and 3 wt.% of nanoalumina particles are 3.95, 3.22, 2.51 and 1.75% respectively. It can be seen that polymerization shrinkage decreases with the increasing in nanoalumina content in the composite. It may be attributed to the fact that there has been a general consensus about the addition of reinforcing filler to a resin matrix in a resin base composite. This is because these inorganic fillers do not undergo any contraction during the setting reaction. In another research, it is reported that the mean linear shrinkage for the 79%, 65 % and 50 % filler experimental Prisma APH composite cone is 0.33 %, 0.35 % and 0.42 % respectively [127]. Hence, increase in filler content decreases the polymerization shrinkage.

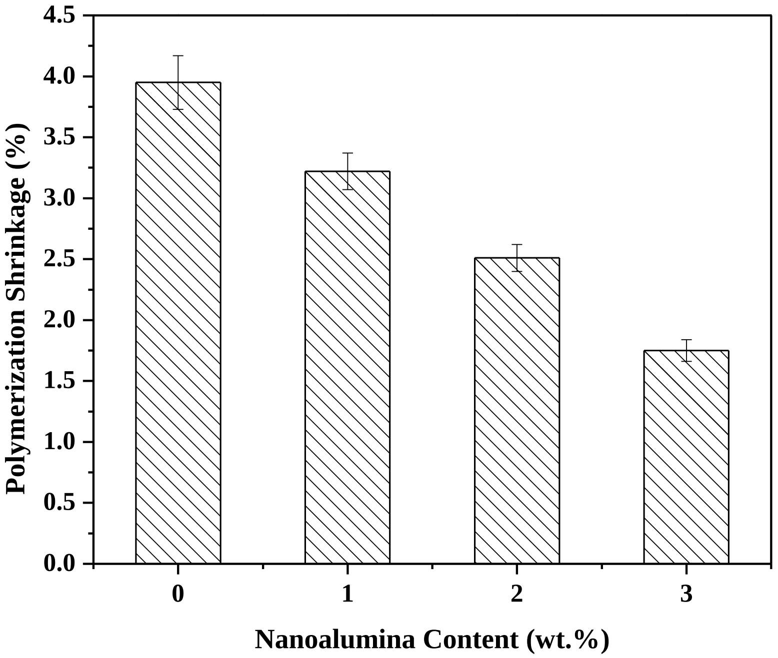


Figure 4.4 Polymerization shrinkages for different weight percentages of nanoalumina filled dental composites

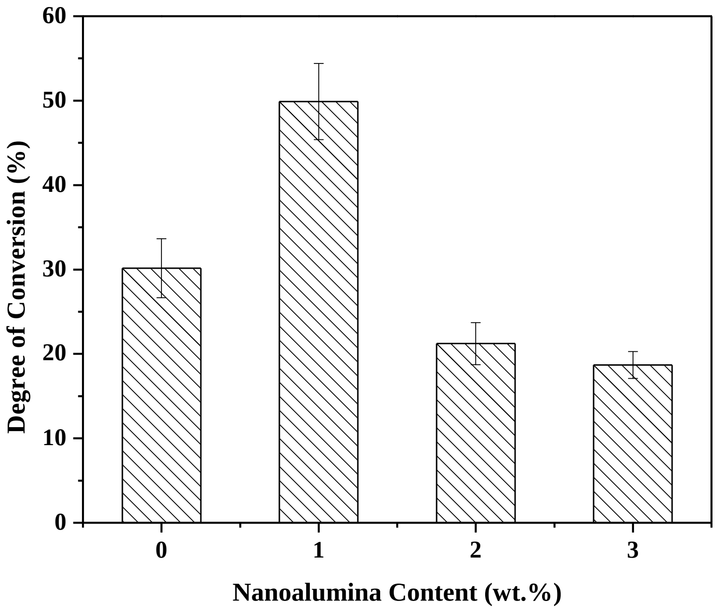


Figure 4.5 Degree of conversion for different weight percentages of nanoalumina filled dental composites

Degree of conversion for the dental composite filled with different weight percent of nanoalumina is shown in Figure 4.5. The degree of conversion of dental composite with 0 wt. %, 1 wt. %, 2 wt. % and 3 wt. % are 30.14, 49.88, 21.22, 18.69 % respectively. Since polymerization shrinkage of composites depend up on the degree of conversion of monomers during polymerization. Hence, the physical and mechanical properties of resin composites strongly depend upon degree of conversion which is defined as the percentage of converted or cured C=C bonds from the total dimethacrylate monomers present in the resin [128].

4.1.5 Sorption and solubility of nanoalumina filled dental composites

Water Sorption and solubility of the dental composites after immersion in water for one week are presented in Table 4.2. The composite filled with 1wt. % silane treated nanoalumina content indicates lowest solubility due to maximum degree of conversion (Figure 4.5). The maximum degree of conversion indicates that the maximum unsaturated bond is converted into saturated bond or un-reacted monomers are converted into polymer during polymerization reaction. The solubility of composites filled with 0,1,2 and3 wt. % of alumina content is found to be 1.14, 0.48, 0.95 and 2.65 μg/mm^3 respectively. In oral environment, dental composites absorb water and then release components like nanoalumina particles etc. which can shorten the service life of restoration and it can create clinical problem.

As summarized in Table 4.2, the sorption result indicates that increase in sorption is attributed to the increase in void content of the composite material. More void content could increase the available free volume for water to be absorbed. The water sorption of composites filled with 0, 1, 2 and 3 wt. % of alumina filler are 1.25, 1.58, 1.81 and 2.5 μg/mm^3 respectively

Table 4.2 Sorption and solubility of nanoalumina filled dental composites

Composite	Sorption in μg/mm^3	Solubility in μg/mm^3
NADC-0 (Composite without nanoalumina)	1.25	1.14
NADC-1 (Composite with 1 wt.-% nanoalumina)	1.58	0.48
NADC-2(Composite with 2wt.-% nanoalumina)	1.81	0.95
NADC-3(Composite with 3 wt.-% nanoalumina)	2.5	2.65

Part II

4.2 Physical and chemical characterization of nanozirconia filled dental composites

4.2.1 Fourier transform infrared analysis of nanozirconia filled dental composites

Figure 4.6 shows the FTIR spectra of zirconia nanofiller before (ZrBS) and after silane treatment (ZrAS). The major peaks appearing in the FTIR spectra of silane treated nanozirconia and untreated nanozirconia could be related to the following: In the silane treated nanozirconia filler, an intense absorbing band close to 1049.45 cm^{-1} and 1101.69 cm^{-1} are attributed to the formation of Si-O bond and stable siloxane group (Si-O-Si) respectively.

Again the similar absorbing band is seen in the range of 1040–1100 cm^{1} bands corresponds to a siloxane network Si–O–Si. The band at 1720.78 cm^{-1} indicates the presence of silane on the surface of the filler. The carbonyl peak for the grafted composite is appeared at 1716 and 1728 cm^{-1}, indicating the presence of different carbonyl groups arising from the acrylic acid and the silane coupling agent. The absorbing band at 1406.70 cm^{-1} is due to presence of C=O stretching vibration due to acrylate group on the surface of treated filler. The absorption bands around 2954.20 cm^{-1} and 3126.20 cm^{-1} are attributed to stretching vibrations of C–H bonds in alkyl and methoxy groups, respectively [129].

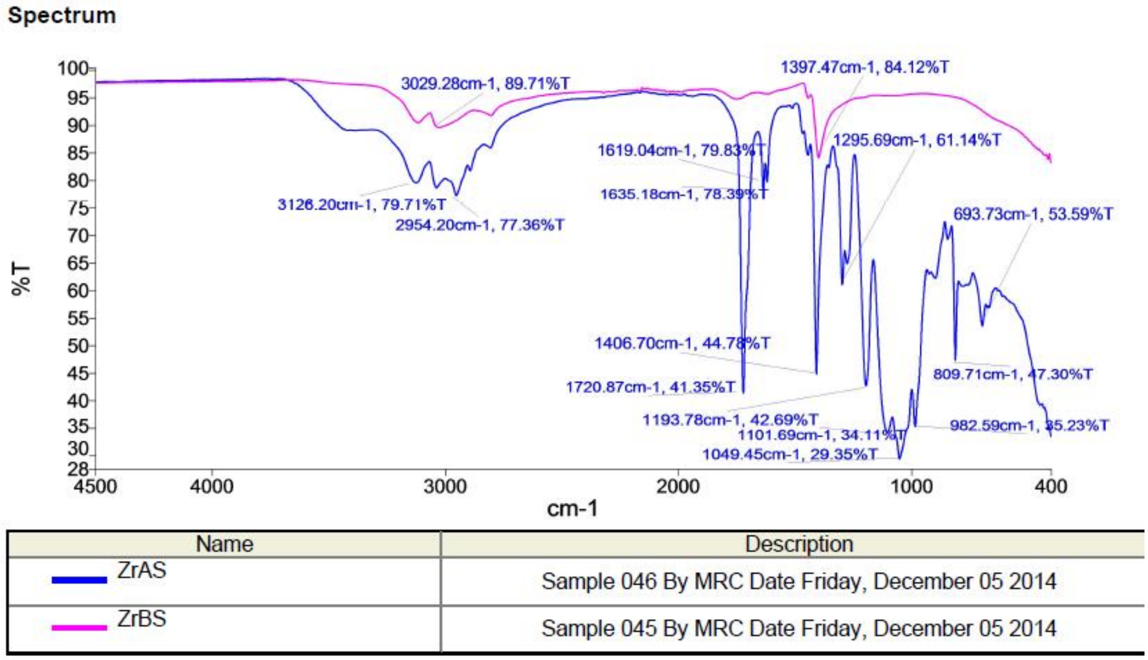
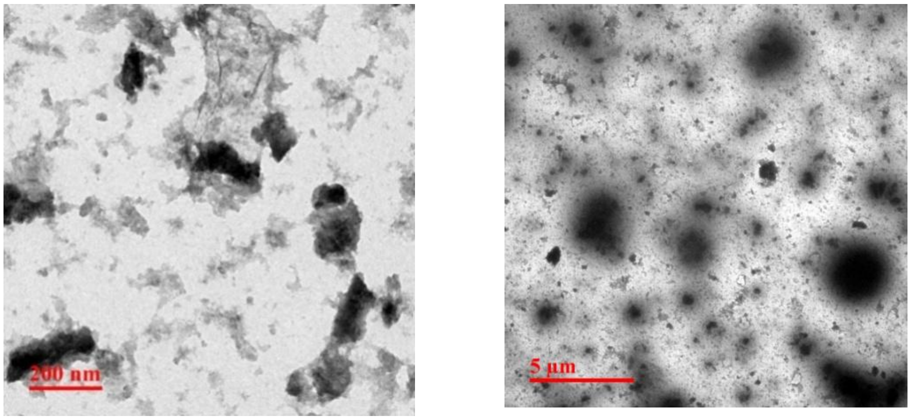


Figure 4.6 Infrared spectra of nanozirconia filler before (ZrBS) and after silane treatment (ZrAS)

4.2.2 Transmission electron microscopy analysis of nanoalumina filled dental composites

Images of the nanofiller before and after silane treatment under Transmission Electron Microscope (TEM) are shown in Figure 4.7. TEM observation revealed that the zirconia nanoparticles with average size about 20 nm distributed homogeneously in the resin matrix.



(a) Before Silane treatment (b) After Silane treatment

Figure 4.7 TEM images of nanozirconia before and after silane treatment

Hence, the filler particles are covered or surrounded by silane. It can be concluded that the effect of coupling agent plays an important role in dispersion of the nanoparticles and hence Figure 4.7 (b) indicates better dispersion than Figure 4.7 (a). The relatively strong interactions between resin matrix and zirconia nanoparticles are responsible for observing nanoparticles with almost spherical shapes.

4.2.3 Effect of void content on nanozirconia filled dental composites

The void contents of the composites are computed by using equation given below. These values are slightly higher than the apparent density values, also presented in Table 4.3. Reduction in the density of composites compared to the expected values is attributed to the entrapment of air in the matrix material in the process of mechanical mixing of the resin. This entrapped air, referred as voids, is undesired because it could adversely affect the mechanical properties of the composite. Table 4.3 indicates that the void content for the dental composite with 0,1,2 and 3 wt.% of nanozirconia filled composite are 0.42, 0.49, 0.69 and 1.15 % respectively.

Table 4.3 Effect of void content on nanozirconia filled dental composites

S. No.	Composition	Theoretical Density(gm/cc)	Apparent Density(gm/cc)	Void Content (%)
1	NZDC-0 (Composite without Zirconia)	1.1833	1.1783	0.42
2	NZDC-1 (Composite with 1% Zirconia)	1.1809	1.1751	0.49
3	NZDC-2 (Composite with 2% Zirconia)	1.1786	1.1704	0.69
4	NZDC-3 (Composite with 3% Zirconia)	1.1762	1.1626	1.15

4.2.4 Depth of Cure, Polymerization Shrinkage and Degree of Conversion of nanozirconia filled dental composites

Figure 4.8 indicates the depth of cure for the composite filled with different weight percentage of nanozirconia particles.

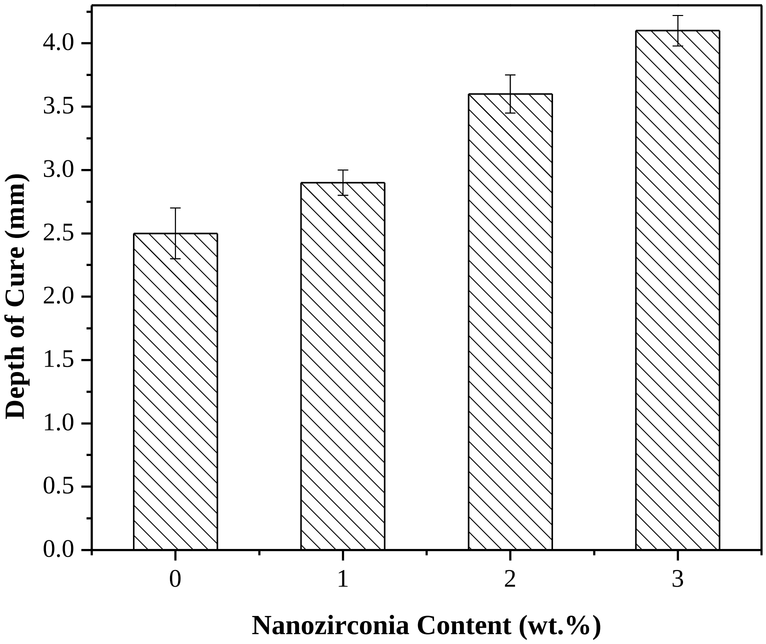


Figure 4.8 Depth of cure for different weight percentages of nanozirconia filled dental composites

The depth of cure for the dental composite with 0, 1, 2 and 3 wt. % of nanozirconia particles are 2.5, 2.9, 3.6 and 3.89 respectively. It can be seen that depth of cure increased with the increased in nanozirconia content in the composite. Dental composite with 3wt. % nanozirconia content exhibited maximum depth of cure. Increase in depth of cure with increase in nanozirconia content is attributed to the fact that with the increased in silane treated filler increases the coupling with the resin matrix and a precise mixture allows light transmission for deep layer [130]. Figure 4.9 indicates the polymerization shrinkage for the composite filled with different wt. % of nanozirconia particles. The polymerization shrinkage for the dental composite with 0, 1, 2 and 3 wt. % of nanozirconia particles is 3.89, 2.94, 2.77 and 1.47 respectively. It can be seen that polymerization shrinkage decreased with the increasing in nanozirconia content in the composite. It may be attributed to the fact that there has been a general consensus about the addition of reinforcing filler to a resin matrix in a composite resin. This is because these inorganic fillers do not undergo any contraction during the setting reaction.

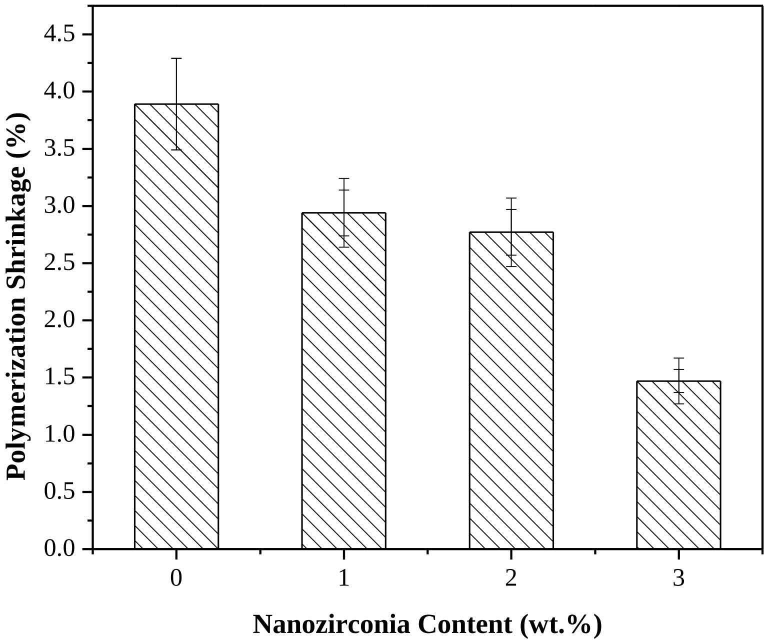


Figure 4.9 Polymerization shrinkages for different weight percentages of nanozirconia filled dental composites

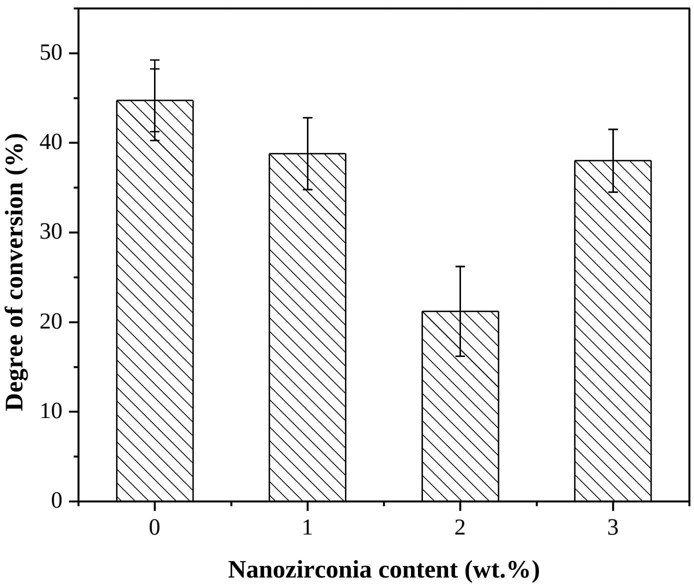


Figure 4.10 Degree of conversion for different weight percentages of nanozirconia filled dental composites

Figure 4.10 indicates the degree of conversion of dental composite filled with different weight percentage of nanozirconia. Degree of conversion of dental composites filled with 0,1,2 and 3 wt.% nanozirconia are 44.75%, 38.80%, 21.2% and 38.01% respectively. It can be seen that degree of conversion decreased for 0 to 2wt. % filled dental composite and then further increased for 3wt.% filled dental composite. Because it is known that the polymerization shrinkage of composite depends on the degree of conversion of monomers during polymerization. Greater the degree of polymerization, greater will be shrinkage. The physical and mechanical properties of resin composites are strongly influenced by the degree of conversion, defined as the percentage of reacted aliphatic C=C bonds from the dimethacrylate monomers present in their polymeric matrices [131].

4.2.5 Sorption and solubility of nanozirconia filled dental composites

Sorption and solubility of the resin composites after immersion in water for one week are presented in Table 4.4. The sorption result showed that the water sorption of composites filled with 0, 1, 2 and 3 wt. % of nanozirconia filler are 1.43, 1.67, 2.70 and 2.86 respectively. The solubility of composites filled with 0,1,2,3 wt. % of nanozirconia content is found to be 0.68, 1.14, 1.00 and 1.23, 0.33 respectively. The composite filled with 3wt.% nanozirconia content indicates lowest water solubility.

Table 4.4. Sorption and solubility of nanozirconia filled dental composites

Composite	Sorption in μg/mm^3	Solubility in μg/mm^3
NZDC-0: (Composite without 0 wt.% nanozirconia)	1.43	0.68
NZDC-1: (Composite with 1 wt.% nanozirconia)	1.67	1.00
NZDC-2: (Composite with 2 wt.% nanozirconia)	2.70	1.14
NZDC-3: (Composite with 3 wt.% nanozirconia)	2.86	0.33

Note: NZDC: nanozirconia filled dental composite

It is revealed that solubility and sorption decreased with increasing filler content. In practice, dental composites absorb water and then can release components like nanozirconia particles etc within the oral environment which can shorten the service life of restoration and it can create clinical problem. The sorption and solubility of all the composites studied are lower than the ISO 4049 [132] in which the maximum affordable values of water sorption and solubility for the dental resins are: 40μg/mm^3 and 5μg/mm^3 respectively. The composites prepared in this paper showed the potentially clinical application.

Part III

4.3 Physical and chemical characterization of nanosilica filled dental composites

4.3.1 Fourier transform infrared analysis of nanosilica filled dental composites

Infrared spectra of nanosilica filler before and after silane treatment have been recorded in Figure 4.11 Silane treated nano filler indicates the formation of stable and strong siloxane group (Si-O-Si) with an intense absorbing band at 1078.97 cm^{-1}. The intensity of this band is found to be decreased with the addition of silane. But Si-O bond absorption peak at 412 cm^{-1} are rarely visible in silane treated nano filler. Hence, it can be concluded that the modification with silane decreases the absorption intensity of Si-O. The intense absorbing band at 1723 cm^{-1} is due to the free carbonyl C=O stretching vibration, which comes from carbonyl groups of silane. Similar absorbing band is obtained by Yu et al.

[133] at 1724 cm^{-1} during FTIR spectroscopy of silane functionalized graphene/thiol-ene. Hence, the absorbing band at 1619.37 cm^{-1} indicates C=C stretching vibration of bond in silane. However, some weaker features near 2944.86 cm^{-1} and 2841.60 cm^{-1} are caused by CH_2 stretching vibration. The formation of Si-O-Si on the surface of silane treated filler are in agreement with Pantoja [134] who indicated that formation of siloxane group is due to the condensation process of silane which occurs as soon as it comes into contact with the air and it reacts with atmospheric water. In another study, Fadeev et al. [135] studied the self-assembled monolayers of organosilicon hydrides on surface of titanium, zirconium, and hafnium dioxides. They observed that the intense band with a complex structure appeared at 1040–1100 cm^{-1} and they assigned 1040–1100 cm^{-1} band to a siloxane network Si–O–Si.

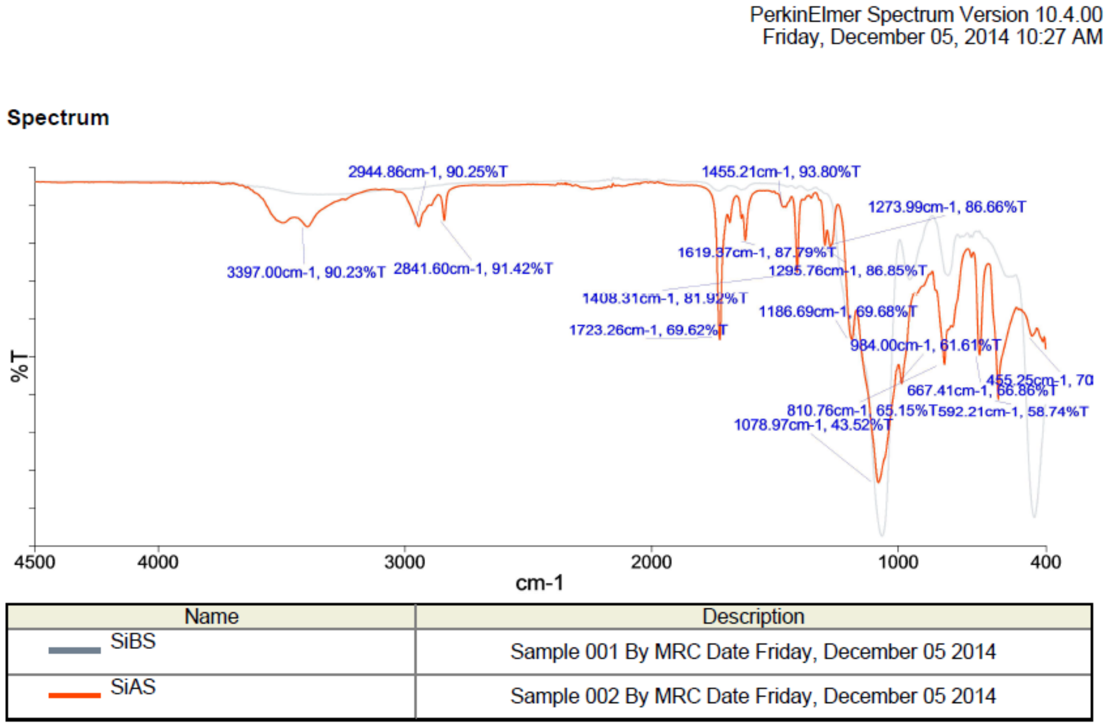
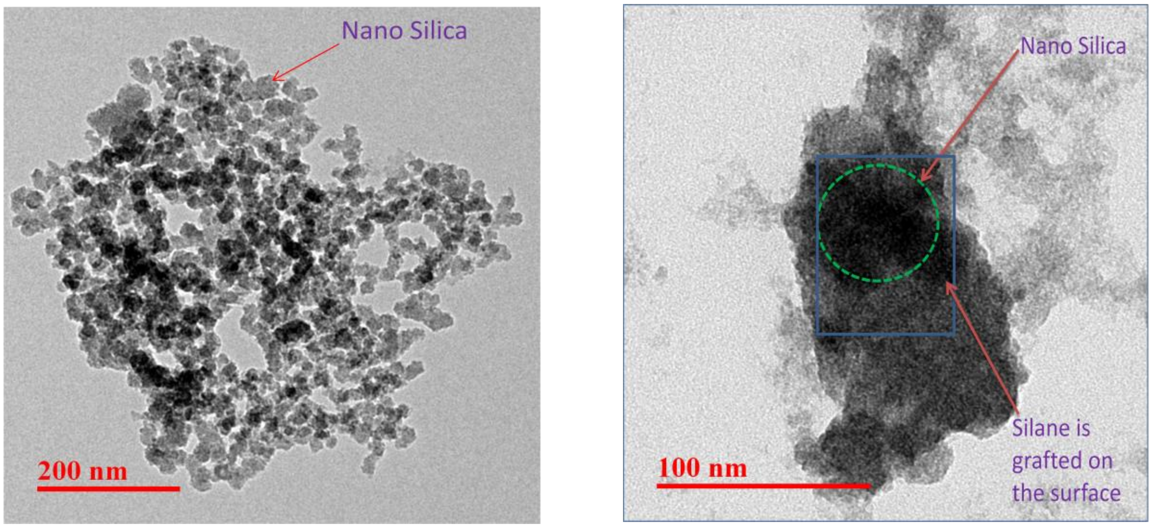


Figure 4.11 Infra Red Spectra of Nanofiller before (SiBS) and after silane treatment (SiAS)

4.3.2 Transmission electron microscopy analysis of nanosilica filled dental composites

Images of the nanofiller before and after silane treatment under TEM are shown in Figure 4.12. Figure 4.12(a) clearly indicates the dispersed and agglomerated silica particles. For better mechanical properties, the inter-particle forces should be reduced by coating the particle surfaces with additives that make the surfaces more compatible with the surrounding polymer. The surface of silica is modified with surfactant chemicals such as the silanes. Similarly, Figure 4.12(b) represents silane treated silica with great diversity in the ultra structure which is observed between fillers with and without silane treatment. For untreated nanosilica filler, views of their ultra structures are consistent at both low and high magnification modes. For silane treated nanosilica filler, the filler particles are covered or surrounded by silane.

It can be observed that the effect of coupling agent plays an important role in dispersion of the nanoparticles. The relatively strong interactions between resin matrix and Silica nanoparticles are responsible for observing nanoparticles with almost spherical shapes. The improvement in adhesion properties of the composite is attributed to the formation of Si–O–Si bonds between the filler and the resin, as well as to the organic phase mobility and flexibility properties of the filler in the stress support of the sample which is in agreement with [136]



(a) Before Silane treatment (b) After Silane treatment

Figure 4.12 TEM images of nanosilica before and after silane treatment

4.3.3 Effect of void content on nanosilica filled dental composites

The theoretical and apparent density values of the nanosilica filled dental composites are presented in Table 4.7. The apparent density of the proposed dental composites is calculated by simple water immersion techniques. It can be seen that theoretical values are slightly higher than the apparent density values. Reduction in the density of composites compared to the expected values is attributed to the entrapment of air in the matrix material in the process of curing or during the mixing of filler and resin. This entrapped air, referred as voids, is undesired because it adversely affects the mechanical properties of the composite. Table 4.5 indicates that the void content for the dental composite Si-0 is much lower than other the dental composites. Increase in void content with increase in filler is attributed to presence of large surface area of nanosilica. Due to increase in surface area the resin matrix may not be able to wet the all surface of nanosilica and may result into increase in viscosity. This makes it difficult to disperse the Nanofiller uniformly in the resin matrix. In similar work, Guo et al. [105] concluded that high fiber loading could lead to the formation of voids in the composites due to the fiber–fiber agglomeration which also contributes to non-uniform stress transfer.

Table 4.5 Effect of void content on nanosilica filled dental composites

S. No.	Composition	Theoretical Density (gm/cc)	Experimental Density (gm/cc)	Void Content (%)
1	NSDC-0: (Composite without Silica)	1.1918	1.1905	0.109
2	NSDC-1: (Composite with 1 wt.-% Nanosilica)	1.1973	1.189	0.693
3	NSDC-2: (Composite with 2 wt.-% Nanosilica)	1.2028	1.1923	0.872
4	NSDC -3: (Composite with 3 wt.-% Nanosilica)	1.2084	1.1938	1.208

Note: NSDC: Nanosilica reinforced dental composite

4.3.4 Depth of cure, Polymerization Shrinkage and degree of conversion of nanosilica filled dental composites

Figure 4.13 indicates the depth of cure for the composite filled with different wt. percentage of nanosilica particles. The depth of cure for the dental composite with 0, 1, 2 and 3 wt. % of nanosilica particles are 2.6, 3.1, 3.5 and 4.2 mm respectively. It can be seen that depth of cure increased with the increasing in silica content in the composite. It may be attributed to the fact that with the increased in silane treated filler increases the coupling with the resin matrix and a precise mixture allows light transmission for deep layer.

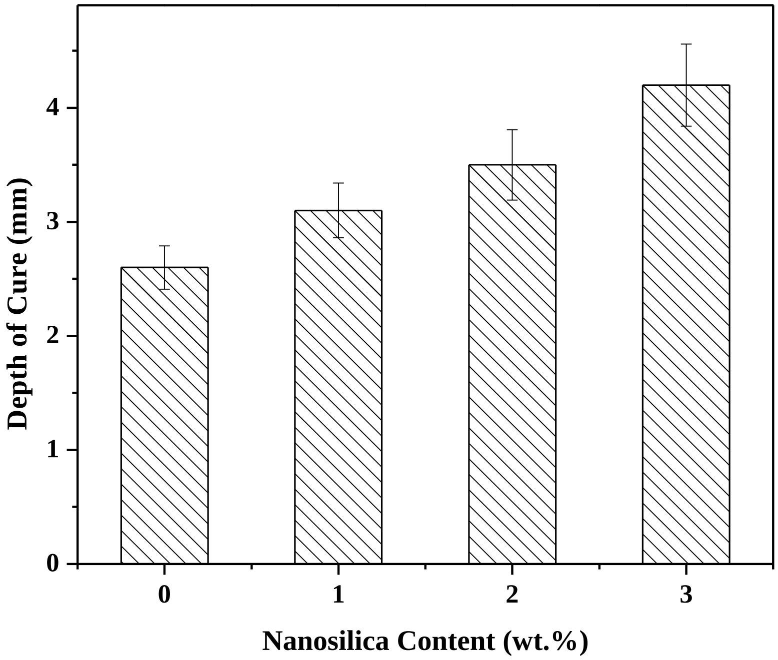


Figure 4.13 Depth of cure for different weight percentages of nanosilica filled dental composites

The results of the present study go with those of Rueggeberg et al. [137], who concluded that, the filler type is one of the most influential factors in the depth of cure. Figure 4.14 indicates the polymerization shrinkage for the composite filled with different wt. % of nanosilica particles. The polymerization shrinkage for the dental composite with 0, 1, 2 and 3 wt. % of nanosilica particles is 3.75, 2.38, 1.92 and 1.53 respectively. It can be seen that polymerization shrinkage decreased with the increasing in silica content in the composite. It may be attributed to the fact that increase in silane treated filler decreased the volume of resin matrix resulting in strong coupling with the resin matrix and formation of strong and stable polymer chain with more molecular weight. This allowed low volume shrinkage upon curing.

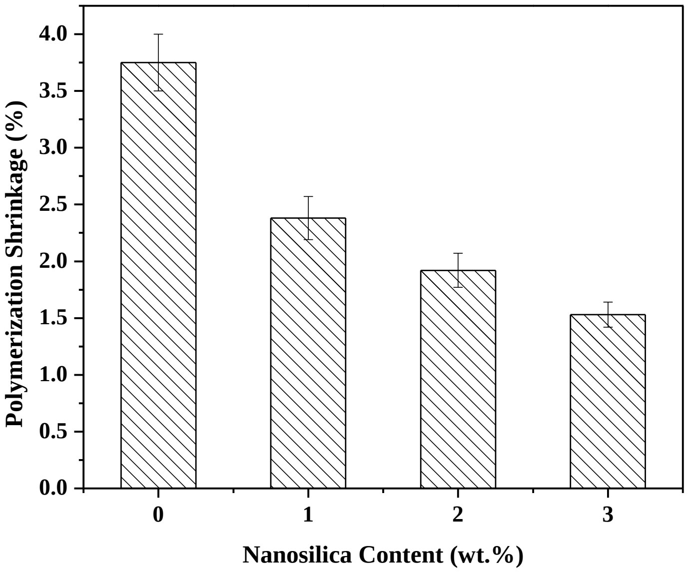


Figure 4.14 Polymerization shrinkages for different weight percentages of nanosilica filled dental composites

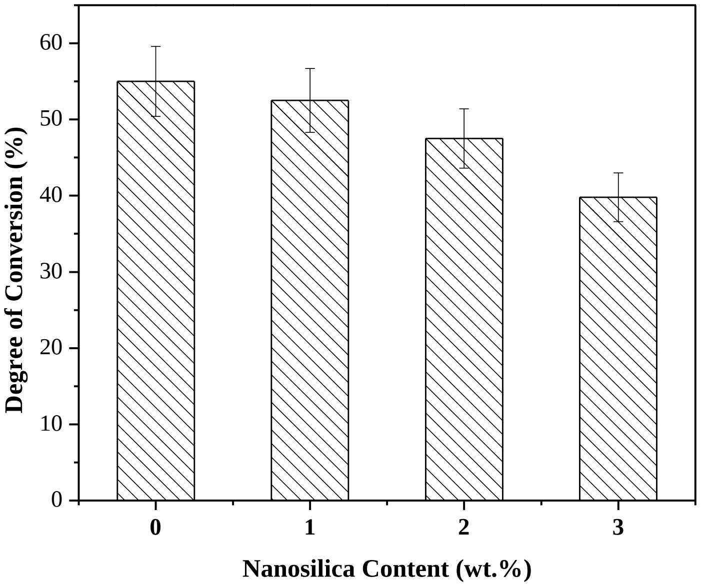


Figure 4.15 Degree of conversion for different weight percentages of nanosilica filled dental composites

A trend of degree of conversion of Figure 4.15 is obvious. Because it is known that the polymerization shrinkage of composite depends on the degree of conversion of monomers during polymerization. Greater the degree of polymerization, greater will be shrinkage [138].

4.3.5 Sorption and solubility of nanosilica filled dental composites

Sorption and solubility of the resin composites after immersion in water for one week are presented in Table 4.6. The composite filled with 3wt.% silica content indicates lowest water sorption. The solubility of composites filled with 0,1,2 and 3 wt. % of silica content is found to be 0.63, 0.95, 2 and 1.23 respectively. In mouth, dental composites absorb water and then release components like nanosilica particles etc within the oral environment which can shorten the service life of restoration and it can create clinical problem.

Table 4.6 Sorption and solubility of nanosilica filled dental composites

Composite	Sorption in µg/mm^3	Solubility in µg/mm^3
NSDC-0: (Composite without Silica)	1.54	0.63
NSDC-1: (Composite with 1 wt.-% Nanosilica)	2.23	0.95
NSDC-2: (Composite with 2 wt.-% Nanosilica)	2.38	2.00
NSDC -3: (Composite with 3 wt.-% Nanosilica)	2.50	1.23

As summarized in Table 4.6, the sorption result showed that the water sorption of composites filled with 0, 1, 2 and 3 wt. % of silica filler are 1.54, 2.23, 2.38 and 2.50 respectively. Decrease in solubility and increase in sorption may be attributed to the decrease in void content and polymerization shrinkage of composite material. The sorption and solubility of all the composites studied are lower than the ISO 9000's standard in which the maximum affordable values of water sorption and solubility for the dental resins are: 40µg/mm^3 and 5µg/mm^3 respectively. The composites prepared in this paper showed the potentially clinical application.

Part IV

4.4 Physical and chemical characterization of gypsum filled dental composites

4.4.1 Fourier transform infrared analysis of gypsum filled dental composites

Figure 4.16 shows Fourier infrared spectroscopy of gypsum filler particle before and after silanization process. The deep absorption peak at 1043 cm^{-1} indicates the presence of strong and stable siloxane group i.e. Si-O-Si. This siloxane group comes from Si-$(OCH_3)_3$ of 3 methacryloxy propyltrimethoxy Silane. Since during silane treatment, the silane is mixed in the solution of water and acetone. pH of solution is adjusted to 4.5–5.5 with acetic acid. Continuous reaction with water or moisture results in the elimination of all OCH_3 groups in the form of alcohol and their replacement with hydroxyl units forming silanols. Low pH is chosen to form stable and coordinated network of Si-O-Si.

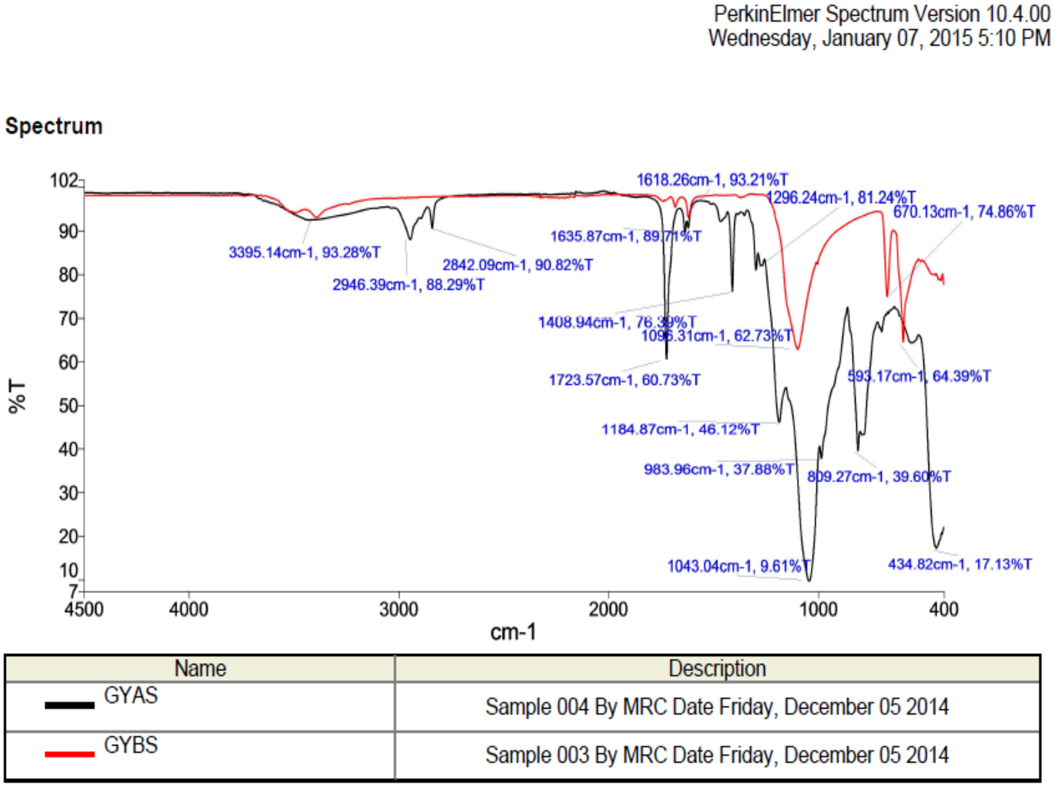
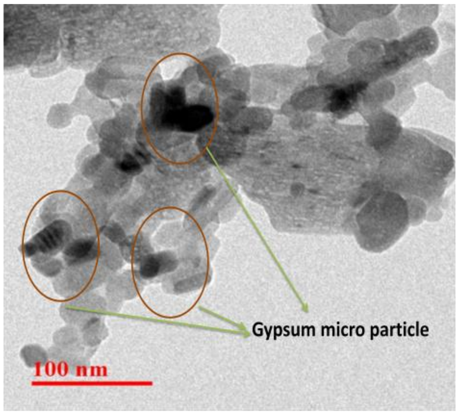


Figure 4.16 Infra Red Spectra of Gypsum Filler before (GYBS) and after silane treatment (GYAS)

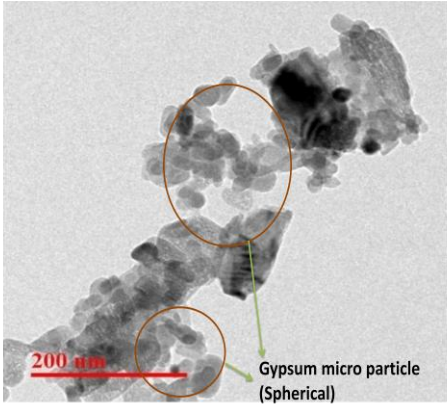
This is in agreement with the Xanthos et al. [139] who concluded that intensities of silane hydrolysis and condensation vary with respect to pH of solution. When pH is low, silane will hydrolyze quickly to form stable silanol but if pH is neutral it will hydrolyze very slowly to silanols that are unstable and will condense. Thus, in both cases, there is a slow reaction in the transition from silanes to Si-O-Si networks. At pH higher than eight, silanes are highly reactive and form silanols very quickly. These silanols are very unstable and condense rapidly to uncoordinated Si-O-Si networks. The buildup of Si-O-Si networks cannot be controlled, and the uniform coating of the filler surface becomes more difficult, resulting in thicker, uncoordinated layers. A strong peak at 1723.57 cm^{-1} is due to formation of carbonyl band (i.e. C=O) arising from the methyl acrylate and the methylacryloxy propyltrimethoxy silane. The presence of absorption peak at 2946 and 2842 is due to symmetric and asymmetric stretching vibration of the –CH3 and –CH2– groups of silane.

4.4.2 Transmission electron microscopy analysis of gypsum filled dental composites

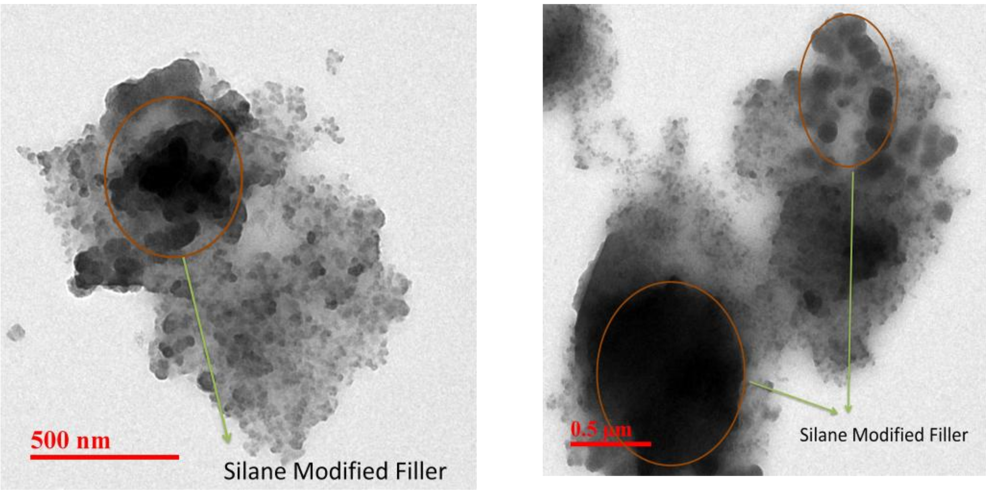
The morphology of gypsum and silane functionalized gypsum is identified using TEM. Images of the Filler before and after silane treatment under TEM are shown in Figure 4.17. The TEM images show that the size of gypsum is made up of particles greater than 20 µm. It can be seen that the silane functionalized gypsum particles are well dispersed in the polymer matrix. The coating of silane on the surface of filler is also uniform, thin and coordinated layers. It can be seen that that the effect of coupling agent plays an important role in dispersion of the micro sized gypsum filler.



(a) Before Silane treatment



(b) Before Silane treatment



(c) After Silane treatment (d) After Silane treatment

Figure 4.17 TEM images of Gypsum filler before and after silane treatment

4.4.3 Effect of void content on gypsum filled dental composites

The theoretical and apparent density values of the gypsum filled dental composites are presented in Table 4.7. The apparent density of the proposed dental composites is calculated by simple water immersion techniques. It can be seen that theoretical values are slightly higher than the apparent density values. Reduction in the density of composites compared to the expected values is attributed to the entrapment of air in the matrix material in the process of curing or during the mixing of filler and resin. This entrapped air, referred as voids, is undesired because it adversely affects the mechanical properties of the composite.

Table 4.7 Effect of void content on gypsum filled dental composites

Composite	Theoretical Density (gm/cc)	Apparent Density(gm/cc)	Void Conten (%)
MGDC-0: (Composite without Gypsum)	1.1765	1.1716	0.41
MGDC-1: (Composite with 1 wt.-% Gypsum)	1.1853	1.1783	0.59
MGDC-2: (Composite with 2wt.-% Gypsum)	1.1809	1.1707	0.86
MGDC-3: (Composite with 3 wt.-% Gypsum)	1.1762	1.1626	1.16

4.4.4 Depth of cure, Polymerization Shrinkage and degree of conversion of gypsum filled dental composites

Figure 4.18 shows that the depth of cure for the dental composite material reinforced with different weight percentage of micro sized gypsum particles is 2.7, 2.9, 3.5 and 3.9 respectively. Dental composite with 3wt.% gypsum indicates the deepest cure. Increase in depth of cure with increase in gypsum filler content is attributed to the fact that increased weight percentage of gypsum particles lead to decrease in volume of resin matrix. Hence the increased volume of gypsum filler permits the light to travel deeper length. All the dental composite materials tested are in agreement with the manufacturer instruction to a depth of cure of at least 2 mm fulfilling the requirement of ISO 4049. Figure 4.19 indicates the polymerization shrinkage for the composite filled with different weight percentage of micro sized gypsum particles. The polymerization shrinkage for the dental composite with 0, 1, 2 and 3 wt. % of micro sized gypsum particles are 4.25, 3.52, 2.42 and 2.02 % respectively.

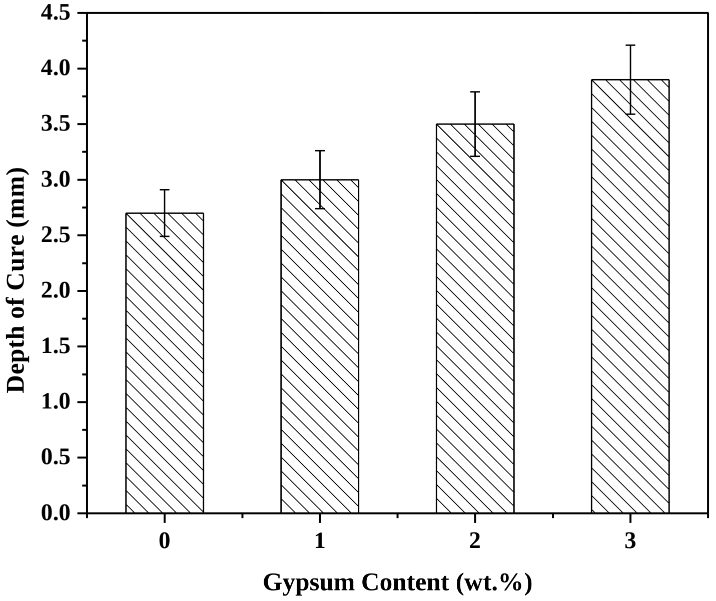


Figure 4.18 Depth of cure for different weight percentages of gypsum filled dental composites

The decreasing trend of polymerization shrinkage with increasing gypsum content can be seen. This decreasing trend may be attributed to the fact that increase in gypsum filler decreased the resin matrix content resulting in strong binding between resin matrix and filler. It leads to formation of strong and stable polymer chain with more molecular weight resulting into low volume shrinkage upon curing. Figure 4.20 indicates the degree of conversion for dental composite filled with different weight fraction of gypsum. The degree of conversion for dental composite filled with different weight percentage of gypsum is 13.12, 15.63, 17.27, and 15.19 % respectively.

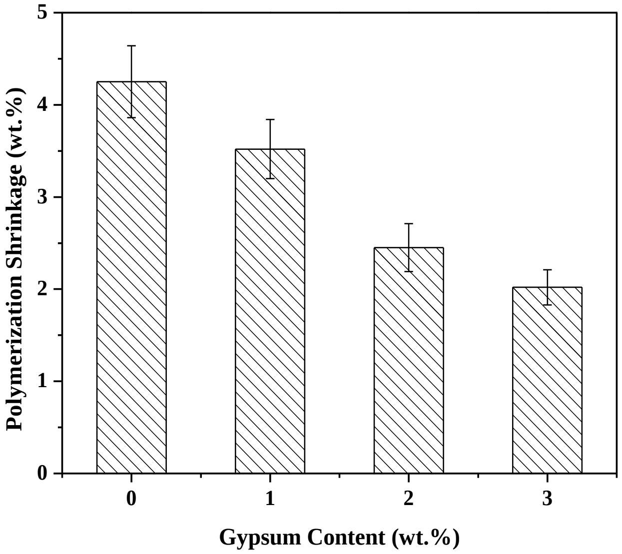


Figure 4.19 Polymerization shrinkages for different weight percentages of gypsum filled dental composites

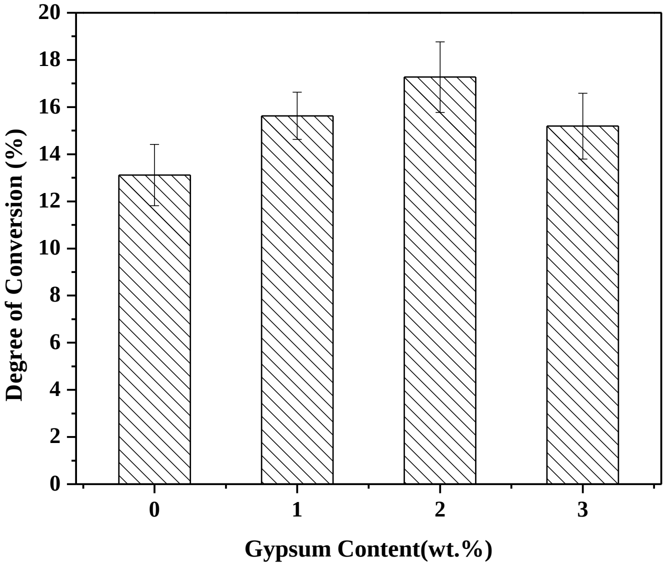


Figure 4.20 Degree of conversion for different weight percentages of gypsum filled dental composites

Increased in degree of conversion with the increased in filler content may be due to the fact that with the increased in filler content reduces the volume of resin matrix, increases the viscosity and resists the molecular mobility inside the resin matrix during polymerization which results into low degree of conversion.

4.4.5 Water sorption and solubility characterization of gypsum filled dental composite

Sorption and solubility of the resin composites after immersion in water for one week are presented in Table 4.8. The water sorption of composites filled with 0, 1, 2 and 3 wt. % of gypsum filler are 1.25, 1.17, 1.26 and 2.77 respectively. The solubility of composites filled with 0,1,2,3 wt. % of gypsum content is found to be 0.63, 0.23, 0.69 and 2.5 respectively. The composite filled with 3wt. % gypsum content indicates maximum water sorption and maximum solubility. This may be attributed to low shrinkage of composite. The sorption and solubility of all the composites studied are lower than the ISO 9000's standard [115] in which the maximum affordable values of water sorption and solubility for the dental resins are: 40μg/mm^3 and 5μg/mm^3 respectively. The composites prepared in this work have potential to be used for dentistry application.

Table 4.8 Sorption and solubility of micro sized gypsum filled dental composites

Composite	Sorption in μg/mm^3	Solubility in μg/mm^3
MGDC-0: (Composite without Gypsum)	1.17	2.5
MGDC-1: (Composite with 1 wt.-% Gypsum)	1.25	1.63
MGDC-2: (Composite with 2wt.-% Gypsum)	1.26	1.23
MGDC-3: (Composite with 3 wt.-% Gypsum)	2.77	1.69

Note: MGDC: Micro sized gypsum filled dental composite

Chapter Summary

This chapter concluded that:

- This chapter presents the physical and chemical properties of the fabricated dental composites.
- The filler particles such as nanosilica, nanoalumina, nanozirconia, and micro sized gypsum particles are successfully modified with MPS.

- Different sets of resin based dental composites have been fabricated. The composites with the highest filler loading exhibited the highest depth of cure (3.9 mm) and lowest polymerization shrinkage (2.02%). According to ISO 4049-2009 standard, the depth of cure value should not be less than 2 mm. In this study, depth of cure of unfilled composite particles is found to be 2.7 mm which is within the limit specified by ISO 4049-2009 standard.
- The mechanical properties such as compressive strength, hardness and flexural strength of dental composite increased with increase in filler content.

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Chapter 5

Mechanical and Thermo-mechanical characterizations of dental composite

Chapter 5

Mechanical and Thermo-Mechanical Properties of Dental Composites

Introduction

This chapter presents the Mechanical and Thermo-mechanical properties of dental composites. The mechanical characterizations include determination of hardness, compressive strength, and flexural properties of dental composite. The Thermo-mechanical characterizations include Dynamic mechanical analysis (DMA) and Simultaneous Thermal Analysis (STA). The interpretation of the results and the comparison among various composite samples are also presented. This chapter consists of four parts: part I consists of dental composited reinforced with nanoalumina filler, part II consists of dental composited reinforced with nanozirconia filler, part III consists of dental composited reinforced with nanosilica filler and part IV consists of dental composited reinforced with micro sized gypsum filler.

Part-I

5.1 Mechanical and thermo-mechanical characterization of nanoalumina filled dental composite

5.1.1 Mechanical characterization of nanoalumina filled dental composite

The variation in mechanical properties such as compressive strength, hardness, and flexural strength of nanoalumina filled dental composite are shown in Figure 5.1. The results indicate that compressive strength of the nanoalumina filled composite increases with the increased in filler content from 0 wt.% to 2wt.% respectively. This is attributed to the stronger coupling between resin and nanoalumina filler which results into increase in mechanical properties because load is transferred from resin to ceramic filler. The reinforcement in a polymer matrix composite increases the strength and stiffness of the relatively weak matrix. The function of the matrix is to bond the reinforcements together and transmit the loads between them [140]. However, with the increasing in percentage of nanoalumina filler from 2wt.% to 3wt.% , there is decrease in compressive strength. This is in agreement with literature [83] which has shown that composites containing a combination of mesoporous and nonporous fillers have better mechanical properties than the composites having either of these fillers alone. This is also in line with the work by Manhart et al. [46] who concluded that

Solitaire, a commercial composite material containing high filler fraction volume of 90% (66 wt. %), demonstrated the significantly lowest mechanical parameters.

Figure 5.2 shows the plot between Vickers hardness vs. nanoalumina filler content (in wt. %) for the resin based dental composites. The composite with different weight percentages of nanoalumina particles demonstrate significantly higher hardness compared to the unfilled resin matrix. The Vickers hardness of the composite with 1, 2, and 3 wt.% of nanoalumina particles exhibits 17.5, 20, and 25 Hv respectively, while the unfilled resin matrix indicates lower values of hardness i.e. 15 Hv. The increase in hardness with the increased in filler content is attributed to the fact that stiffer inorganic oxides are more brittle than the resin matrix. However, addition of filler particles in the matrix material stiffens the elasticity and improves the matrix surface resistance to the indentation. This fact is in line with the literature [141] in which it is concluded that the filler amount contributes to the material performance as well as increased in hardness are due to increase in percentage of the hard phase of nanoalumina particles in the ductile resin matrix.

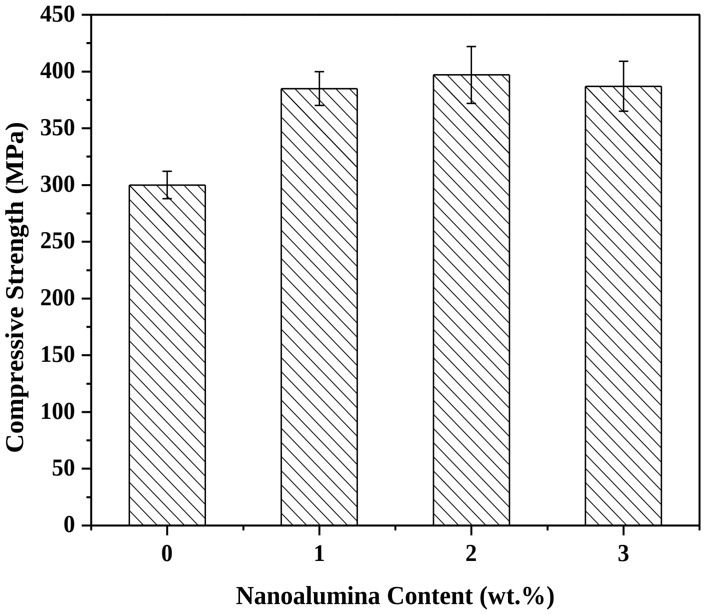

Figure 5.1 Effect of compressive strength on Nanoalumina filled dental composites

In another research, similar observation is also reported by Foroutan et al. [78] and concluded that a more efficient nanoparticle dispersion combined with higher loadings may lead to an even more improved composite dental restorative materials irrespective of the size of the nanofiller in the matrix material [142].

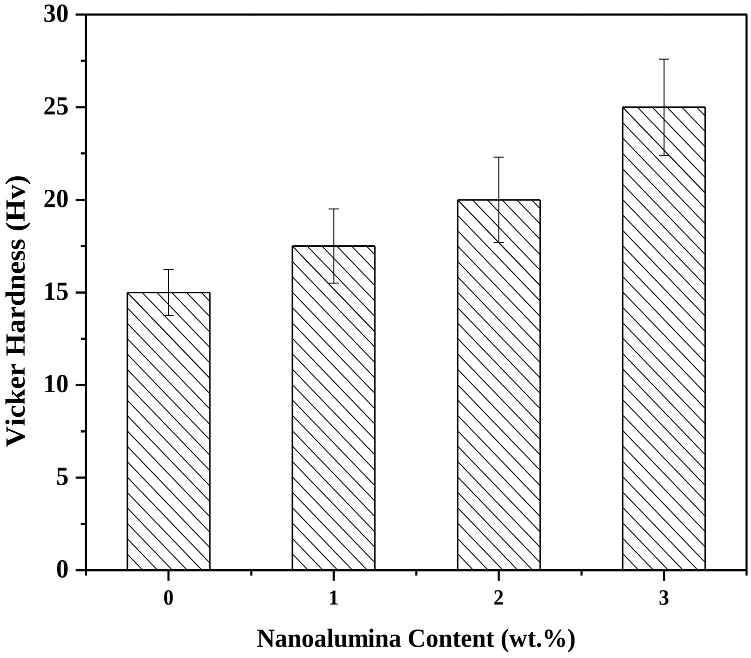

Figure 5.2 Effect of Vickers hardness of Nanoalumina filled dental composites

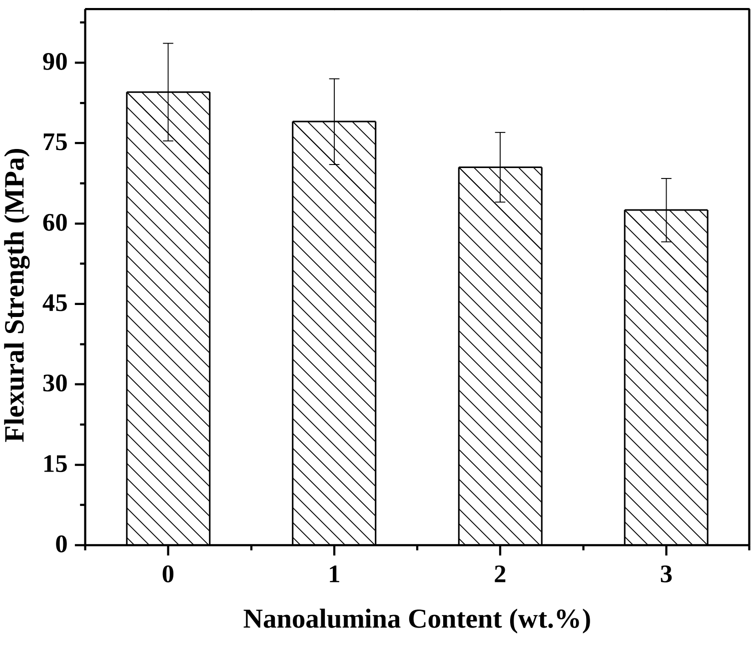

Figure 5.3 Effect of flexural strength on Nanoalumina filled dental composites

Figure 5.3 shows the flexural strength values of the resin matrix filled with different ratios of nano Al_2O_3 particles. It can be seen that the flexural strength for the composites having 0, 1, 2, and 3 wt.-% of alumina is 84.5, 79, 70.5, 62.5 MPa respectively. The result of this study reveals that when the weight percentage of Al_2O_3 particles is increased in the resin matrix, the flexural strength values are found to be slightly decreased. The decrease in flexural strength is attributed to the increase in loading of filler of inadequate shape. Since inadequate particulate fillers do not hinder crack propagation as compared to fiber shaped filler.

In this study, the minimum flexural strength value of resin matrix filled with 3 wt. % nanoalumina particles is reached up to 62.5 MPa which is within the specified limit as per ISO 4049 standard. According to ISO 4049 standard for polymeric restorative dental material, the flexural strength for dental composites should not be less than 50 MPa.

5.1.2 Dynamic mechanical analysis of nanoalumina filled dental composites

The dynamic mechanical properties of the composites in terms of variation in storage modulus (E') and loss modulus (E") and Tan δ with temperature are shown in Figures 5.4a, 5.4b and 5.4c respectively. Conceptually E' and E" correspond to the extent of elastically recoverable response and non recoverable viscous response due to dissipation via frictional and internal motions of the composites. Storage modulus defines the energy stored elastically in the material, while loss modulus corresponds to the energy loss as heat [143]. Storage modulus describes the relative stiffness or rigidity of a material. A stiff composite will require a higher load to deform to the same extent as a more elastic one. From this point of view a composite placed in stress-bearing areas it is required to withstand at least the active masticatory forces to avoid stress concentration at the tooth-restoration interface. Ideally the elastic modulus of dental composites should be matched to those of dental tissue they are supposed to replace. Figures 5.4a represents storage modulus (E') vs. temperature curve for all four dental composites. It can be seen that during low temperatures range (30-50°C), there is decrement in storage modulus and afterward at high temperatures (50-120°C), abrupt decrease is recorded and finally it become constant. The abrupt decrease in the storage modulus as a function of temperature is attributed to the glass transition region of the material. Region between 50–80°C is due to the thermal curing reaction occurring during the test, because of increased in temperature. Hence, with the increased in temperature, the storage modulus (E') decreases for all dental composites. The decrease in storage modulus with the increase in temperature was due to the fact that the increase in temperature led to increase the molecular mobility inside the polymeric matrix resulting into softening the polymeric material. From 30-50°C, the molecules were closely packed and storage modulus was high. This decreased drastically in the region of glassy to rubbery stage. After transition stage, it became nearly constant in the rubbery state.

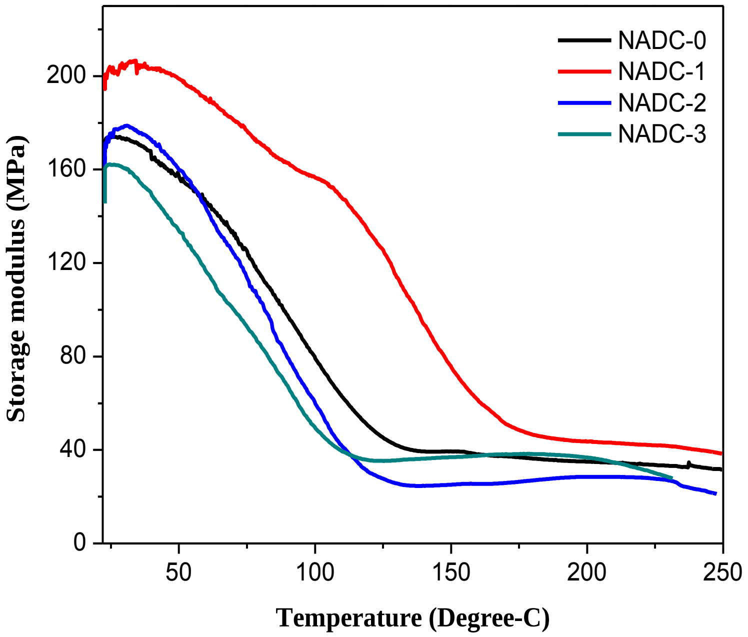

Figure 5.4a Variation of the storage modulus (E') as a function of temperature for Nanoalumina filled in dental composite

It is known that the quick reaction in light-curing of dimethacrylates at room temperature induces incomplete conversion of their functional groups. Initially the storage modulus increases with the increased in filler content up to 1wt.% and on further addition of nanoalumina filler in the matrix material the storage modulus starts decreasing in trend as shown in Figures 5.4a [144]. Hence, dental composite with 1wt.% nanoalumina filler content exhibited maximum storage modulus which is 17.64% more than that of unfilled composite.

The loss modulus (E") generally represents the viscous nature of the material and higher viscous modulus suggests greater ability to relieve excess energy built up through moderate viscous flow during tooth function. It can be seen that loss modulus of nanoalumina filled composite is higher than that of unfilled composite (Figures 5.4b). This may be due to uniform dispersion of nanoparticles in the resin matrix and therefore interaction between matrix and nanofiller is stronger with the increased in interfacial area. Figure 4b shows the three different stages of loss modulus variation i.e. from 30-50°C slope variation is more between composites, from 100-120°C abrupt loss modulus and from 120°C-250°C gradual loss modulus pattern.

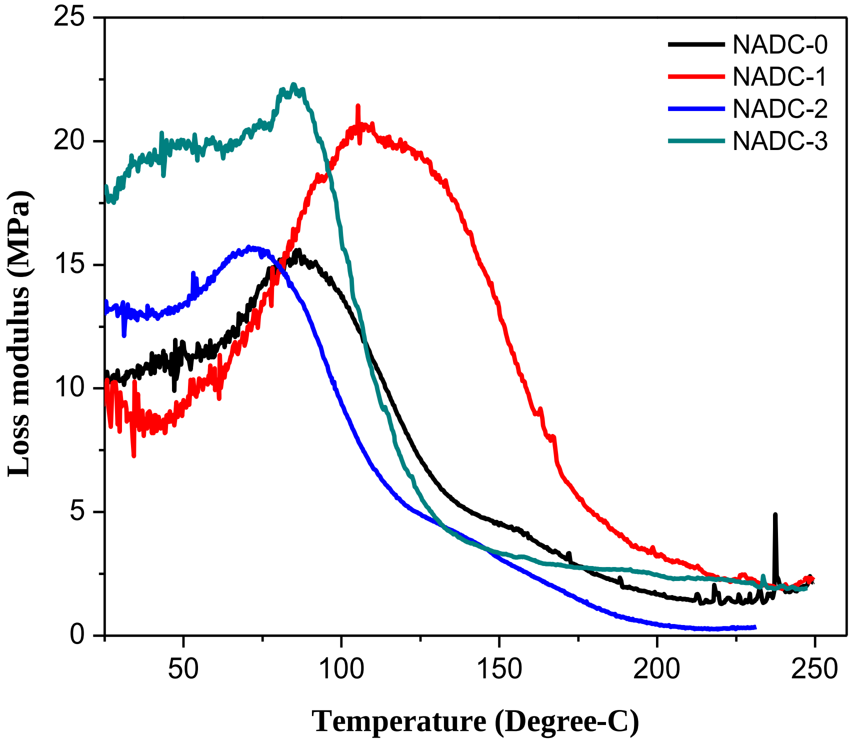

Figure 5.4b Variation of the loss modulus (E") as a function of temperature for Nanoalumina filled dental composite

Figures 5.4c represents Tan δ versus temperature curves obtained for different composite at a constant frequency 1 Hz. It is clear that the composite with 1 wt.% nanoalumina filler content shows least damping ratio as compared to the other composites because addition of nanoalumina particle improves the chain mobility of filler particles inside the resin matrix and less energy is dissipated. However, on further increasing in filler loading with respect to increase in temperature the Tan δ also increases. Therefore, increased in the value of Tan δ indicates that the number of the mobile chains during the glass transition is increased. Composite with 1wt. % nanoalumina content shows broad Tan δ at half of the peak has the widest temperature range more than 100°C. Glass transition temperature of dental composite filled with 1wt. % nanoalumina is 160°C which is maximum among all filled and unfilled composite.

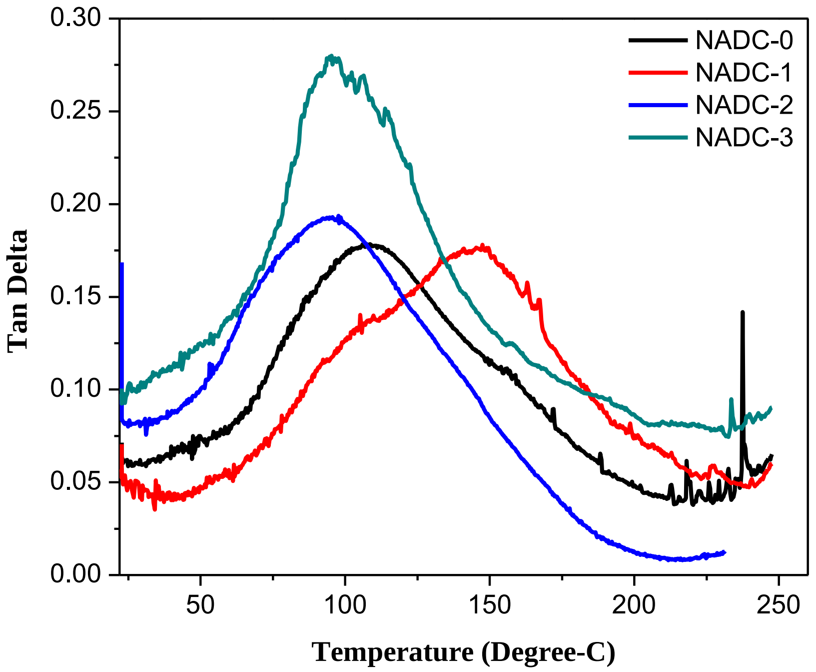

Figure 5.4c Variation of the Tan Delta (Tan δ) as a function of temperature for Nanoalumina filled dental composite

5.1.3 Simultaneous Thermal Analysis of nanoalumina filled dental composites

The thermal characteristics of all the fabricated nanoalumina filled dental composites have been investigated by Simultaneous Thermal Analysis (STA) as presented in Table 5.1 and shown in Figure 5.5. Earlier study reported the glass transition temperature ranging from 40 to 110°C [145, 146] for untreated micro zirconia / silica reinforced dental composites. However, in the present analysis with silane treatment nanoalumina filled dental composites the glass transition temperature is slightly shifted to higher temperature i.e. about 45 ºC higher than those values from 110 to 155°C (Table 5.1). Composite with 1wt.% nanoalumina content exhibits lowest glass transition temperature, crystallization temperature and melting temperature. However composite with 3wt. % nanoalumina content indicates maximum glass transition crystallization and melting temperature. It may be due to presence of maximum void (Table 4.1). Table 5.1 also indicates that the endothermic peak around 40–45°C in the first run corresponds to the evaporation of water and appeared in all the composite samples. The glass transition temperature and crystallization temperature occur in the interval of around 125-155°C and 170-180°C respectively. These results show a decomposition temperature for dental composites around 265–320 °C, a temperature range that's agreement would be checked with the highest weight loss observed in TGA.

Table 5.1 DSC Analysis on nanoalumina filled dental composites

Sl. No.	Composition	1st Endothermic Peak (°C)	Glass Transition (°C)	Crystallization temperature (°C)	Biopolymer decomposition (°C)
1	NADC-0	45-50	125-130	170-175	300
2	NADC-1	55-60	150-160	180-200	260
3	NADC-2	45-50	140-145	170-175	310
4	NADC-3	50-55	150-155	175-180	320

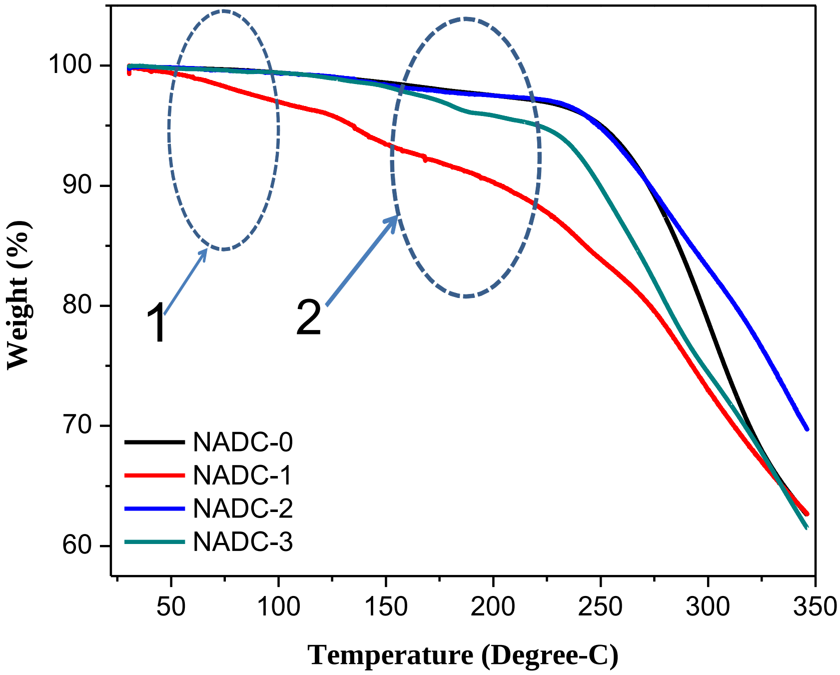

Figure 5.5 TGA thermograms of Nanoalumina filled dental composite

These results show a decomposition temperature for dental composites around 275–310°C, a temperature range that agrees with the highest weight loss observed in TGA. Figure 5.5 shows TGA curves of nanoalumina filled composites. It is revealed that the weight loss and consequent degradation for all nanoalumina filled resin composites studied began around 240°C. The thermal behavior is observed for these composites can be described in two main steps: the first mass loss (5-7%) from 30–150°C is due to the loss of bound-water. The second step is from 220–330°C, with mass decreasing from 8%–45%, this is associated with a complex process that includes depolymerization and decomposition of the polymer unit. Mass losses initiated around 200°C except the composite filled with 1 wt.% nanoalumina which indicates thermally unstable behavior throughout the temperature range from 30 to 350°C. The unstable behavior of 1wt.% nanoalumina filled composite can be seen under dotted circle 1 and 2 (Figure 5.5). The greater the percentage of filler content, higher the polymer structure homogeneity and hence higher the glass transition temperature [147, 148].

Part-II

5.2 Mechanical and thermo-mechanical characterization of nanozirconia filled dental composite

5.2.1 Mechanical characterization of nanozirconia filled dental composite

Several of the forces during mastication are of compressive nature. Hence, compressive strength of dental composite is needed to be determined for long service life of dental composite. From Figure 5.6, it can be seen that compressive strength of dental composite filled with 1wt.%, 2wt.% and 3 wt.% are 291.5, 296.24, 311.44MPa whereas unfilled composite exhibits compressive strength of 287.7MPa. It can be observed that the compressive strength increases with the increase in nanosilica filler contents. The increase in compressive strength with the increase in nanosilica filler content is attributed to the presence of stronger coupling between resin and nanozirconia filler which leads to increase in mechanical properties because load is transferred to ceramic fill. The reinforcement in a polymer matrix composite increases the strength and stiffness of the relatively weak matrix.

The Vickers hardness values of the dental composite filled with different weight percentage of nanozirconia (0, 1, 2 and 3wt. %) are depicted in the Figure 5.7. It is revealed that addition of nanozirconia filler enhances the hardness of dental composite significantly. The hardness of unfilled dental composite indicates lower hardness value of 15.1Hv whereas hardness of dental composite with 1, 2, and 3 wt. % of nanozirconia particle reached 22.5, 28.2, and 35.6Hv respectively.

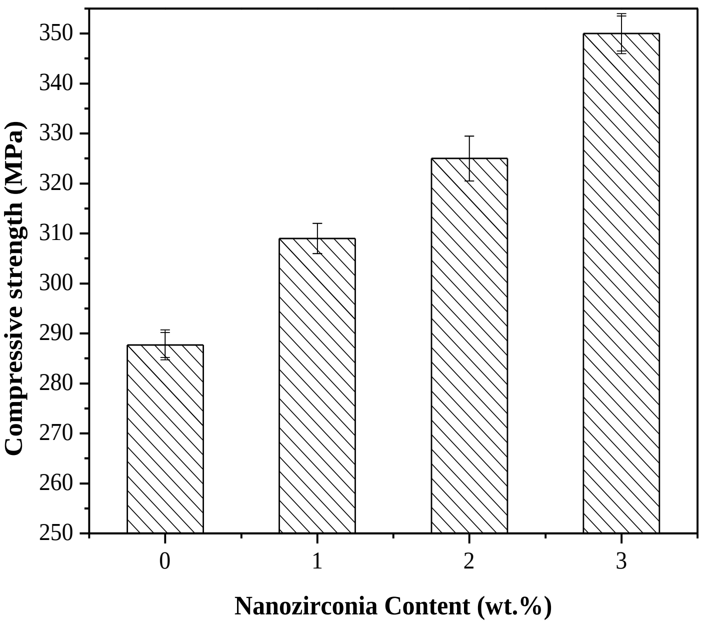

Figure 5.6 Effect of compressive strength on nanozirconia filled dental composites

This is due to increase in ceramic like filler which are much stiffer and brittle as compared to ductile resin matrix. Masouras et al. [141] concluded that the filler amount contributes to the material performance. McCabe et al. [149] proposed that hardness increases almost monotonically with filler volume fraction for silanated fillers but there is no such clear relationship when fillers are unsilanated. Figure 5.8 shows the flexural strength values of the resin matrix filled with different ratios of nanozirconia particles. It can be seen that the flexural strength for the composites having 0, 1, 2, and 3 wt. percent of nanozirconia is 75.5, 80.6, 99.2, 112.5MPa respectively. It is found that flexural strength of dental composite increased with the increase in nanozirconia content. This result is in agreement with Kim et al. [9]. They concluded that the morphological characteristics of the fillers must also be considered, since they have been shown to be determining factors in both the filler loading and the material strength. Smooth spherical shaped filler particles are related to an increased volume fraction of the filler due to the improved packing of the particles and also to higher flexure strength [150].

However, in another result, no correlation between the highest filler wt.% and the highest mechanical properties is observed, which indicates that they are some other factors than the filler weight percentage are involved in the mechanical behaviour of the composites [151].

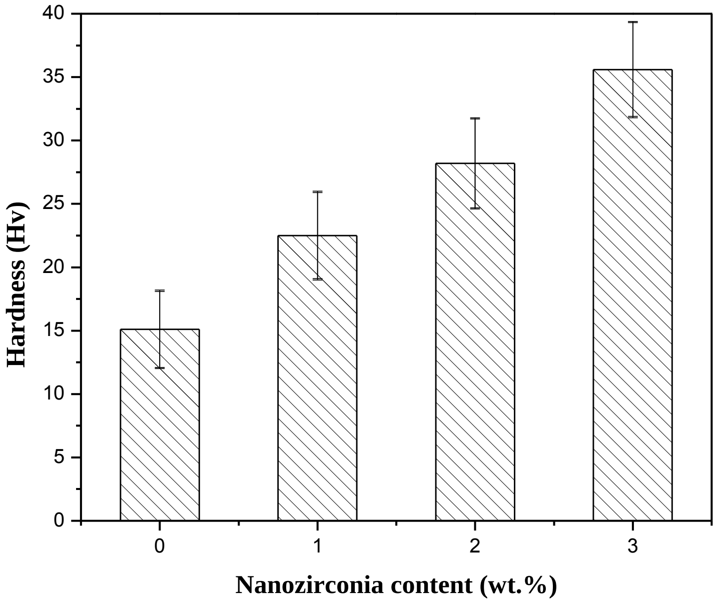

Figure 5.7 Effect of Vickers hardness of nanozirconia filled dental composites

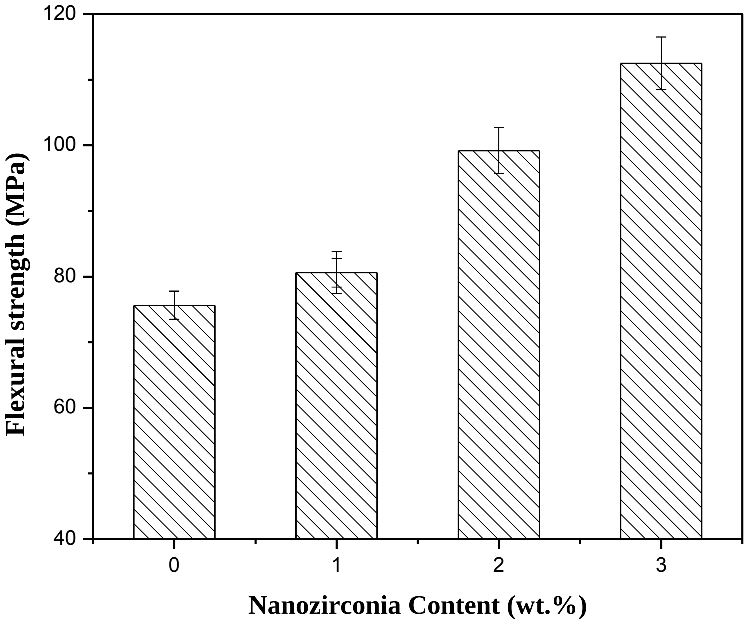

Figure 5.8 Effect of flexural strength on nanozirconia filled dental composites

5.2.2 Dynamic mechanical analysis of nanozirconia filled dental composites

In oral environment, dental composites are exposed to dynamic loading rather than static loading hence dynamic tests, having variable such as time, temperature and surrounding medium, needs to be conducted. The dynamic mechanical properties of the composites in terms of variation in storage modulus (E') and loss modulus (E") and

Tan δ with temperature are shown in is shown in Figure 5.9a, Figure 5.9b and Figure 5.9c respectively. Conceptually E' and E" correspond to the extent of elastically recoverable response and non recoverable viscous response due to dissipation via frictional and internal motions of the polymer. Storage modulus defines the energy stored elastically in the material, while loss modulus corresponds to the energy loss as heat.

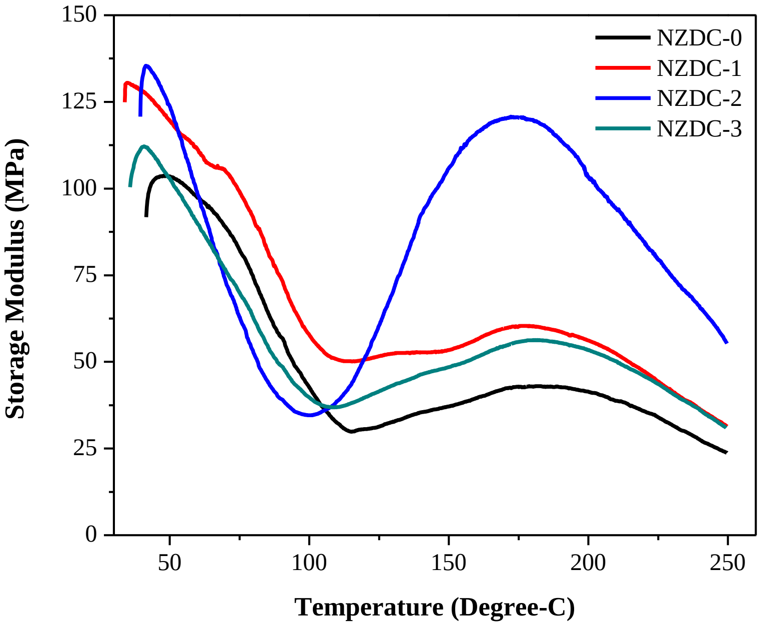

Figure 5.9a Variation of the storage modulus (E') as a function of temperature for nanozirconia filled in dental composite

Figure 5.9a represents storage modulus (E') vs. temperature curve for all the four dental composites. It is revealed that during the low temperatures (30-50°C), some increment in storage modulus is reported but during the temperatures (50-100°C), there is abrupt decrement in storage modulus. The abrupt decrease in the storage modulus as a function of temperature is attributed to the glass transition region of the material. Region between 50–80^{o}C is due to the thermal curing reaction occurring during the test, because of the temperature increase. It is known that the fast reaction in light-curing of dimethacrylates at room temperature induces incomplete conversion of their functional groups. However, during the temperature range 100-250°C, there is again increment in storage modulus up to 200°C and it further decreased up to 250°C. The decrease in the value of storage modulus is much lower than that at room temperature showing molecular mobility in composite. This behavior occurs due to increase in molecular mobility in polymer chain above T_g which results in strongly weakening of filler-matrix interfacial bond. The value of storage modulus is increased with the increased in nanozirconia filler content up to 2 wt. %. This may be due to great stress transfer at the interface of fiber and matrix. For further increased in nanozirconia filler reinforcement from 2wt.% to 3wt.%, there may be improper interfacial bonding which results in reduction in value of E′. Hence, dental composite with 2wt. % nanozirconia filler content exhibits maximum storage modulus which is 30% more than that of unfilled composite. However the dental composite filled with 2 wt. % of nanozirconia indicates two peaks of storage modulus. This may be due to the fact that dental composite exhibits two peaks at 25°C and 175°C indicating again the presence of two phases. The peak at 25°C corresponds to silane treated filler and the one at 175°C relates to composite material [152].

The loss modulus (E) represents the viscous nature of the material. Higher viscous modulus suggests greater ability to relieve excess energy built up through moderate viscous flow during tooth function. Figure 5.9b represents the loss modulus of composite of different wt.% of nanozirconia filler. It can be seen that loss modulus of 2wt. % nanozirconia filled composite is higher than that of unfilled composite.

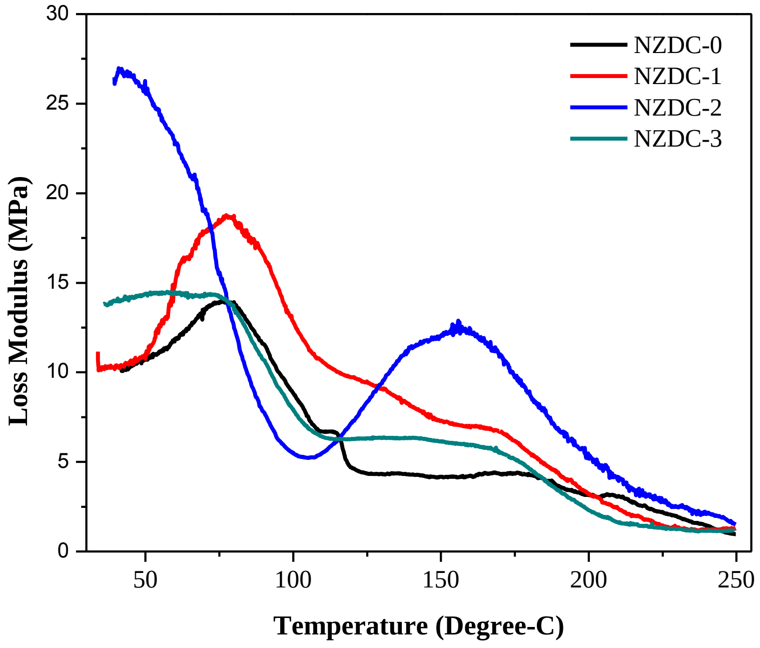

Figure 5.9b Variation of the loss modulus (E") as a function of temperature for nanozirconia filled dental composite

It may be due to uniform dispersion of nanoparticles in the resin matrix. Therefore interfacial area is larger and interaction between matrix and Nanofiller is stronger. Within the range (30-75^{o}C), loss modulus for different composite increased with different slopes. After attaining maximum loss modulus, it decreased abruptly during (75-120^{o}C). Loss modulus of dental composite with 2wt. % nanozirconia exhibits maximum value. Decrease in loss modulus is reported when filler content increased from 2 to 3 wt. %.

Tan δ represents the ratio of the viscous to elastic response of a viscoelastic material or in another word the energy dissipation potential of the material. To make it simple, assume that you apply a load to a polymer, some part of the applied load is dissipated by the energy dissipation mechanisms (such as segmental motions) in the bulk of polymer, and other part of the load is stored in the material and will be release upon removal of the load (such as the elastic response of a spring). Figure 5.9c represents

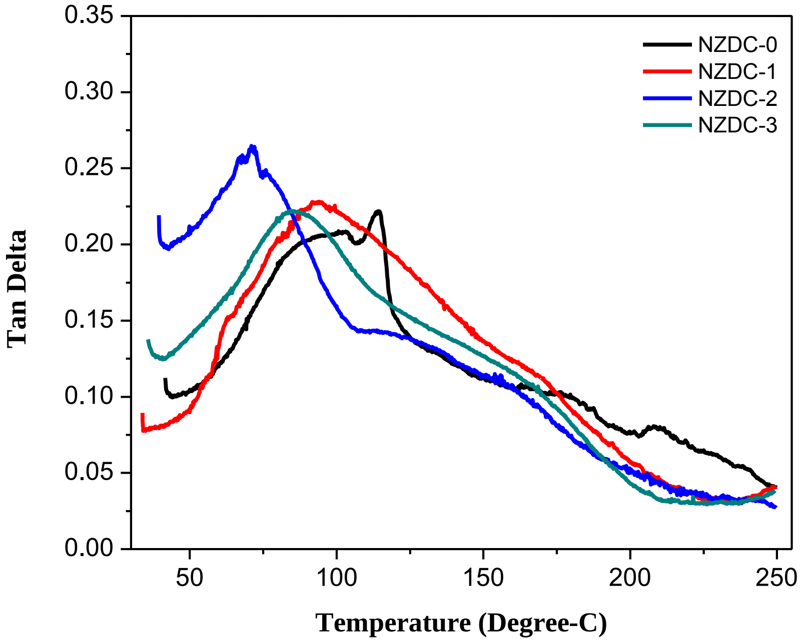

Figure 5.9c Variation of the Tan Delta (Tan δ) as a function of temperature for nanozirconia filled dental composite

Tan δ versus temperature curves obtained for different composite at a constant frequency 1 Hz. It is observed that, in transition region the damping factor increases with increase in temperature. It reaches to maximum value and further in rubbery region it falls. It is also observed for all composites the damping factor value below T_g

is quite low due to polymeric chains are in frozen in this temperature range. Glass transition temperature decreases with increasing filler content. This may be attributed to the decrease in rate of energy loss. This also may be possible due to enhancement of storage modulus of composite could limit the degree of freedom of the polymeric network at atomic level. Highest value of damping factor is observed for 2wt. % nanozirconia filled composite at glass/rubbery transition region. The trend in variations of T_g from damping factor curve is in good agreements with T_g as obtained from E″ curve.

5.2.3 Simultaneous Thermal Analysis of nanozirconia filled dental composites

The thermal characteristics of all the fabricated composites have been investigated by STA as shown in Table 5.2 and Figure 5.10 respectively. Table 5.2 shows a DSC thermograph and indicates that there is slight change in glass transition, crystallization and melting temperature. Composite with 1 wt. % nanozirconia content exhibits lowest glass transition temperature (T_g = 125°C), crystallization temperature (T_c=160°C) and melting temperature (T_m=310°C). However unfilled composite indicates maximum glass transition temperature (T_g =140°C), crystallization temperature (T_c=220°C), melting temperature (T_m=320°C).

From Table 5.2, it can be observed that the endothermic peak around 40–45°C in the first run corresponds to the evaporation of water and appeared in all the composite samples. The next endothermic peak around 130 °C can be assigned to the glass transition temperature. The peak at 180 °C can be assigned to the crystallization temperature. The peak at 300°C could be ascribed to total biopolymer decomposition. These results show a decomposition temperature for dental composites around 275–310 °C, a temperature range that agrees with the highest weight loss observed in TGA.

Table 5.2 DSC Analysis on nanozirconia filled dental composites

Sl. No.	Composition	1st Endothermic Peak (°C)	Glass Transition (°C)	Crystallization temperature (°C)	Biopolymer decomposition (°C)
1	NZDC-0	48-50	130-140	175	320
2	NZDC-1	40-42	135-145	170	325
3	NZDC-2	42-45	120-125	175	330
4	NZDC-3	48-50	130-140	195	350

Figure 5.10 shows TGA curves of nanozirconia filled composites. It is revealed that the weight loss and consequent degradation for all resin composites studied began around 250ºC. The thermal behavior observed for these composites can be described in two main steps: the first mass loss (0-5%) from 30–250°C is due to the loss of bound-water. The second step is from 250–330 °C, with mass decreasing from 5%–30%, this is associated with a complex process that includes depolymerization and decomposition of the polymer matrix. The unstable behavior of 1wt.% filled composite can be seen under dotted circle 1 and 2 in the Figure 5.10. From the dotted circle 2 it can be seen that the mass loss initiated around 250 °C except the composite filled with 1% nanozirconia which indicates thermally unstable behavior throughout the temperature range (30-350) ºC.

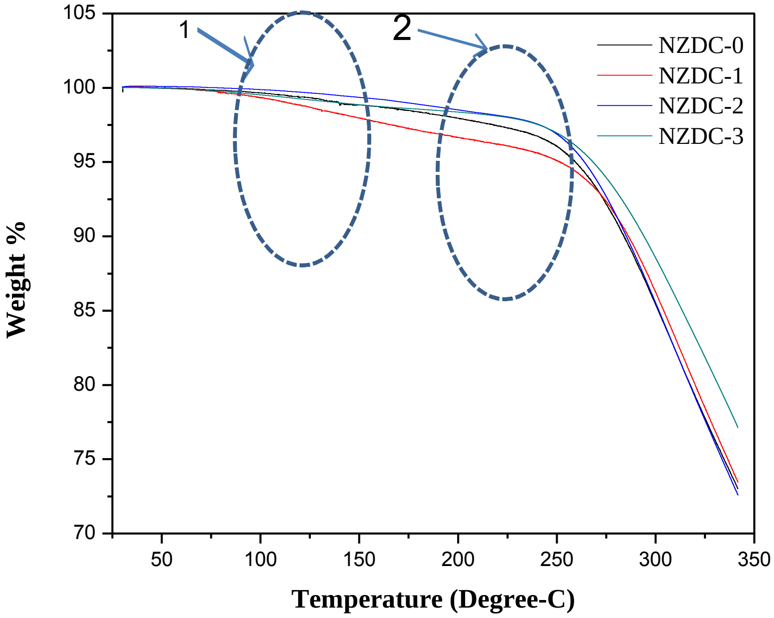

Figure 5.10 TGA thermograms of nanozirconia filled dental composites

The addition of nanofiller increased the mass loss rate but later when filler content is increased from 1 wt. % to 2 wt. %, its thermal stability slightly improved but again its thermal stability decreases upon increase in filler loading i.e. from 2 to 3%. All results from TGA revealed that the weight loss and consequent degradation for all resin composites studied began around 250 ºC. The weight loss of composite is attributed to the fact that the sample containing moisture is heated, with increase in temperature moisture get evaporated that result in decrease in the weight of sample correspond to the moisture.

Part-III

5.3 Mechanical and thermo-mechanical characterization of nanosilica filled dental composite

5.3.1 Mechanical characterization of nanosilica filled dental composite

The variation in mechanical properties such as compressive strength, hardness, flexural modulus and flexural strength of dental composite filled with different wt.-% of nanosilica are shown in Figure 5.11. Compressive strength has a particularly important role in the mastication process since several of the masticatory forces are of compressive nature. From Figure 5.11, it can be seen that with the increased in nanosilica content (1 to 3 wt. %), the compressive strength of dental composite increases. This is attributed to increase in silane treated nanosilica particles. Increase in silane treated filler lower the volume of resin matrix by increasing the coupling strength between composite and fillers and forming comparatively more strong and stable chain containing siloxane group. However, unfilled dental composite exhibits maximum compressive strength. This may be attributed to the facts that unfilled composite reported maximum polymerization shrinkage (Figure 4.14) lowest void content (Table 4.5).

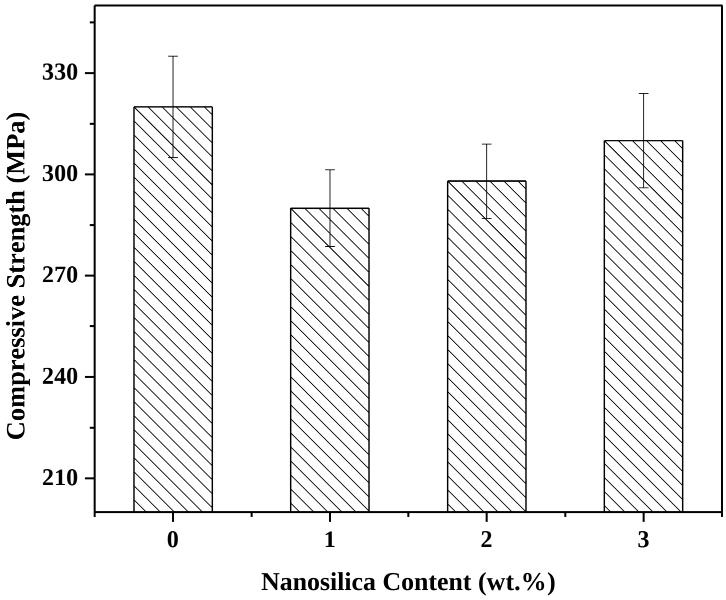

Figure 5.11 Effect of compressive strength on nanosilica filled dental composites

Figure 5.12 shows the Vickers hardness values of the dental composite filled with different wt. % of nanosilica content. It can be seen that the composite with different wt. % of nanosilica particles demonstrated significantly higher hardness compared to the unfilled resin matrix. The hardness of the composite with 0, 1, 2, and 3 wt% of nanosilica particle reached to be 22, 24.5, 28.5, and 33.6 respectively. The increase in hardness value with increase in nanosilica filler content is attributed to the increase in stiffer and brittle inorganic oxide as compared to resin matrix therefore, it is reasonable that increased nanosilica particles led to increased in hardness of dental composite. This is in agreement with Nevas et al. [153] who established a direct correlation between filler content and Vickers hardness number. They finally concluded that hardness increases uniformly with filler amount. Figure 5.12 also indicates that the dental composite having maximum weight percent of nanosilica exhibits maximum hardness and from previous chapter i.e. Figure 4.8 (Chapter-4), same composite has indicated maximum depth of cure. This is in line with study by El-Nawawy et al. [154] who reported that there must be direct correlation between depth of cure and micro hardness of composite. They observed that composite material filled with higher wt.-% of nanosilica content exhibited maximum hardness and minimum depth of cure.

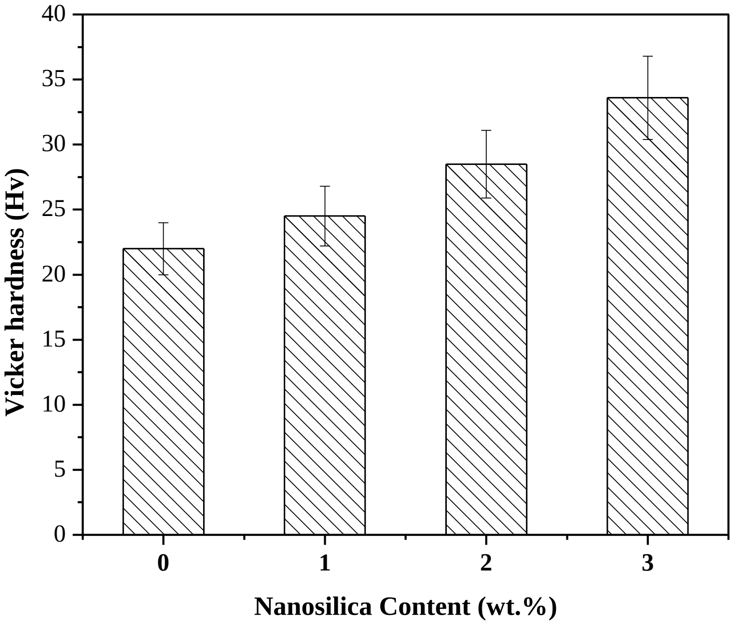

Figure 5.12 Effect of Vickers hardness of nanosilica filled dental composites

Figure 5.13 shows the flexural strength values of the resin matrix filled with different ratios of SiO_2 particles. It can be seen that the flexural strength for the composites having 0, 1, 2, and 3 wt. percent of silica is 115, 80.2, 72.5, 65.5 MPa respectively. It is found that unfilled dental composite exhibits maximum flexural strength which is much more than that of other composite. This can be attributed to having lowest void content or maximum polymerization shrinkage of composite. However, increase in the weight percentage of SiO_2 particles resulted in decrease in flexural strength. This result is in agreement with Pereira et al. [155] and Willis and Masters [156] who observed that increasing the amount of filler loading led to a decrease in strength. This is due to the increased loading of filler of inadequate shape. It is known that particulate fillers do not hinder crack propagation through a composite material as effectively as fibre- shaped fillers. Hence, Polymer-reinforced fibres have high specific strength compared to conventional polymer materials [157]. These observations are within the specified limit as per ISO 4049-2009 standard which states the flexural strength value should not be less than 50 MPa. In this study, the flexural strength value of resin matrix filled with 3wt. - % of nanoSiO_2 particles reached 65.5 MPa. Hence, it may be suitable for the dental restoration application.

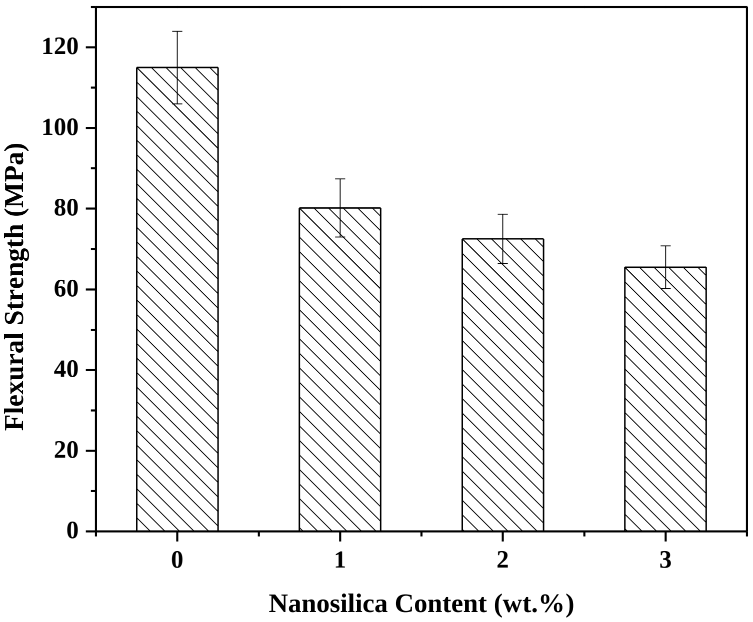

Figure 5.13 Effect of flexural strength on nanosilica filled dental composites

5.3.2 Dynamic mechanical analysis of nanosilica filled dental composites

In oral environment, dental composites are exposed to dynamic loading rather than static loading hence dynamic tests needs to be conducted. Dynamic tests better mimic the cyclic masticatory loading to which dental composites are clinically subjected. Dynamic tests such as dynamic mechanical analysis (DMA) is particularly well suited to characterizing viscoelastic materials and has been suggested as a valuable tool for obtaining information regarding the crosslink density and structural heterogeneity of polymer networks, since the method measures both elastic and viscous responses. DMA measures stiffness and damping, these are reported as modulus and tan delta. Because after applying sinusoidal force, storage modulus is expressed as an in-phase component, loss modulus as out of phase component. The storage modulus is the measure of the sample's elastic behaviour. The ratio of the loss to the storage is the tan delta and is often called damping. It is a measure of the energy dissipation of a material under cyclic load. Figure 5.14a represents storage modulus (E') vs. temperature curve for all the four dental composites.

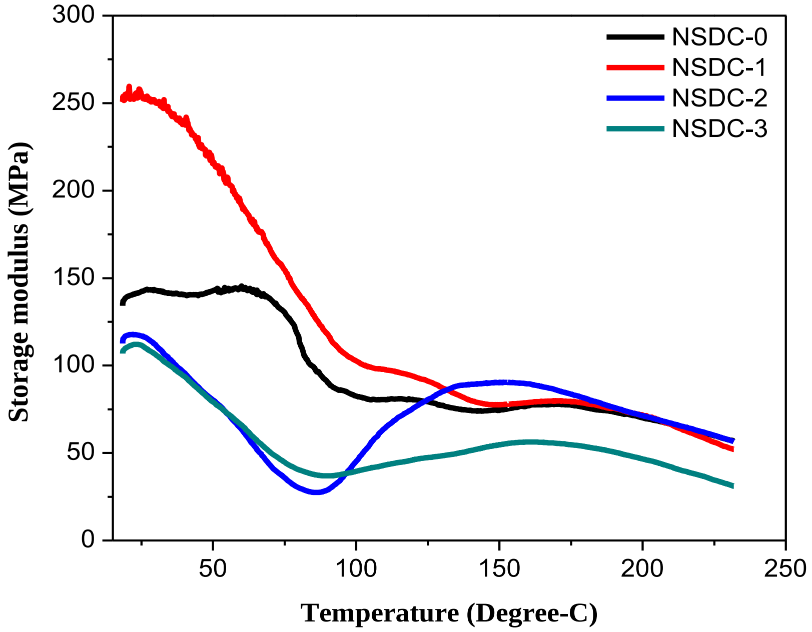

Figure 5.14a Variation of the storage modulus (E') as a function of temperature for nanosilica filled in dental composite

It can be seen that during the low temperatures (30-80^{o}C), there is abrupt decrement in storage modulus except the case of unfilled composite and afterward at high temperatures (80-150^{o}C), decrease is recorded at slow rate and finally it became constant. But the trend reported by dental composite filled with 2 wt. % of nanosilica indicates two peaks of storage modulus. This may be due to the fact that dental composite exhibits two peaks at 25°C and 150°C indicating again the presence of two phases. The peak at 25°C corresponds to silane treated filler and the one at 150°C relates to composite material. Region between 50–120°C is attributed to the thermal curing reaction occurring during the test due to increase in temperature. It is known that the fast reaction in light-curing of dimethacrylates at room temperature induces incomplete conversion of their functional groups. On increasing the temperature, E' decreases for all composites, due to the increased molecular mobility of the polymer chains. Increase in storage modulus is reported when filler content increased from 0 to 1%. Further increased in filler content from 1 to 3 wt. % decreased the storage modulus. Hence, dental composite with 1wt.% of nanosilica filler content exhibits maximum storage modulus. As can be observed, the dental composite with 1wt.-% of nanosilica filler shows an increased value for E' at 30 °C, reaching 250MPa, which means a 92.30% higher value than the unfilled composite whose E' is 120MPa.

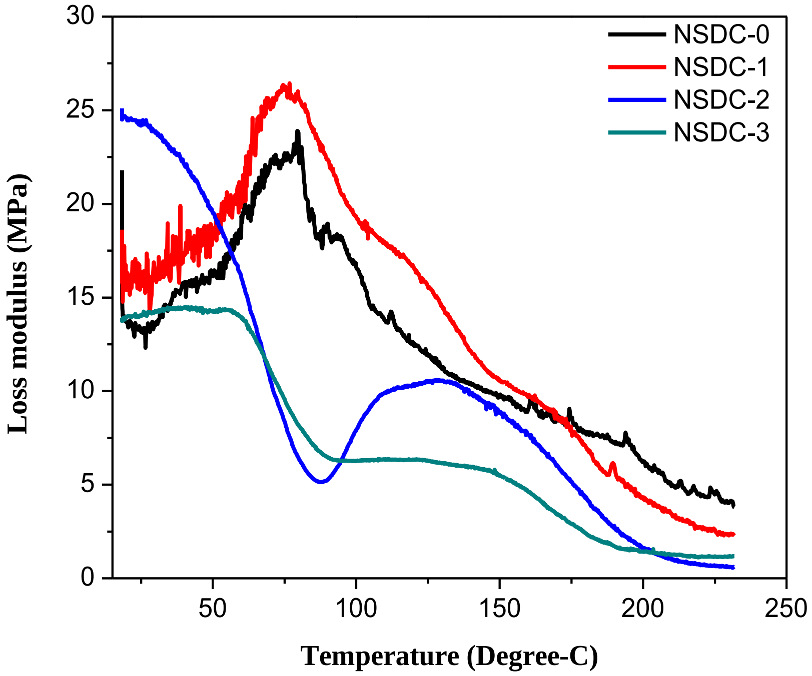

Figure 5.14b Variation of the loss modulus (E") as a function of temperature for nanosilica filled dental composite

Figure 5.14b represents the loss modulus of composite of different wt.- % of nanosilica particles. It can be seen that loss modulus of 1% silica filled composite is higher than that of unfilled composite. It may be due to uniform dispersion of nanoparticles in the resin matrix. Therefore interfacial area is larger and interaction between matrix and Nanofiller is stronger. Within the range (30-80^{o}C), loss modulus for different composite increased with different slopes. After attaining maximum loss modulus, it decreased abruptly during (80-120^{o}C). Loss modulus of dental composite with 1% wt fraction nanosilica exhibits maximum value. Decrease in loss modulus is reported when filler content increased from 1 to 3wt.%. It may be due to agglomeration of nanoparticle in the composite.

Figure 5.14c represents Tan δ versus temperature curves obtained for different composite at a constant frequency 1 Hz. All samples showed a wide range of widths of the Tan δ curves. But the Tan δ peak heights (damping behavior) of 1wt.% nanosilica filled dental composite reported least among the other filled and unfilled composite. It is due to the fact that addition of nanosilica particle improved the chain mobility of filler particles inside the resin matrix and less energy is dissipated. However, on further increasing of filler loading, Tan δ increased at all temperatures. Therefore, increase in the value of Tan δ indicates that the number of the mobile chains during the glass transition is increased. Composite with 1wt.-% nanosilica content showed a broad tan delta peak, in which the efficient damping (Tan δ> 0.15) has a wide temperature range more than 100^0C. The tan *δ* value of nanocomposite comes from the contribution of both composite and filler materials.

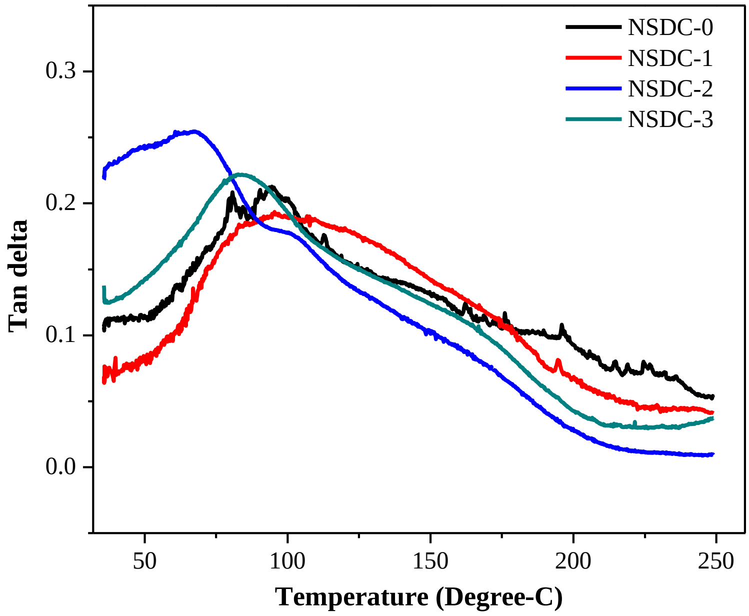

Figure 5.14c Variation of the Tan Delta (Tan δ) as a function of temperature for nanosilica filled dental composite

5.3.3 Simultaneous Thermal Analysis of nanosilica filled dental composites

The thermal characteristics of all the fabricated composites have been investigated by STA and the thermograms obtained are shown in Figures 5.15a and 5.15b.

Simultaneous Thermal Analysis (STA) generally refers to the simultaneous application of Thermo-gravimetry analysis (TGA) and Differential Scanning Calorimetry (DSC) to one and the same sample in a single instrument.

Figure 5.15a shows DSC curves for dental composites filled with different wt.-% of nanosilica. It can be revealed that the endothermic peak around 50–55°C in the first run corresponds to the evaporation of water and appeared in all the composite samples. The next endothermic peak around 150°C can be assigned to the glass transition temperature. The peak at 220°C can be assigned to the crystallization temperature. The peak at 280°C could be ascribed to total biopolymer decomposition. These results show a decomposition temperature for dental composites around 275–310°C, a temperature range that agrees with the highest weight loss observed in TGA. The glass transition temperatures of the all filled composite are more than that of unfilled composite. This is due to the fact that the glass transition of filled composite included both the temperature of resin matrix and filler.

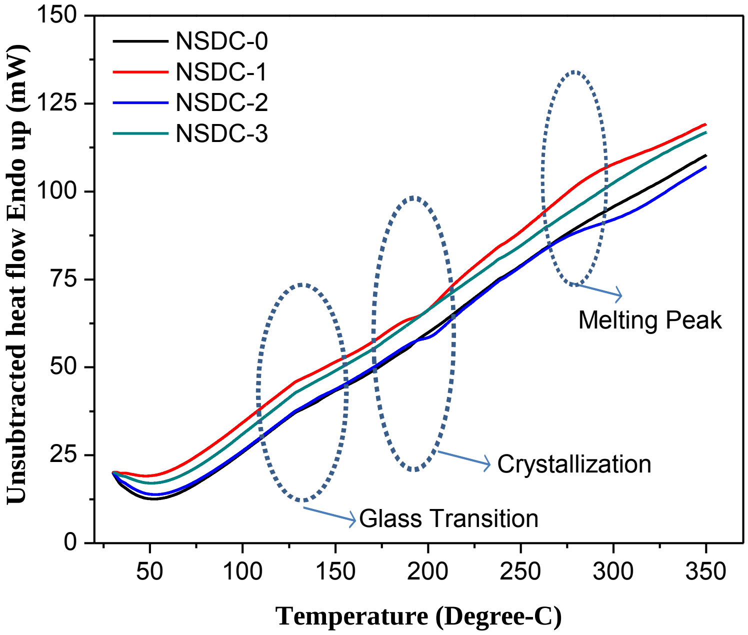

Figure 5.15a DSC thermograms of nanosilica filled dental composites

Figure 5.15a also indicates that the dental composite filled with 1 wt.-% nanosilica content exhibits more unsubtracted heat flow than the other filled and unfilled composite. Also in terms of glass transition, crystallization and melting feature, 1 wt.-% nanosilica filled dental composite indicates better properties than other filled and unfilled composite.

Figure 5.15b shows TGA curves of all the nanosilica filled composites with different weight % of nanosilica filler. It is revealed that the weight loss and consequent degradation for all resin composites studied began around 220ºC. The thermal behavior observed for these composites can be described in two main steps: the first mass loss (5-7%) from 30–150 °C is due to the loss of bound-water. The second step is from 220–330 °C, with mass decreasing from 8%–45%, this is associated with a complex process that includes depolymerization and decomposition of the polymer unit. This behavior of unfilled composite can be seen under dotted circle 1 and 2 in the Figure 5.15b. However, unfilled composite indicates degradation from the start of the curve at 30ºC. The addition of nanofiller decreased the mass loss rate. Hence, increase in filler content increased the thermal stability of the composites and the composite with maximum filler content reported maximum thermal stability.

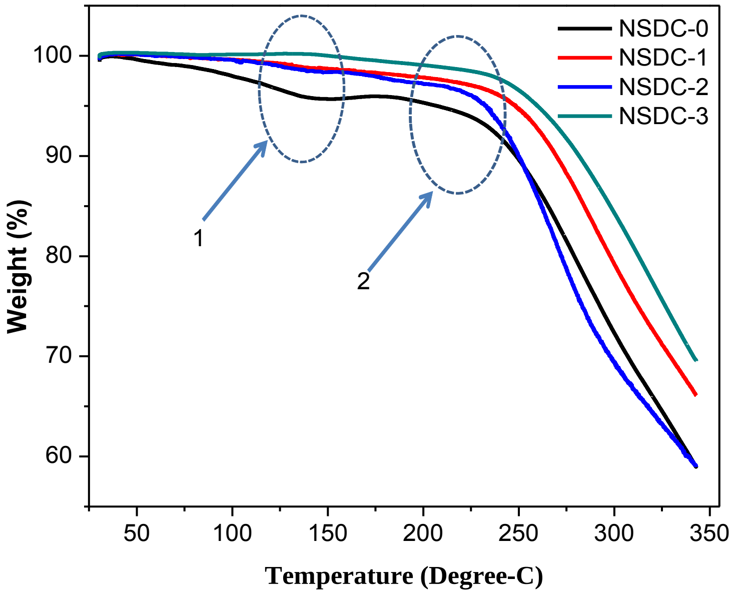

Figure 5.15b TGA thermograms of nanosilica filled dental composites

Part IV

5.4 Mechanical and thermo-mechanical characterization of gypsum filled dental composite

5.4.1 Mechanical characterization of gypsum filled dental composite

Figure 5.16 shows the compressive strength of dental composite filled with 0, 1, 2 and 3 wt. % of gypsum particle is 185.15, 199.39, 295.29 and 308.59 MPa respectively. It can be seen that with the increased in micro sized gypsum content, the compressive strength of dental composite increased. This is attributed to increase in silane functionalized micro sized gypsum particles. Hence, increased in hard phase silane functionalized filler lowers the volume of ductile resin matrix and increases the coupling strength between composite and fillers, which forms comparatively more strong and stable chain containing siloxane group.

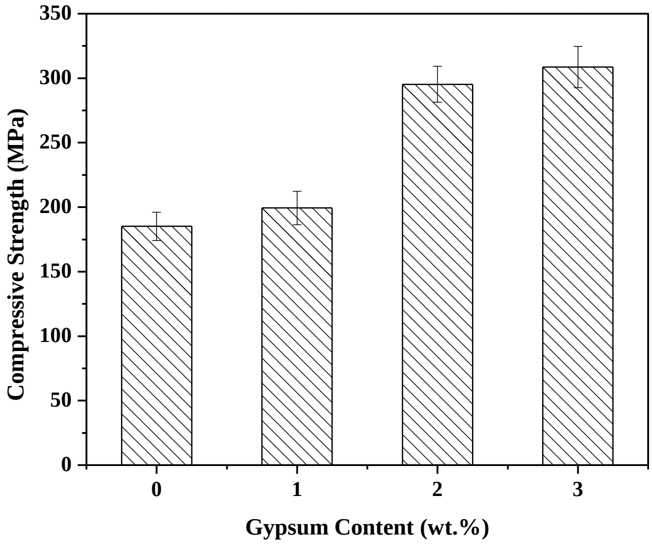

Figure 5.16 Effect of compressive strength on gypsum filled dental composites

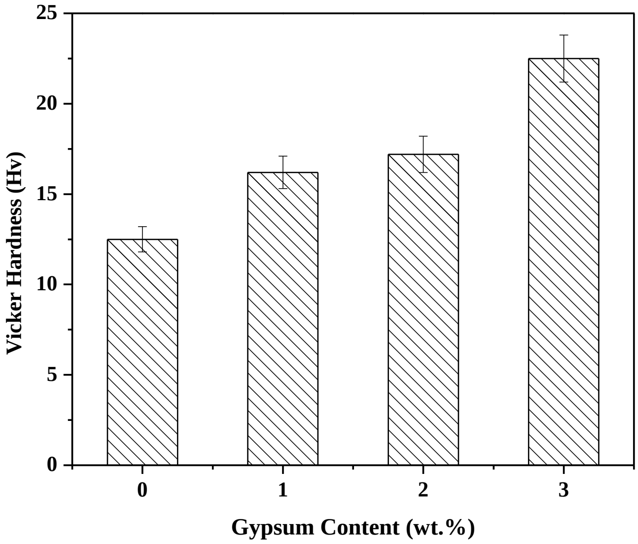

Figure 5.17 Effect of Vickers hardness of gypsum filled dental composites

Figure 5.17 shows the Vickers hardness values of the dental composite filled with different weight percentage of micro-sized gypsum content. It can be observed that composite with different weight percentage of gypsum particles demonstrated significantly higher hardness compared to the unfilled composite. The hardness of the composite with 1, 2, and 3 wt.% of gypsum particle reached 16.2Hv, 17.2Hv, and 22.5Hv respectively, while the unfilled resin matrix indicates lower hardness value of 12.5 Hv. Increased in hardness with increase in gypsum content may be attributed to viscoelasticity of dental composite. Major part of the present dental composite is resin and rest inorganic filler which is brittle in nature. Therefore, role of filler plays an important role in determining the hardness of dental composites. Hardness of composite depends upon resin chemistry, filler morphology, filler concentration, quality of silane treatment etc. According to Mota et al. [158], rounded filler resulted into higher hardness. The increased in hardness with increase in filler content is in agreement with Alsharif et al. [12]. Finally, it can be concluded that the major factor for determining mechanical properties of dental composite is the filler morphology and concentration. As the filler content increases, the mechanical properties of the gypsum based dental composites is increased in the present analysis. Figure 5.17 also indicates the dental composite having maximum weight percent of micro sized gypsum particle exhibits maximum hardness and from Figure 4.18 (in Chapter 4), same composite has indicated maximum depth of cure. Hence, it can be concluded that there must be direct correlation between depth of cure and micro hardness of the dental composites. Figure 5.18 shows the flexural strength of the resin matrix filled with different ratios of gypsum particles.

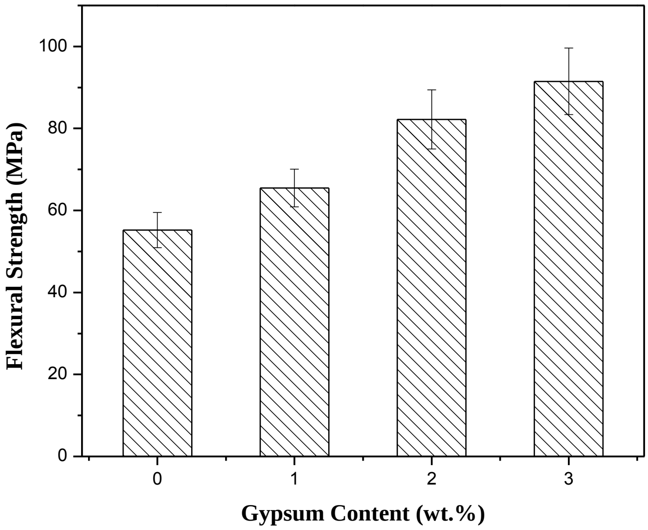

Figure 5.18 Effect of flexural strength on gypsum filled dental composites

It can be seen that the flexural strength for the composites having 0, 1, 2, and 3 wt. percent of gypsum is 55.2, 65.5, 82.2 and 91.5 MPa respectively. It is found that dental composite filled with 3wt. % of gypsum filler exhibits maximum flexural strength. These observations are within the specified limit as per ISO 4049-2009 standard which states the flexural strength value should not be less than 50 MPa. In this study, the flexural strength value of resin matrix filled with 3wt.% of gypsum particles reached 55.2 MPa. Hence, it may be suitable for the dental restoration application.

5.4.2 Dynamic Mechanical Analysis of gypsum filled dental composite

Dynamic Mechanical Analysis (DMA) has been used to acquire useful information about visco-elastic characteristics of dental composite material as a function of time, temperature, and frequency. Figure 5.19a indicates the variation of storage modulus (E') as a function of temperature for different weight percentage of gypsum filler. It can be seen that storage modulus increased with increasing filler content [159]. The dental composite with 3wt.% gypsum filler content reported maximum storage modulus. Increase in storage modulus with increase in gypsum content is due to the fact that storage modulus is generally related to molecular elastic response i.e. stiffness of dental composite material.

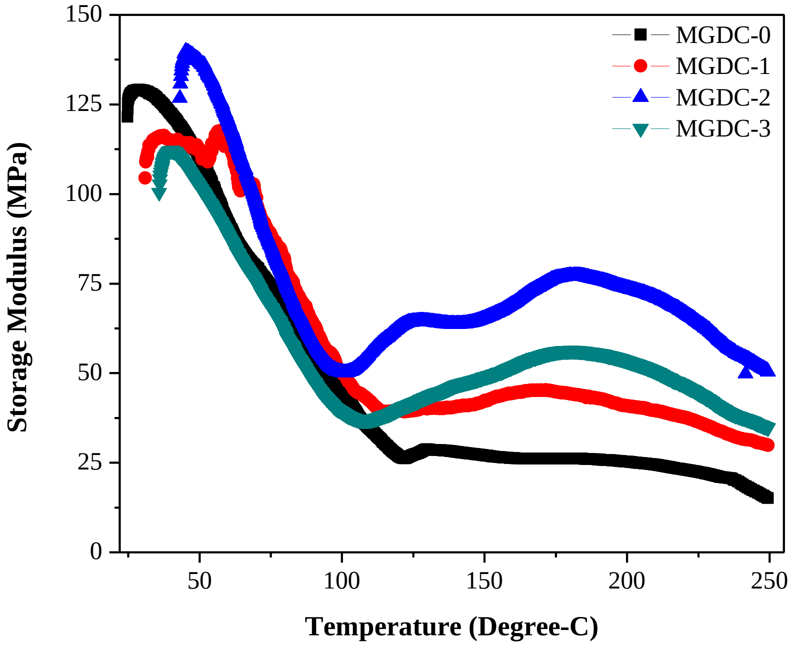

Figure 5.19a Variation of the storage modulus (E’) as a function of temperature for gypsum filled in dental composite

Therefore, with the increased in gypsum filler content is directly proportional to increase in stiff and brittle fillers in the resin matrix which finally results into increase in storage modulus. Storage modulus decreases with increased in temperature for all gypsum filled and unfilled dental composites. It is due to the fact that with the increased in temperature leads to softening of resin matrix which finally results into decreased in storage modulus. However, at higher filler content composites (2 and 3 wt.%) indicates reverse in trend after attaining certain temperature (90-100°C). Both the dental composites are attained another peak around 180°C and then further storage modulus decreases with the increased in temperature.

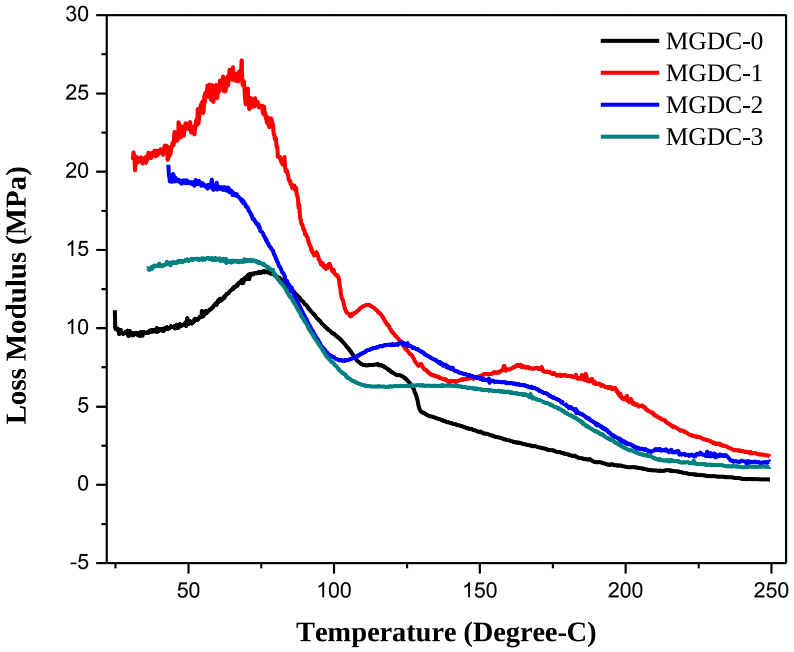

Figure 5.19b Variation of the loss modulus (E") as a function of temperature for gypsum filled dental composite

Figure 5.19b represents the loss modulus of composite filled with different wt. % of micro sized gypsum particles. It can be seen that with increasing temperature, loss modulus curve increases up to transition peak around 75°C and then decreases. Loss modulus is a measure of absorbed energy due to relaxation and is related to viscous response of material. Loss modulus increased with increasing filler content from 0wt.% to 1wt.%. loss modulus of 1wt.% gypsum filled composite is higher than that of unfilled and other filled composite. It is due to the fact that presence of gypsum filler (2 or 3 wt.%) in the resin matrix restrict the mobility of the polymer molecules or increase then viscosity. However, for other composite filled with 2 and 3wt.% gypsum filled composite reported reverse trend. Increase in gypsum content from 1 to 3 wt.%, decreases the loss modulus. It seems to be due to number of factors like resin chemistry, filler size, composition, morphology, and amount of initiators and the quality of silanization. Figure 5.19c represents Tan δ versus temperature curves obtained for different composite at a constant frequency 1 Hz. Tan δ of dental composite increased with increase in filler content. Hence the composite with 3wt.% Gypsum filler content showed least damping as compared to the other composites because addition of micro sized gypsum particle improved the chain mobility of filler particles inside the resin matrix and less energy is dissipated. However, dental composite with 1 wt.% gypsum reported higher damping (Tan δ value) than unfilled composite.

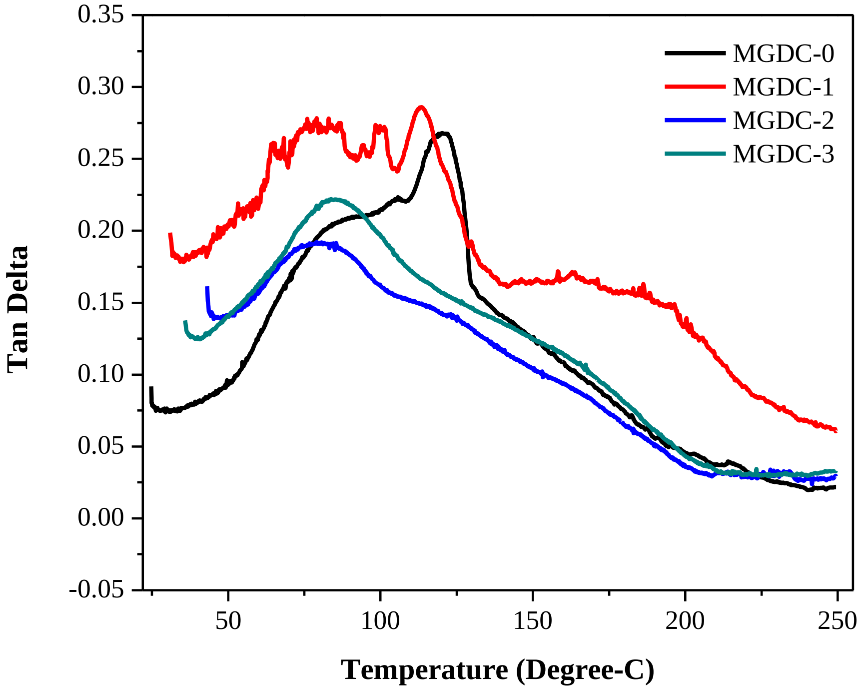

Figure 5.19c Variation of the Tan Delta (Tan δ) as a function of temperature for gypsum filled dental composite

5.4.3 Simultaneous Thermal Analysis of gypsum filled dental composite

The thermal properties of dental composite filled with different weight percent of gypsum filler have been investigated by Simultaneous Thermal analysis (STA).

Table 5.3 DSC Analysis on micro-sized gypsum filled dental composites

Sl. No.	Composition	1st Endothermic Peak(°C)	Glass Transition (°C)	Crystallization temperature (°C)	Biopolymer decomposition (°C)
1	MGDC-0	45-48	145-150	175-180	300-320
2	MGDC -1	40-42	135-140	160-165	290-300
3	MGDC -2	45-50	150-155	180-185	330-350
4	MGDC -3	40-45	140-145	165-175	300-310

Table 5.3 indicates the variation in unsubtracted heat flow as a function of temperature for dental composites filled with different weight percent of gypsum filler. It can be seen glass transition temperature decreased as filler increased. It may be due to dehydration of gypsum starts at lower temperature. However results showed that the glass transition temperature obtained in this study is in line with the literature. Melting and crystallization peak of gypsum filled dental composite are found to be better than the unfilled composite. Dental composite filled with 2wt.% gypsum filler exhibits maximum range of first endothermic peak (corresponds to the evaporation of water), glass transition, crystallization and decomposition temperature (Table 5.3).

Figure 5.20 shows TGA curves of all the microsized gypsum filled composites with different weight percentage of Gypsum filler.

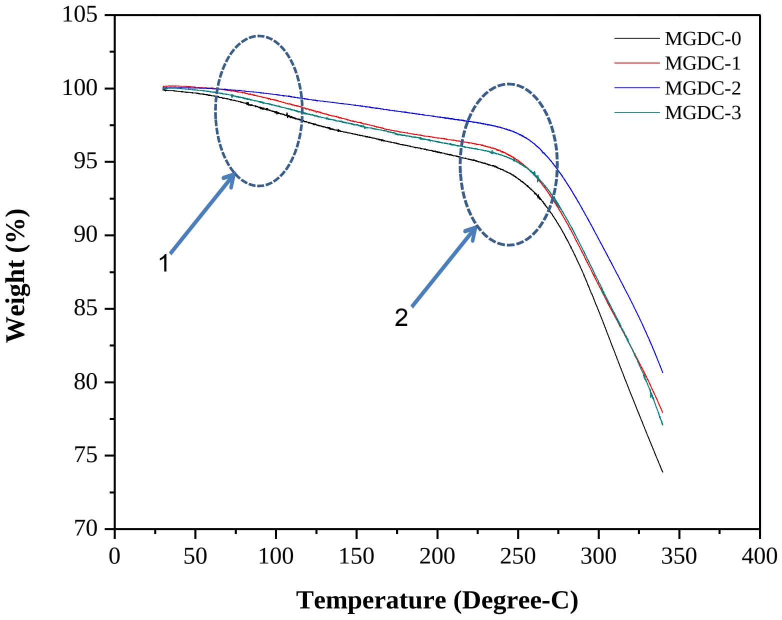

Figure 5.20 TGA thermograms of gypsum filled dental composites

It can be seen that the dental composite filled with 2 wt.% of gypsum micro-filler reported maximum thermal stability. Two step thermal degradation behaviour of dental composite is seen. In first step represented by dotted circle1 in Figure 5.20, slow weight loss is reported for all dental composite after 75°C. In second step denoted by dotted circle 2 in same Figure 5.20, a drastic weight loss and consequent degradation for all resin composites began around 250°C. It can be seen that thermal stability increased with increasing filler content.

Chapter Summary

This chapter concluded that:

- The composites with the highest filler loading exhibit the highest depth of cure and lowest polymerization shrinkage. According to ISO 4049-2009 standard, the flexural strength value should not be less than 50 MPa. In this study, the minimum flexural strength value is reported to be 65.5 MPa which is in line with ISO 4049-2009 standard and is acceptable for dentistry applications.
- The compressive strength of unfilled dental composite indicates maximum value. This is due to presence of lowest void content and maximum polymerization shrinkage in the composite. However, after 1wt.% filler content, composite material indicates increasing trends of compressive strength. The Vickers hardness of the resin-composites increased with increasing filler content.
- The sorption and solubility of all the composites studied are in the range of (0.63-2) μg/mm^3 and (1.54- 2.50) μg/mm^3 respectively which is within the limits prescribed by ISO 9000's standard in which the maximum affordable values of water sorption and solubility for the dental resins are: 40 μg/mm^3 and 5 μg/mm^3 respectively. In this regard the prepared composite is found suitable for dentistry application.
- The Storage modulus and glass transition temperature increased with increase in nanosilica content in the dental composites. Similarly, the thermal stability and degradation temperature shows same pattern also.

The next chapter presents the wear performance of the resin based dental composite under study.

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Chapter 6

Wear characterizations of dental Composites

Chapter 6

Wear Characterization of Dental Composites

This chapter evaluates the wear characteristics of particulate filled dental composite on Dental Wear Simulator in the different working conditions. The interpretation of the results and the comparison among various dental composite samples are also presented. This chapter consists of four parts: part I consists of wear performance of dental composite reinforced with silanized nanoalumina filler (NADC series), part II consists of wear performance of dental composite reinforced with silanized nanozirconia filler (NZDC series), part III consists of wear performance of dental composite reinforced with silanized nanosilica filler (NSDC series) and part IV consists of wear performance of dental composite reinforced with silanized micro sized gypsum filler particles (MGDC series) in food slurry and citric acid medium.

Part-I

6.1 Wear assessment of dental composite reinforced with nanoalumina filler

6.1.1 Steady state condition for wear characterization

6.1.1.1 Effect of Chewing Load on Volumetric wear rate

The effect of variation in the chewing load on the volumetric wear rate of dental composites is presented in the Figure 6.1. It can be seen that the wear rate is increased by increasing chewing load from 40 to 100 N in the step of 20 N under the constant profile speed, chamber temperature and food slurry concentration etc. The range of load considered is in agreement with the available literatures [14,160] and per standard operating conditions. During normal chewing, the loads applied to the teeth are in the range of 10–20 N at the initial contact and are increased to the range of 30–120 N at the end of the chewing cycle. The chewing load depends mainly upon the properties of food particles. As there can be different variety of foods depending up on size, shape, strength, acidity etc., the extent of chewing forces will vary accordingly. Apart from food properties, there are some other factors which influence maximum biting forces for examples gender, age and muscle build etc. Patients suffering from Bruxism, clinching habits etc. can apply occlusal loads of approximately 1,000 N [161]. In the study of wear behavior of human teeth during normal chewing load is of 20 N, according to Hertzian contact stress theory [162], the associated mean contact pressure (208.0 MPa) is below the yield strength of enamel (330MPa) [163, 164].

Increase in wear rate with the increasing in chewing load is due to increase in true contact area. The increase in contact area results into increased in shear force and thrust frictional force [165] and is also resulted into increased coefficient of friction and volumetric wear rate. Increase in hard and brittle inorganic oxide such as nanoalumina filler in the dental composite resulted into decreased in the volume of ductile and flexible resin matrix. Hence, hardness of dental composite is increased with the decreased in volumetric wear rate of the dental composites.

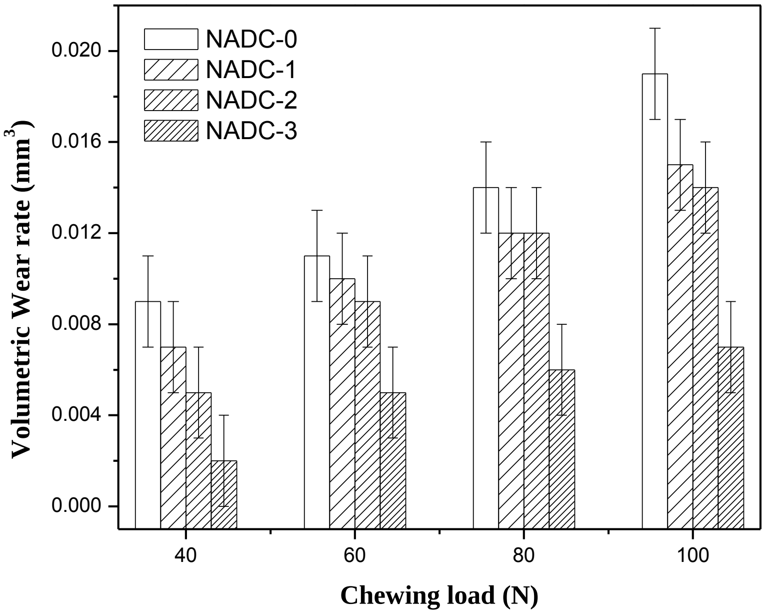


Figure 6.1 Effect of Chewing Load on volumetric wear rate of the dental composites (At constant profile speed 40%, chamber temperature: 35°C

Kaidonis et al. [166] investigated the effect of factors such as load, pH and the nature of the lubricant on the wear behavior of human enamel. It was proposed that apart from the load, pH of lubricating medium also played an important role to influence wear rate of dental composites. Therefore, very low pH can lead to high wear rate under all loading conditions. In the food slurry medium, the applied chewing load is shared by the food particles, participating dental material and antagonist disc. A three-body wear phenomenon of dental material is mainly caused by the abrasion of the moving food particles.

6.1.1.2 Effect of profile speed on volumetric wear rate

Profile speeds are varied in the steps of 20% from a minimum value of 20% to a maximum value of 80% keeping other parameters i.e. chewing load as 40 N, chamber temperature 35°C and food slurry concentration remained constant. Figure 6.2 represents the effect on variation in profile speed in volumetric wear rate of dental composites. It is also indicated that as the filler content increases, the wear rate decreases which is due to increase in hardness of the particulate filled dental composites. Figure 6.2 also indicates that wear rate increases with the increased in profile speed. The increased in wear rate with the increase in profile speed is attributed to the fact that as the profile speed increases, the frictional thrust force and shear force is increased which results into increased in wear rate.

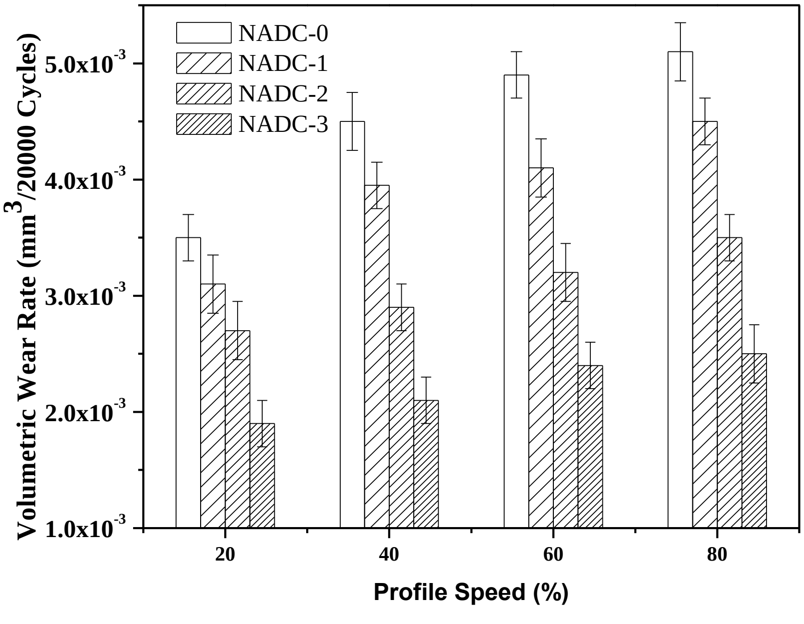


Figure 6.2 Effect of profile speed on volumetric wear rate of the dental composites (At constant Chewing Load 40 N, chamber temperature 35^{o}C)

6.1.1.3 Effect of chamber temperature on volumetric wear rate

Figure 6.3 shows the variation in volumetric wear with chamber temperature of silanized nanoalumina filled dental composites (NADC series) under constant chewing load of 40N and profile speed of 40% respectively. It is observed that as the temperature increases, the wear rate of the nanoalumina filled dental composites with variation of filler content increases up to two third of the proposed temperature and then shows in a decreasing trend which completely satisfies with the available literature [167]. The increased in wear rate with increase in temperature (5-25°C) is due to the fact that the increase in temperature increases the true contact area, friction forces and polymer chain mobility etc. Further increased in temperature in the range of 25-35°C results into slight decreased in the wear rate because of presence of resin matrix in the composites.

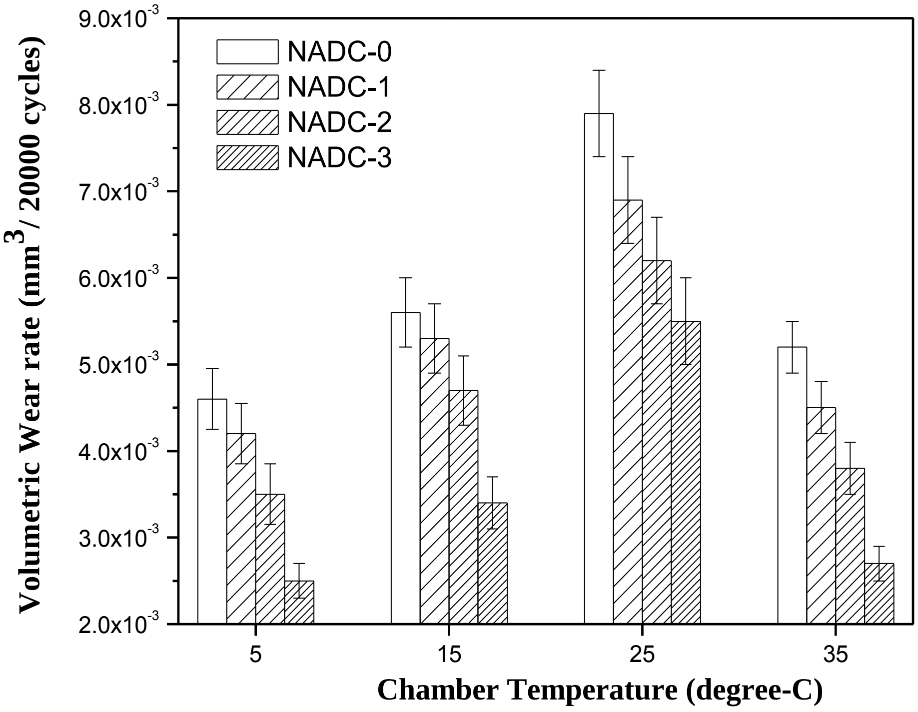


Figure 6.3 Effect of Chamber temperature on volumetric wear rate of the dental composites (At constant chewing load 40N, profile speed 40%)

The result is in agreement with the available literature [168, 169]. It is reported that the wear rate of particulate reinforced composite increased with temperature. They further obtained a critical temperature which depicted the transition from mild to severe wear in particulate reinforced composite. It is also reported that dispersion of hard ceramic particles such as alumina or SiC improves the stiffness and wear resistance of the dental composites [170-174].

6.1.2 Taguchi experimental results for nanoalumina filled dental composite

In design of experiment, Taguchi method is applied to improve the performance output in both the food slurry and citric acid medium. In Table 6.1, seventh column represents S/N ratio of the volumetric wear rate of the composites.

Table 6.1. Taguchi experimental results for NADC series composite

S.No	Filler content (%)	Chewing load (N)	Profile Speed (%)	Chamber Temperature (degree-C)	Volumetric Wear Rate in food slurry (mm^3/ 20000 cycles)	S/N ratio (dB)	Volumetric Wear Rate in acidic medium (mm^3/ 20000 cycles)	S/N ratio (dB)
1	0	40	20	5	0.0028955	50.77	0.00333	51.88
2	0	60	40	15	0.0046617	46.63	0.00528	47.45
3	0	80	60	25	0.005791	44.74	0.006443	45.86
4	0	100	80	35	0.0069204	43.20	0.008135	44.52
5	1	40	40	25	0.0019962	54.00	0.00228	55.36
6	1	60	20	35	0.0017154	55.31	0.002063	61.38
7	1	80	80	5	0.003993	47.97	0.004792	49.34
8	1	100	60	15	0.0024328	52.28	0.002851	61.38
9	2	40	60	35	0.0018426	54.69	0.002051	55.36
10	2	60	80	25	0.002764	51.17	0.003156	51.84
11	2	80	20	15	0.0024067	52.37	0.002821	55.36
12	2	100	40	5	0.0039673	48.03	0.004622	49.34
13	3	40	80	15	0.0017411	55.18	0.001988	55.29
14	3	60	60	5	0.0013216	57.58	0.0015	61.31
15	3	80	40	35	0.0028372	50.94	0.003354	51.77
16	3	100	20	25	0.0017725	55.03	0.001982	61.31
Mean Volumetric Wear Rate (mm^3/ 20000 cycles)					0.002657		0.00354	

The overall mean for the S/N ratio of the specific wear rate is found to be 47.50 db for the dental composite filled with different wt. % of nanoalumina particulates. The analysis is performed using the software MINITAB 16 to analyze the wear rate of the nanoalumina particulate filled dental composites. From this analysis (Figure 6.4) it is observed that the factor combination of A4, B1, C1 and D2 gives minimum volumetric wear rate for dental composite filled with different wt. % of nanoalumina. It means the dental composite filled with 3 wt. % nanoalumina at chewing load of 40N and with profile speed 20% and at chamber temperature 15 °C exhibits minimum wear rate.

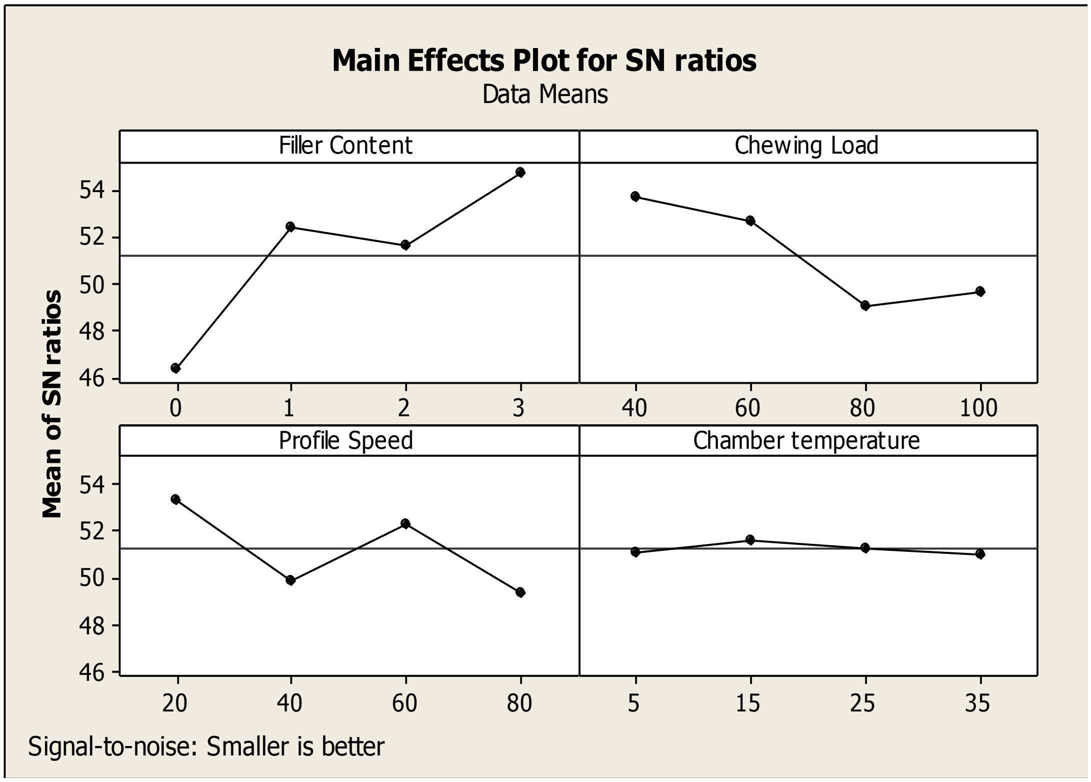


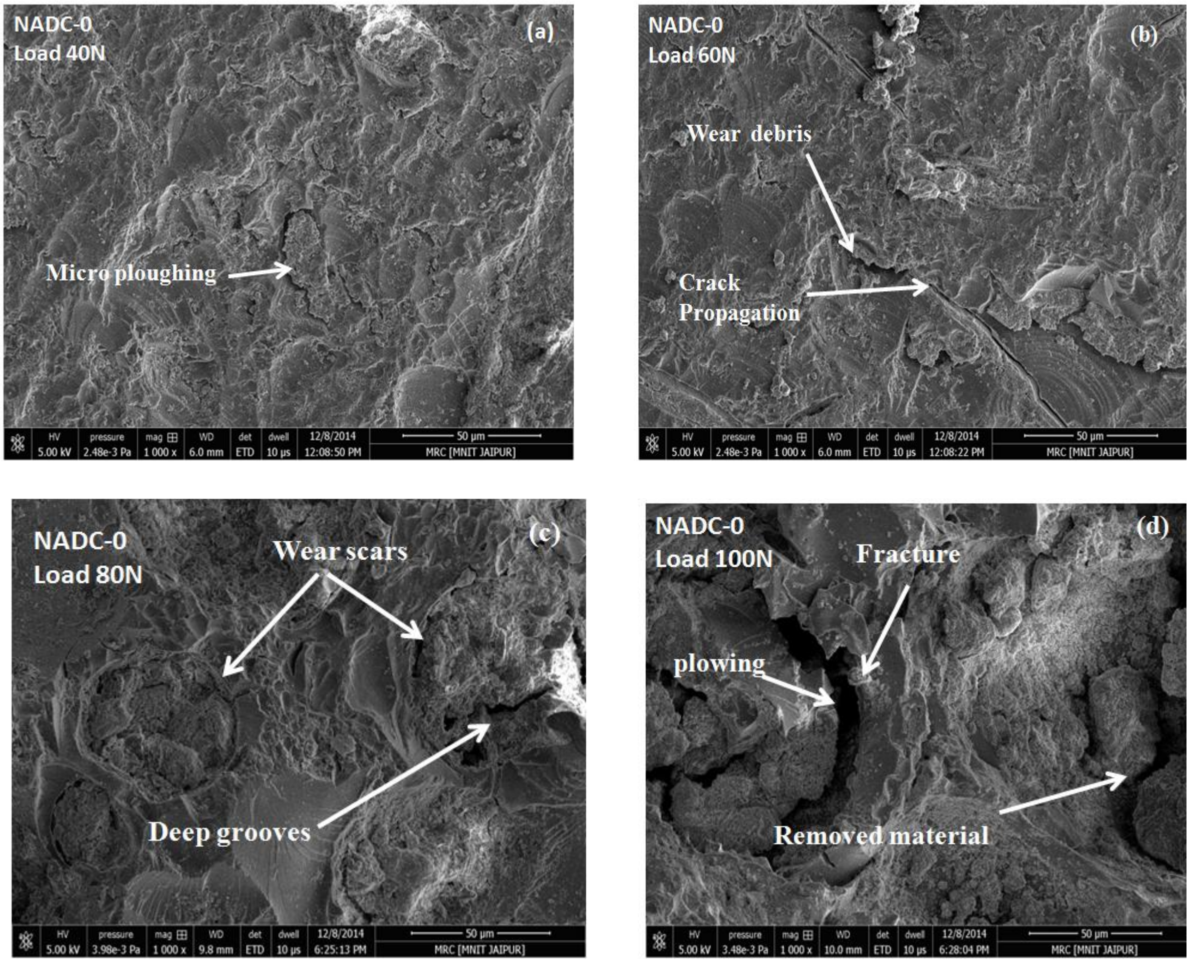
Figure 6.4 Effect of control factors on the wear rate of dental composites

6.1.3 Surface morphology

The worn surface morphology of the nanoalumina filled dental composites is studied under steady state conditions using FE-SEM is presented in the Figures 6.5-6.7. All the wear analysis is conducted under limited number of cycle's i.e. 20,000 cycles per test sample.

6.1.3.1 Micrograph for varying Chewing Load for unfilled dental composite

Figure 6.5 consists of seven micrographs to study the variation in chewing load and filler content. In Figure 6.5(a-d), the effect of variation of chewing load on volumetric wear rate of unfilled dental composite is studied. Whereas, Figure 6.5(a),(e),(f),(g), show the effect of variation of filler content on volumetric wear rate at constant chewing load 40N. Figure 6.5(a-d) represents the worn surfaces morphology of unfilled dental composite under variable chewing load i.e. 40N, 60N, 80N and 100N respectively at constant profile speed 40% and chamber temperature 35°C respectively. Figure 6.5(a) indicates the SEM micrograph of the unfilled dental composite under chewing loading of 40N, profile speed 40%, and chamber temperature: 35^{o}C respectively. Here, micro ploughing can be seen, crack is generated but still wear is less and the surface is rough. But as the chewing load is increased from 40N to 60N (as in Figure 6.5b), cracks propagation and wear debris is seen on the surface. Further increased in load from 60N to 80N, the unfilled composite has shown deep grooves in the abraded position and the wear scars are also observed. At last when chewing load is reached to the maximum value of 100N, fracture on the surface starts to be visible.



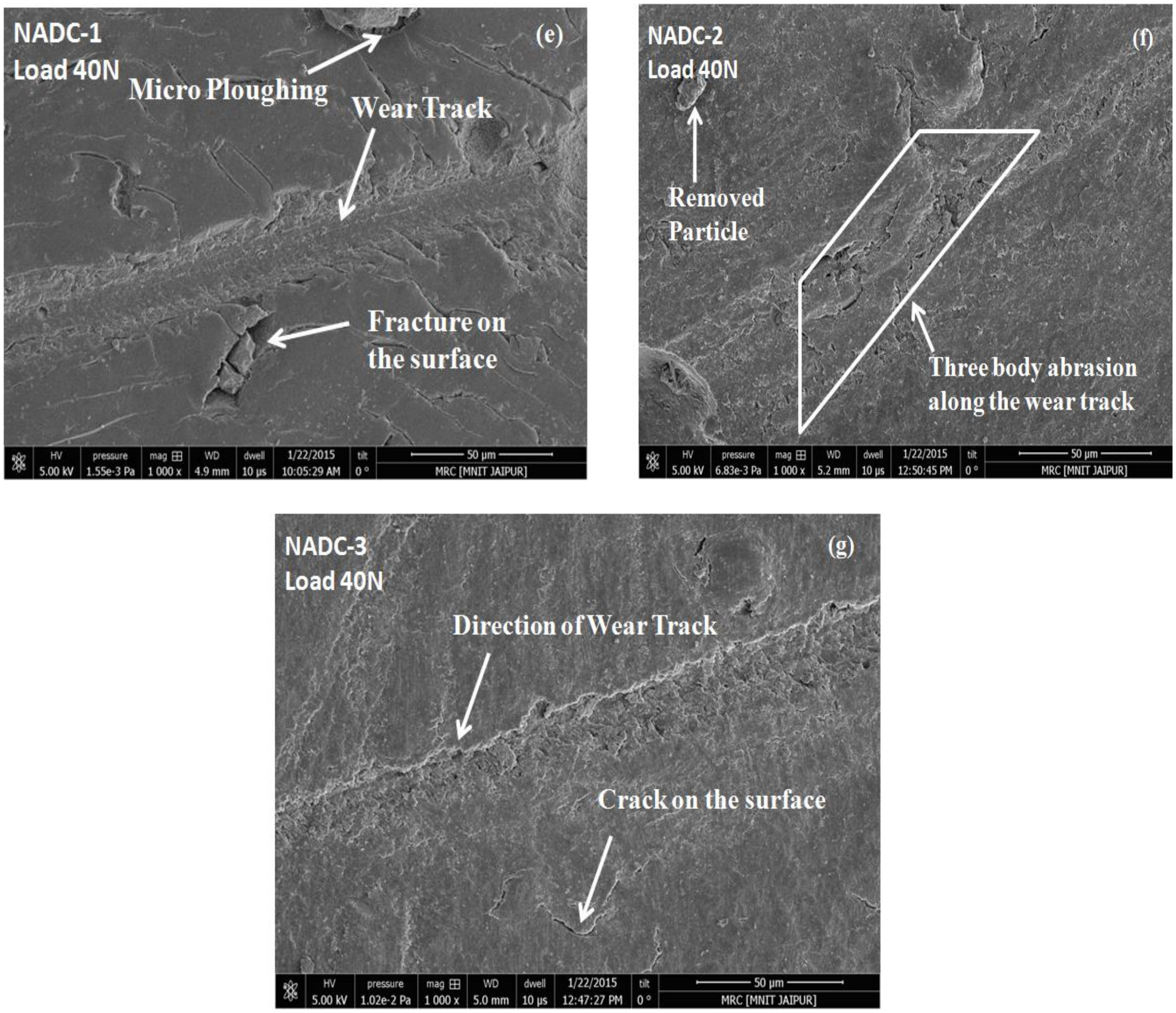


Figure 6.5 FE-SEM images of worn surfaces of composite NADC under the profile speed 40% and temp 35 °C and varying filler content and chewing load a) 0 wt.% at 40N, b) 0 wt.% at 60N, c) 0 wt.% at 80N, d) 0 wt.% at 100N, e) 1 wt.% , 40N f) 2 wt.% , 40N g) 3 wt.% , 40N.

6.1.3.2 Micrograph for different weight percentage of nanoalumina at constant chewing load, speed and temperature

Figures 6.5(a), 6.5(e), 6.5(f), 6.5(g) indicate the worn surfaces of 0,1,2,3 wt. % nanoalumina filled dental composite after 20000 cycles of experimental run under similar operating conditions (chewing load 40N, profile speed 40%, chamber temperature 35°C). It can be seen that, as the filler content increases, wear rate starts decreasing. In Figure 6.5(e), both micro ploughing and wear track are observed but some fracture surface can also be seen. Minimum wear can be observed in the case of Figure 6.5(g). In Figure 6.5(f), worn particles are presented on the surface. In Figure 6.5(f), least wear is indicated for the dental composite filled with 3 wt.% silanized nanoalumina (NADC-3). It is also observed that the depth of wear track decreases as the filler content increases.

6.1.3.3 Micrograph for varying profile speed

Figure 6.6 shows worn surfaces of the composite filled with 1 wt. % nanoalumina (NADC-1) under the variable profile speed of 20%, 40%, 60% and 80% at constant chewing load of 40N and chamber temperature 35°C. It can be seen that this NADC-1 composite has shown less wear rate than the unfilled composite but still available of blow holes, scratches, wear scars and cracks in the filled composite.

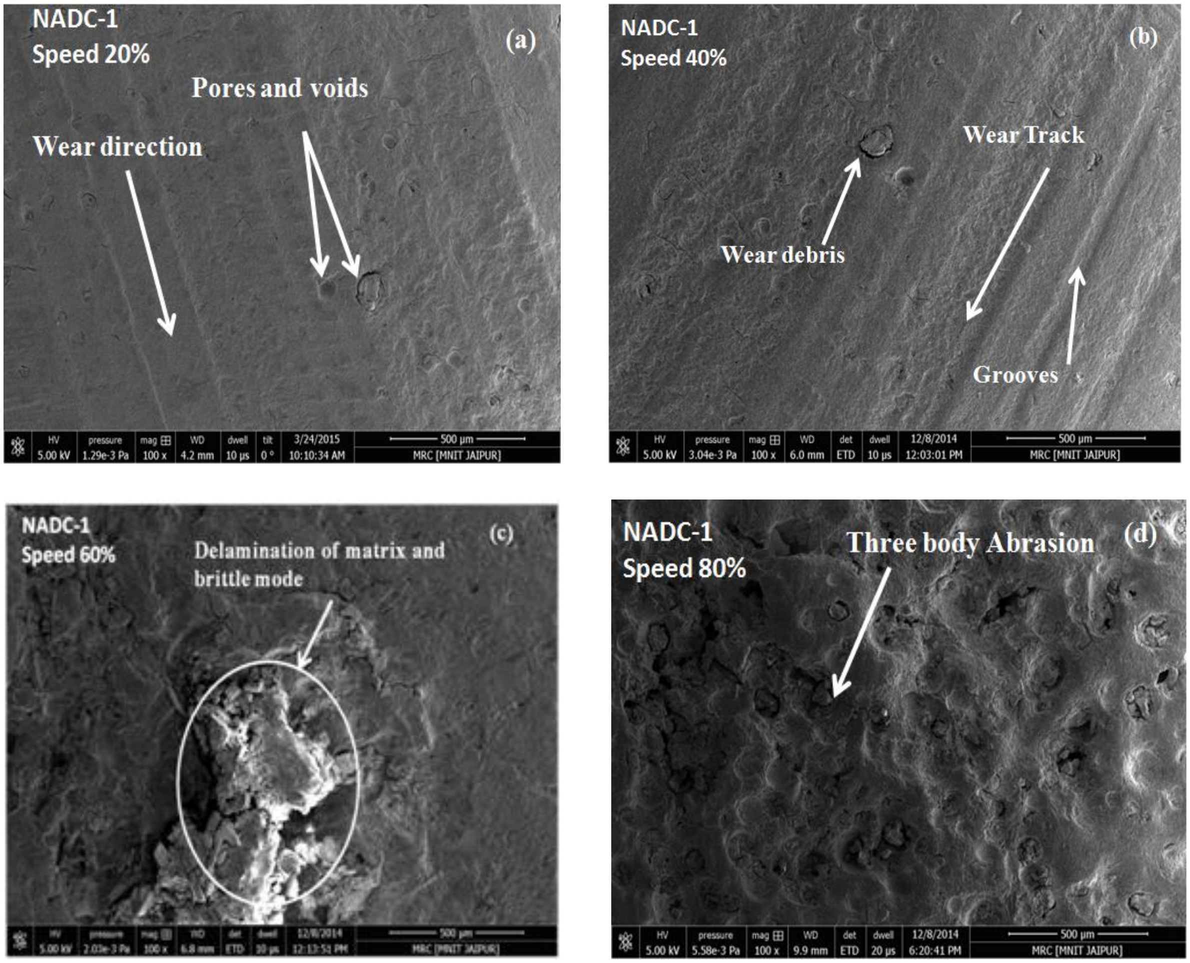


Figure 6.6 FE-SEM images of worn surfaces of composite filled with 1 wt. % nanoalumina under the chewing load 40N, temp 35^0C and the varying profile speed a) 20%, b) 40%, c) 60%, d) 80%

Figure 6.6a shows the micro graph of 1 wt. % nanoalumina filled dental composite studied under constant chewing load 40N, profile speed of 20% and chamber temperature 35°C respectively. At 20% profile speed, wear is less, but wear track direction is visible and few voids and pores are also located in the micrograph. However, with the increased in profile speed from 20% to 40% by keeping other factors remaining constant, the wear rate is found to be slightly higher as shown in Figure 6.2 but when we moved towards the micrograph of Figure 6.6b the surface deformation is very less as compared with Figure 6.6a. This may be due to the fact that at higher profile speed, the removal of matrix material plays a major role instead of matrix deformation mechanism. Again for similar composite (NADC-1) with further increased in profile speed to 60% the wear rate still increases (Figure 6.1) and lot of matrix cracks is observed on the surface of the dental composites. The formation of crack is due to improper binding between the matrix material and nanoalumina particulates at higher profile speed (Figure 6.6c). Similarly, with the further increased in profile speed to 80% the matrix material is completely deformed with higher wear rate as observed in Figure 6.6d and Figure 6.1 (steady-state condition graph) respectively. Therefore, from the above study it is clear from the steady-state graph and their respective micro-graphs, the profile speed is also played major role to increase the wear rate of the particulate filled dental composites.

6.1.3.4 Micrograph for varying chamber temperature

Figure 6.7 indicates the worn surfaces of dental composite filled with 2 wt. % nanoalumina (NADC-2) under varying chamber temperature from 5°C to 35°C in a step of 10°C at constant loading of 40N and profile speed of 40% respectively. NADC-2 composite has shown less wear than unfilled and 1 wt. % particulate filled dental composites. Therefore, crack is generated throughout the composite and its propagation is also visible in the micrograph. Some partially exposed filler particles can be observed on the worn surface. Figure 6.7a indicates that at 5°C chamber temperature, wear is very less. In Figure 6.7b, cracks are generated in the filled composite, plowing grooves and slight scratching are also noticed caused by sharp abrasive particles can be seen on the surface, which is perpendicular to the sliding direction. Some partially exposed filler particles can be observed on the worn surface. Figure 6.7c indicates that some surfaces are burnt due to the increase in temperature. One can be observed that as temperature increases from 5°C to 25°C, more wear scars are found on the surface but afterward at higher temperature i.e. 35°C (Figure 6.7(d)), wear scars on the surfaces slightly decreased. At temperature 35°C, molecular mobility inside the polymer increases its viscosity. Presence of increased viscosity can be seen in Figure 6.7(d).

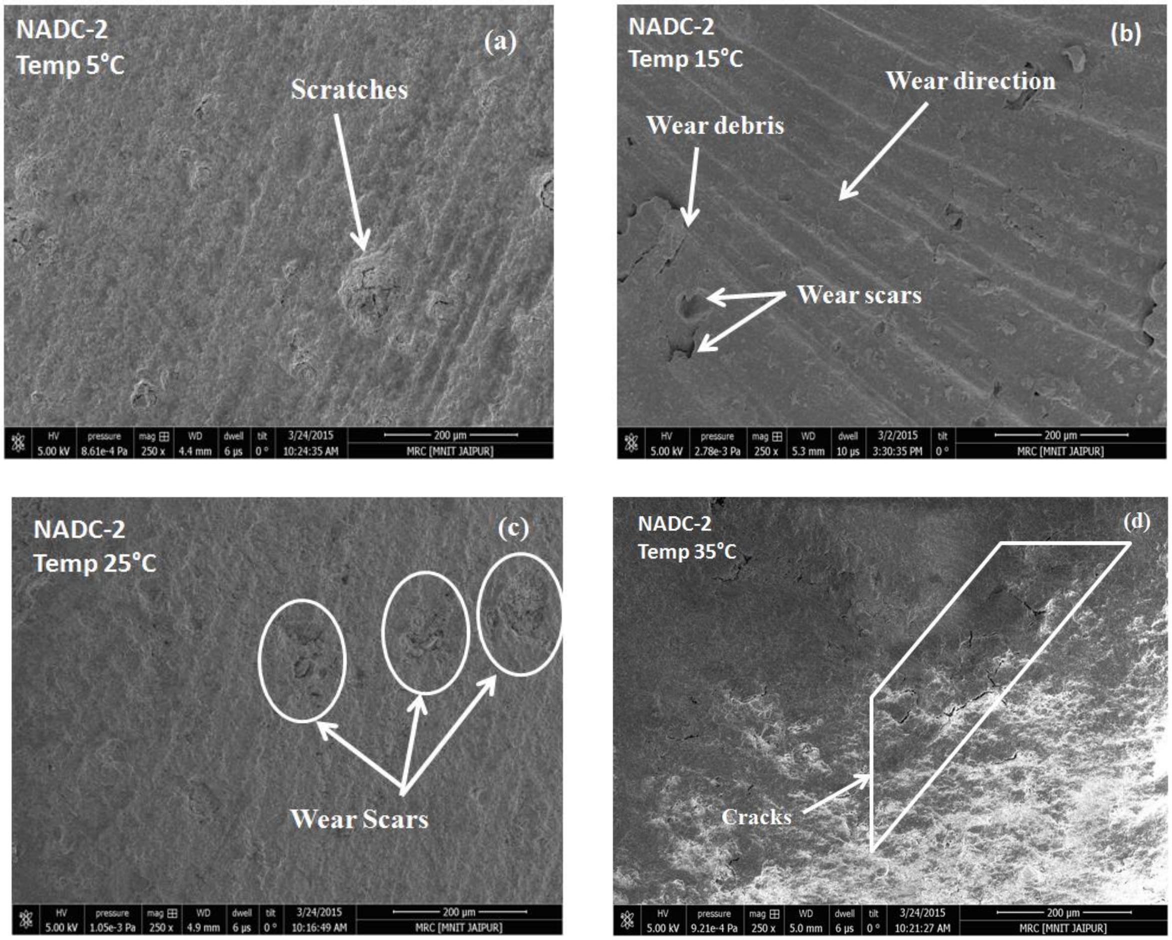
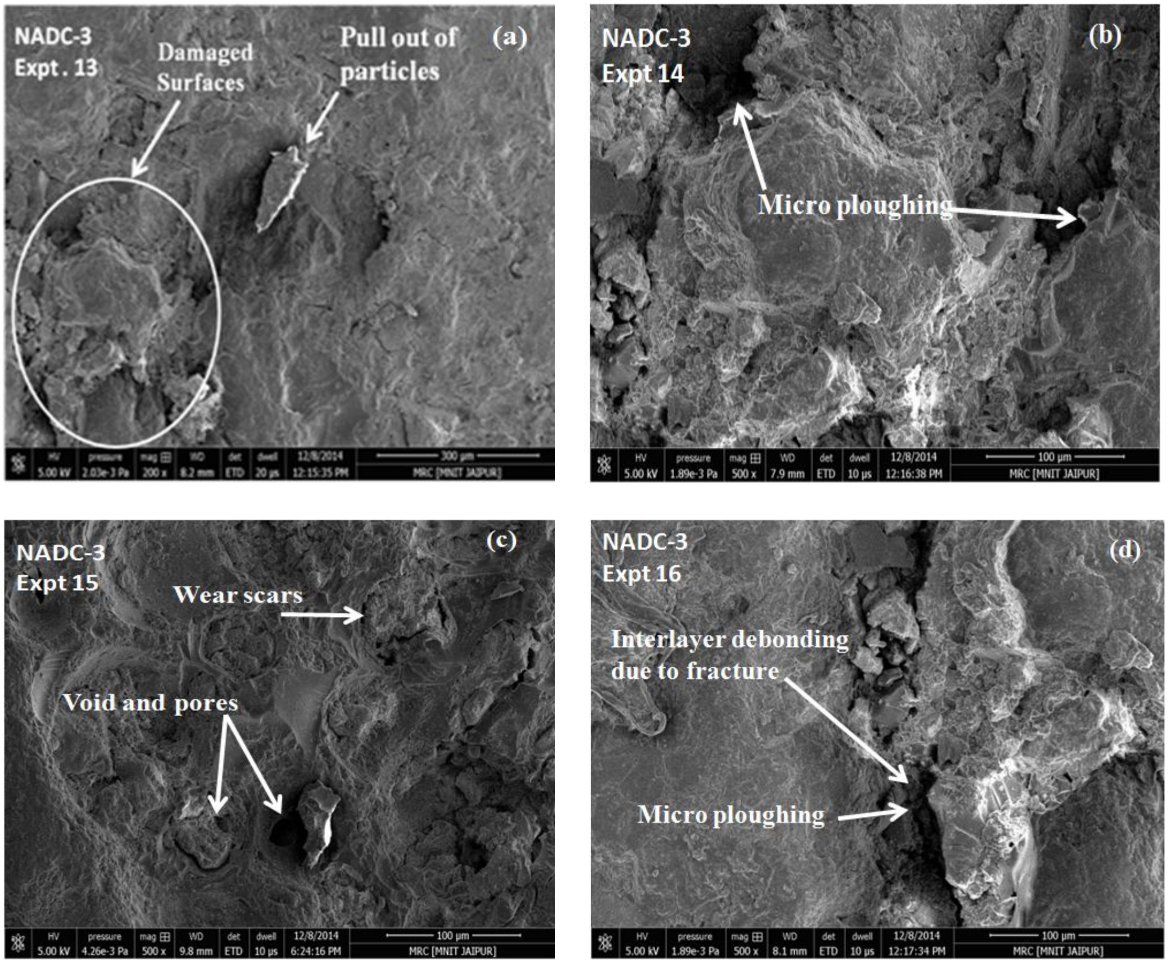


Figure 6.7 FE-SEM images of worn surfaces of composite filled with 2 wt. % nanoalumina under, chewing load 40N, profile speed 40% and varying chamber temperature a) 5°C, b) 15°C, c) 25°C and d) 35°C

6.1.3.5. Micrograph from Taguchi analysis

Figure 6.8 shows worn surfaces of composites filled with 3 wt. % nanoalumina (NADC-3) for four different experimental conditions in Taguchi experimental design during the experiment no 13,14,15,16 in Table 6.1. In these four experiments, large load and high speeds are simultaneously applied and varied. Figure 6.8a indicates the micrograph for the experiment which is performed under high profile speed of 80% at constant chewing load and chamber temperature i.e. 40N and 15°C respectively. Therefore, with the increased in profile speed i.e. 80% the composite surface is completely damaged as indicated in Figure 6.8(a). Removal of particle is due to applied frictional and shear thrust force developed during high profile speed. Figure 6.8(b) shows the micrograph for the experiment performed under profile speed 60%, chewing load 60N and chamber temperature of 5°C respectively. Here, both the high speed and high load are applied simultaneously. Long cracks extending through the polymer matrix along filler boundaries, micro ploughing and severe damage surface are seen. Figure 6.8c shows the micrograph for the experiment performed under high profile speed 40%, chewing load 80N and chamber temperature of 35°C. Severe damages are located because of large numbers of void and pores are visible in the composites. Figure 6.8d shows the micrograph for the experiment performed under high profile speed 20%, chewing load 100N and chamber temperature of 25°C, interlayer debonding due to fractured surface occurs.



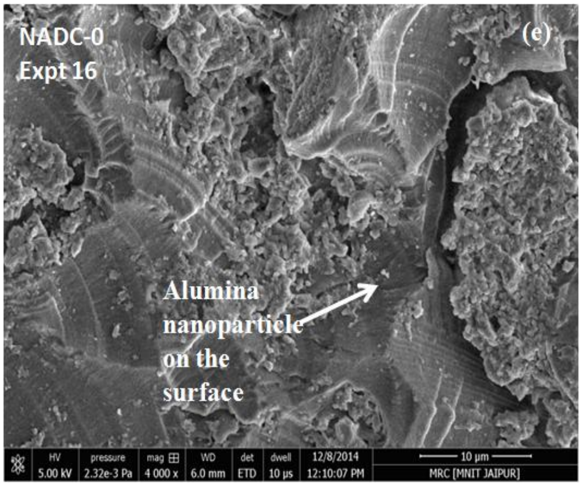


Figure 6.8 FE-SEM images of worn surfaces of composite filled with 3 wt. % nanoalumina under different working condition as in Table 6.1: a) experiment no 13, chewing load 40 N, profile speed 80, Chamber temp 15°C, b) experiment no 14, chewing load 60N, profile speed 60% , Chamber temp 5°C, c) experiment no 15 chewing load 80 N, profile speed 40,the chamber temperature 35°C, d) experiment no 16 chewing load 100 N, profile speed 20%, temperature 25°C, e) experiment no 16 at higher magnification (10000x).

It can be concluded that chewing load and profile speed are the most influencing factor for the volumetric wear rate of dental composite whereas chamber temperature is least influencing factor on the wear rate. Hence, increase in chewing load and profile speed increase the wear rate significantly. NADC-3 indicates least wear among NADC-0, NADC-1, NADC-2 and NADC-3 despite of having maximum void content (Table 4.1). The least wear rate of NADC-3 may conclude that wear rate depends up on number of factors such as resin chemistry, filler shape/size, composition, morphology, amount of initiators, accelerator and the quality of silanization. Figure 6.8d represents the worn surface during the experiment no 16 in Table 6.1. The figure indicates the presence of blow holes, void and pore, exposed wear particles. The scanning electron microscope image (10000X) of Figure 6.8d is shown in Figure 6.8e. The presence of nanoalumina filler particle can be seen in Figure 6.8e.

6.1.4 ANOVA Analysis

Based on the results of Taguchi experimental design, statistical significance of various factors like filler contents, chewing load, profile speed, chamber temperature on volumetric wear rates of dental composite is determined with the help of Analysis of variance (ANOVA). Table 6.2 indicates the results of the ANOVA with the wear rate of dental composites taken in this investigation. The level of confidence of significance for this analysis is 5%.

Table 6.2 ANOVA analysis for nanoalumina filled dental composite

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Filler content (wt.%)	3	149.398	149.398	49.799	74.14	0.003
Chewing load (N)	3	61.862	61.862	30.70	20.621	0.009
Profile Speed (%)	3	43.844	43.844	21.76	14.615	0.015
Chamber Temperature (Degree-C)	3	0.824	0.824	0.41	0.275	0.759
Error	3	2.015	2.015	0.672		
Total	15	257.943				

Note: Where DF stands for Degree of freedom, Seq SS stands for Sequential sum of square, Adj SS stands for Adjacent sum of square. Adj MS stands for Adjacent sum of mean square, F stands for Variance, P stands for percentage contribution of each factor in overall performance)

The last column of the Table 6.2 indicates the level of significance of each factor. From Table 6.2, it is observed that the statistical significance of factor in the descending order follows: filler content (p = 0.003), Chewing load (p = 0.009), profile speed (p = 0.015), chamber temperature (p = 0.759). Hence, filler content, chewing load and profile speed indicates significant effect on volumetric wear rate of the filled composites. However, profile speed and chamber temperature indicates shows less significant contribution on volumetric wear rate of the composites.

Part- II

6.2 Wear assessment of dental composite reinforced with nanozirconia filler

6.2.1 Steady state condition for wear characterization

6.2.1.1 Effect of Chewing Load on volumetric wear rate

Steady state abrasive wear tests are conducted to study the effect of change in wear rate with the change in chewing load. Chewing load are varied in a step of 20 N from minimum value of 40 N to maximum value of 100 N and keeping other parameters such as profile speed: 40%, Profile size 100%, chamber temperature 35°C and food slurry concentration remaining constant. Figure 6.9 shows the effect of change in chewing load with the change in wear rate of dental composites. Wear rate is increased with the increase in chewing load for all dental composite filled with different wt. % of nanozirconia filler particles. The increased in wear rate with increase in chewing load is attributed to the fact that increase in chewing load increases the true contact area of asperities with the opposing surface which resulted into increased in wear of dental composites. The result in this study is in line with Archard equation which said that the wear of a material is directly proportional to increase in true contact area. This observation is also in agreement with the work carried out by Zhang et al. [175] who proposed that in three body abrasive wear, increased in chewing load results into progressive increase in wear rate of human tooth.

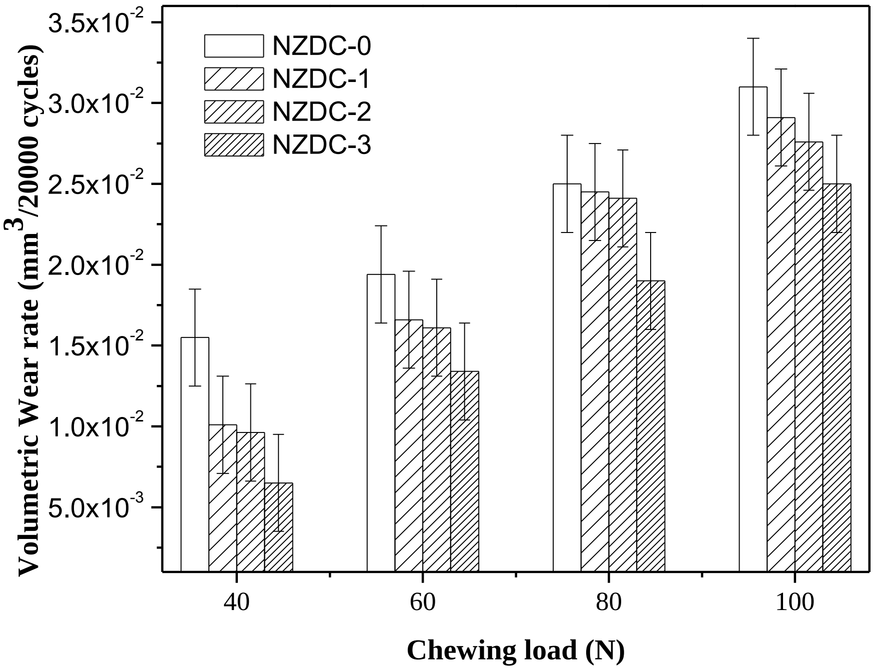


Figure 6.9 Effect of Chewing Load on volumetric wear rate of the dental composites (At constant profile speed 40%, chamber temperature: 35°C

They also concluded that the enamel exhibits lower friction and less wear volume under three-body abrasive wear conditions than under two-body abrasive wear conditions because the chewing in case of mastication in three body abrasive wear is distributed/shared by the food particles and the dental material. Hence, the maximum stress is much lower than in two body condition. In another research Tamura et al. [64] focused on the difference between two different wear assessment techniques such as simulated occlusal wear and tooth brush wear and proposed that a simulated occlusal wear test uses a hard antagonist under relatively high Chewing loading on the specimen's surface which leads to high friction between the surface of specimen and the antagonist, whereas, the toothbrush wear test uses thin flexible filaments of a toothbrush and fine abrasive particles in the dentifrice under lighter loading. Nagarajan [14] determined the in vitro two-body wear resistance of three medium filled composites and proposed that the wear volume of dental composite was increased by ten times when the load increased from 1 to 10 N. From Figure 6.9 it is also revealed that increase in filler content decreased the wear rate. This may be attributed to the fact that increased in nanozirconia filler increases the hardness of dental composite and hence it resulted into decreased in the wear rate.

6.2.1.2 Effect of profile speed on volumetric wear rate

Three body abrasive wear tests are conducted to find the effect of change in wear rate with the change in profile speed of the movement of dental material. Profile speeds are varied in the steps of 20% from a minimum value of 20% to a maximum value of 80% keeping other parameters i.e. chewing load as 40 N, chamber temperature 35^0C and food slurry concentration remaining constant. Figure 6.10 represents the effect on wear rate with the change in profile speed. Wear rate decreases with the increased in nanozirconia content due to increase in hardness. Increase in hardness is attributed to the increase in nanozirconia filler content (Figure 5.7 in Chapter 4). Figure 6.10 also indicates that wear rate increases with the increased in profile speed. The wear rate of dental composite filled with different weight percentage of nanozirconia (NZDC series) is slightly increased with an increase in profile speed up to 40%. Beyond 40%, the wear rate of all composites is increased with higher rate.

Hence, unfilled dental composite exhibited maximum wear rate as compared with other particulate filled dental composites. At 80% profile speed, wear by delamination is observed to occur in unfilled dental composite. This increased in wear rate of unfilled dental composite finally leads to seizure of the material, which is evident from the micrograph shown in Figure 6.14(d). Pihtili and Tosun [176, 177] examined the significance of applied load and sliding speed on the wear behavior of composites. It is concluded that the applied load has more significance than the sliding speed for composites. Various researchers [178-181] showed that value of friction coefficient increases with the increased in normal load. They developed different combinations of polymer and its composite and compared friction coefficient and specific wear rate values of dental composites [182]. Finally, it is observed that the coefficient of friction decreases linearly with the increased in applied pressure values for all material combinations. In the similar study, Unal et al. [183,184] reported that the applied load exerts more influence on the sliding wear of polymer and its composite than the sliding velocity.

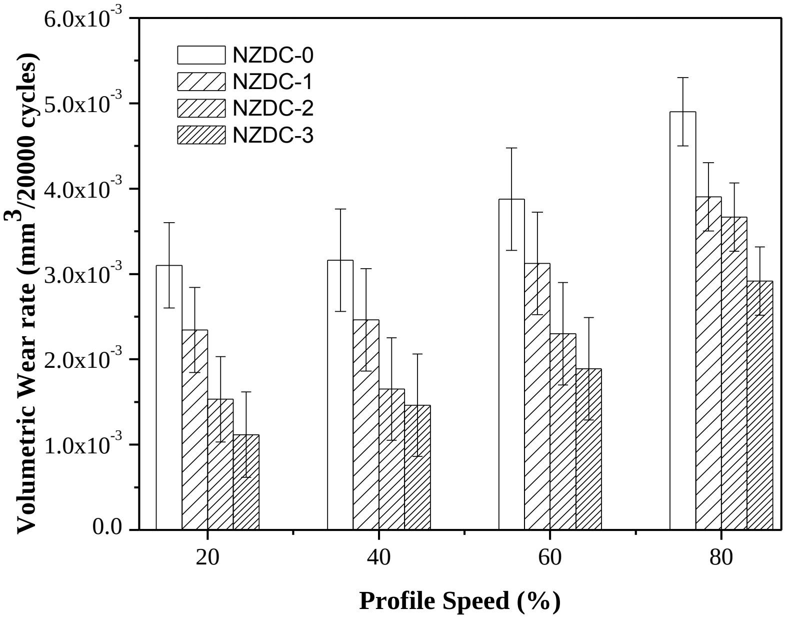


Figure 6.10 Effect of profile speed on volumetric wear rate of the dental composites (At constant Chewing Load 40 N, chamber temperature 35°C)

6.2.1.3 Effect of chamber temperature on volumetric wear rate

Variation in wear rate with temperature of the nanozirconia particulate filled dental composites is shown in Figure 6.11. As the temperature increases, the wear rate of the nanozirconia filled dental composites with variation of filler content also increases up to two third of the proposed temperature and then shows in a decreasing trend. This is in agreement with the study reported by Ramalho et al. [102]. In their work, three different commercially available resins i.e. Synergy, Surefill and Alert have been taken and studied their wear performance with respect to five different temperature ranges (10-50°C). They concluded that the wear rate as well as other mechanical properties such as hardness, elastic modulus, flexural modulus etc show inferior performance at 30°C.

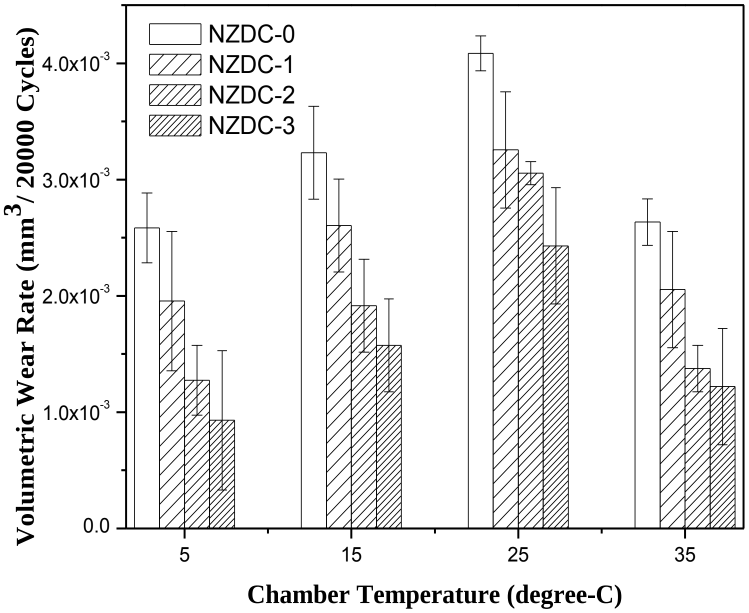


Figure 6.11 Effect of Chamber temperature on volumetric wear rate of the dental composites (At constant chewing load 40N, profile speed 40%

6.2.2 Wear Analysis of experimental results by Taguchi method

In design of experiment, Taguchi method is applied to improve the performance output by optimizing the process parameters and presented in Table 6.3. In Table 6.3, seventh column represents S/N ratio of the volumetric wear rate of the composites. The overall mean for the S/N ratio of the specific wear rate is found to be 47.50 db for the dental composite filled with different wt. % of nanozirconia particulates. From this analysis (Figure 6.12) it is observed that the factor combination of A4, B1, C1 and D4 gives minimum volumetric wear rate for dental composite filled with different wt. % of nanozirconia. It means that dental composite filled with 3 wt. % nanozirconia under chewing load of 40N and with profile speed of 20% and at chamber temperature of 35 °C exhibited minimum wear rate.

Table 6.3 Taguchi experimental results for nanozirconia filled dental composite

S.No	Filler content (%)	Chewing load (N)	Profile Speed (%)	Chamber Temperature (degree-C)	Volumetric Wear Rate dental composite filled with silane treated nanozirconia (mm^3/ 20000 cycles) in food slurry condition	S/N ratio (dB)	Volumetric Wear Rate of silane treated nanozirconia filled dental composite (mm^3/ 20000 cycles) in Citric acid condition	S/N ratio (dB)
1.	0	40	20	5	0.001084	59.2954	0.001504	56.4565
2.	0	60	40	15	0.001332	57.5127	0.002227	53.0470
3.	0	80	60	25	0.001501	56.4718	0.002699	51.3773
4.	0	100	80	35	0.00172	55.2872	0.003295	49.6418
5.	1	40	40	25	0.00098	60.1744	0.001166	58.6628
6.	1	60	20	35	0.001092	59.2327	0.001528	56.3179
7.	1	80	80	5	0.001243	58.1103	0.001974	54.0920
8.	1	100	60	15	0.001508	56.4329	0.002717	51.3179
9.	2	40	60	35	0.000932	60.6154	0.00099	60.0906
10.	2	60	80	25	0.001057	59.5189	0.001418	56.9666
11.	2	80	20	15	0.00111	59.0949	0.001581	56.0201
12.	2	100	40	5	0.001317	57.6063	0.002186	53.2058
13.	3	40	80	15	0.000906	60.8561	0.000883	61.0794
14.	3	60	60	5	0.000973	60.2383	0.001141	58.8505
15.	3	80	40	35	0.001038	59.6723	0.001359	57.3335
16.	3	100	20	25	0.001126	58.9681	0.001631	55.7530
Mean Volumetric Wear Rate (mm^3/ 20000 cycles)					0.001183		0.001769	

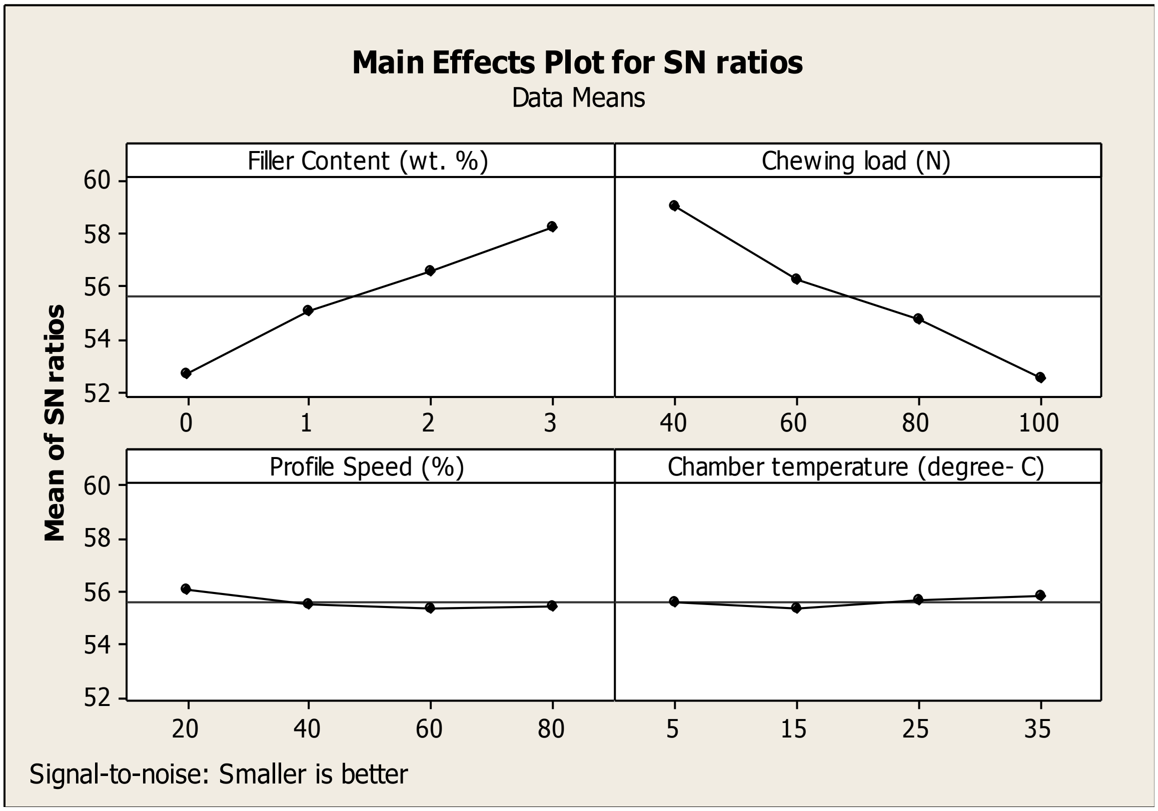


Figure 6.12 Effect of control factors on the wear rate of dental composites

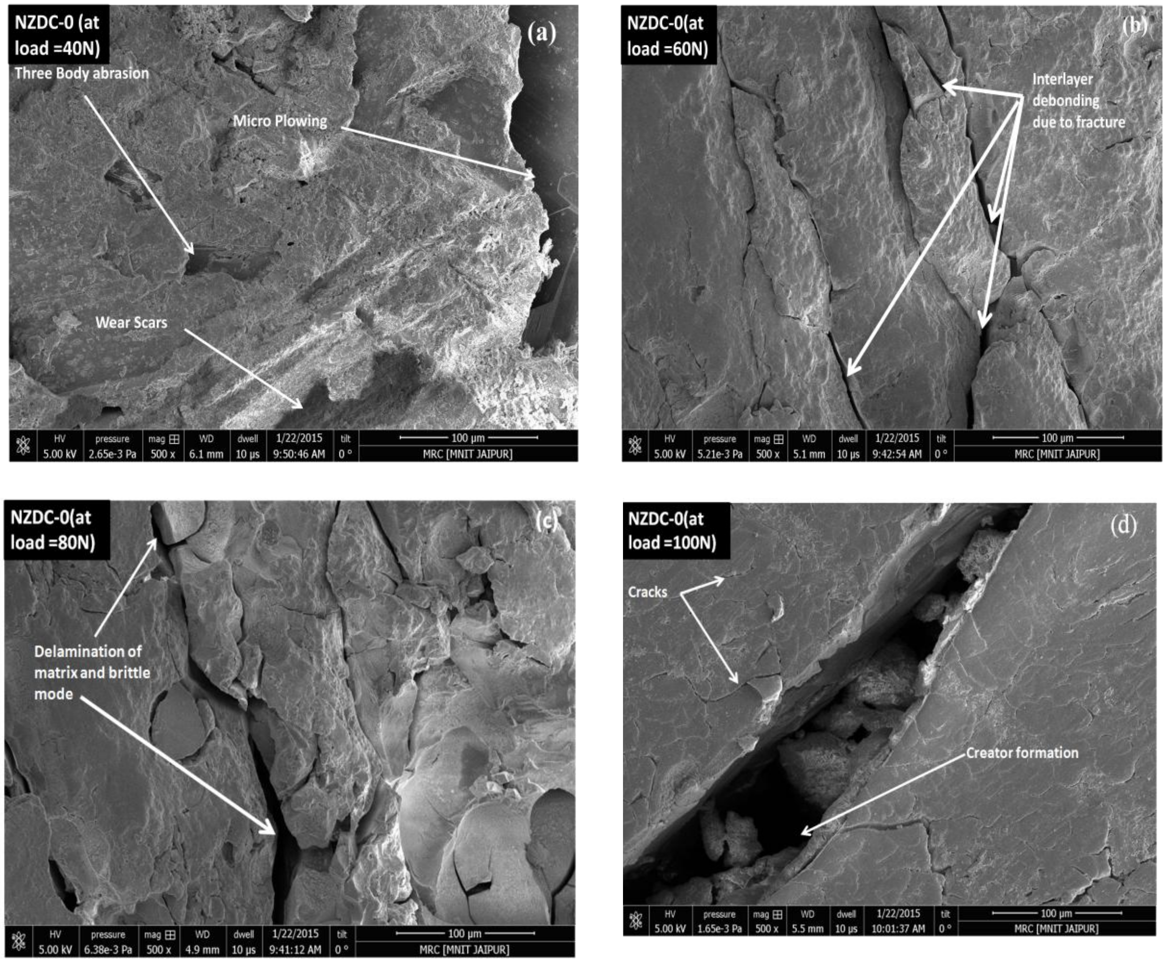
6.2.3 Surface morphology

The worn surface morphology of the nanozirconia filled dental composites studied under steady state conditions using FE-SEM is presented in the Figures 6.13-6.16. All the wear analysis is conducted under limited number of cycle's i.e. 20, 000 cycles per test sample.

6.2.3.1 Micrograph for varying Chewing Load for unfilled dental composite

Figure 6.13 consists of seven micrographs to study variation in chewing load and filler content. In Figure 6.13(a-d), the effect of variation of chewing load on volumetric wear rate of unfilled dental composite is studied. Whereas, in Figures 6.13(a),(e),(f),(g), effect of variation of filler content on volumetric wear rate is studied at constant chewing load 40N.

Figure 6.13 (a-d) represents the worn surface of unfilled dental composite under variable chewing load i.e. 40N, 60N, 80N and 100N respectively at constant profile speed 40% and chamber temperature 35°C. The SEM micro graph of the worn unfilled dental composite is conducted at constant chewing load 40N, profile speed 40%, chamber temperature: 35°C respectively (Figure 6.13). Figure 6.13a indicates the SEM micrograph of the unfilled dental composites under the chewing loading of 40N, profile speed 40%, and chamber temperature: 35°C respectively. From Figure 6.13a it is also observed that among unfilled and particulate filled dental composites under similar boundary conditions (chewing loading of 40N, profile speed 40%, and chamber temperature: 35°C respectively). The unfilled dental composite (NZDC-0) is shown maximum wear rate as in Figure 6.9 and that may be due to presence of blow holes, void and pore as shown in Figure 6.13a. As the load is increased, the same unfilled composite has shown deep furrows in the abrading direction, due to the plowing action by the counter face and hard filler particles (Figure 6.13 (b), Figure 6.13 (c) and Figure 6.13 (d). However, the sizes of the wear scars are bigger than those of the other composites. Typical abrasive wear features, evidenced by plow grooves and striation parallel to the wear direction, and appeared on the worn surface. The substrate plowing is caused by hard asperities on hard filler particles (three-body conditions) [185].



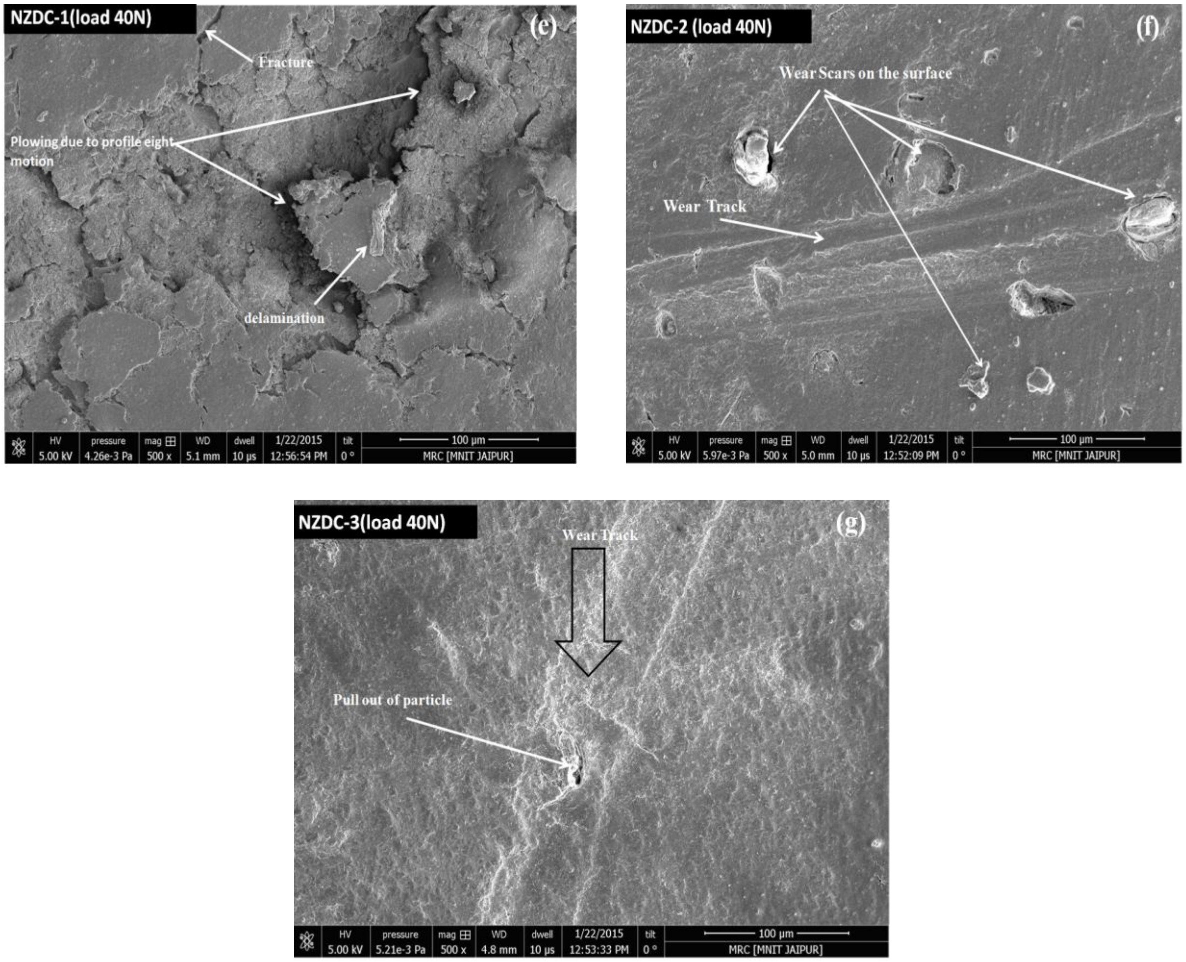


Figure 6.13 FE-SEM images of worn surfaces of composite NADC under the profile speed 40% and temp 35 °C and varying filler content and chewing load a) 0 wt.% at 40N, b) 0 wt.% at 60N, c) 0 wt.% at 80N, d) 0 wt.% at 100N, e) 1 wt.% , 40N f) 2 wt.% , 40N g) 3 wt.% , 40N

6.2.3.2 Micrograph for different weight percentage of nanozirconia at constant chewing load, speed and temperature

Figure 6.13 (e-g) represented the worn surfaces of dental composite with different weight percentage of nanozirconia particles under constant chewing load of 40N, profile speed 40% and chamber temperature 35°C respectively. Figure 6.13a, Figure 6.13e, Figure 6.13f and Figure 6.13g have shown worn surfaces of different dental composites i.e NZDC-0, NZDC-1, NZDC-2 and NZDC-3 respectively after 20000 cycles of experimental run studied under similar operating conditions (chewing load 40N, profile speed 40%, chamber temperature 35°C), Figure 6.13e has shown fracture portion of surface which might be due to applying load in the cross section point of profile eight. In

Figure 6.13f wear scars are less. Minimum wear can be observed in the case of Figure 6.13g.

6.2.3.3 Micrograph for varying profile speed

Figure 6.14 shows worn surfaces of the composite filled with 1 wt. % nanozirconia (NZDC-1) under the variable profile speed of 20%, 40%, 60% and 80% at constant chewing load of 40N and chamber temperature 35°C. It can be seen that this NZDC-1 composite is shown less wear rate than the unfilled composite but still available of blow holes, scratches, wear scars and cracks in the filled composite. Figure 6.14(a) shows the micro graph of 1 wt. % nanozirconia filled dental composite studied under constant chewing load 40N, profile speed of 20% and chamber temperature 35°C respectively. The above boundary condition the upper surface is shown initially rubbing of the resin matrix layer and then subsequently formation of micro-plowing along the sliding direction as shown in Figure 6.14 (a). Low profile speed led to low wear rate of dental composite. However, wear debris is present on the surface, also wear Scars and grooves can be seen with the increased in profile speed from 20% to 40% by keeping other two factors remaining constant, the wear rate is found to be slightly higher as shown in Figure 6.10 (steady state condition graph between sliding speed and volumetric wear rate) but when we moved towards the micrograph of Figure 14 (b) the surface deformation is very less as compared with Figure 6.14 **(**a). This may be due to at higher profile speed the removal of matrix material played major role instead of matrix deformation mechanism. Again for similar composite (NZDC-1), with further increased in profile speed to 60% remaining factors remaining constant, the wear rate is still increased as shown in Figure 6.10 (Steady state graph) and lot of matrix cracks is observed on the surface of the dental composites. The formation of crack is may be due to improper binding between the matrix material and nanozirconia particulates at higher profile speed Figure 6.14 **(**c). Lack of binding resulted into formation of marginal gap. Three body abrasions can be easily seen as in Figure 6.14 (c).

Similarly, with the further increased in profile speed to 80% , sever damages are seen and the matrix material is completely deformed with higher wear rate as observed in Figure 6.14 (d) and Figure 6.10 (steady-state condition graph). Therefore, to summaries the above study it is clear from the steady-state graph and their respective micro-graphs the profile speed played a major role to increase the wear rate on the particulate filled dental composites.

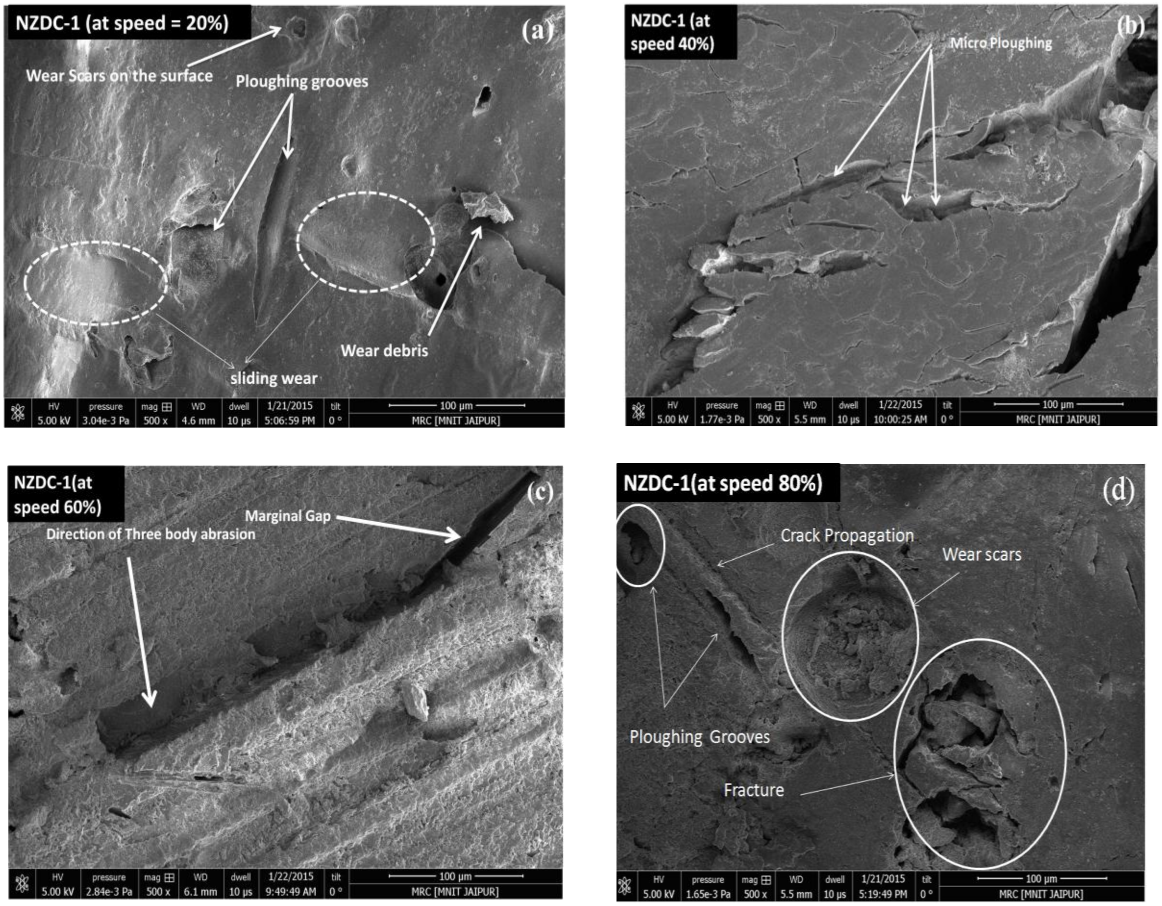


Figure 6.14 FE-SEM images of worn surfaces of composite filled with 1 wt. % nanozirconia under the chewing load 40N, temp 35^{0}C and the varying profile speed a) 20%, b) 40%, c) 60%, d) 80%

6.2.3.4 Micrograph for varying chamber temperature

Figure 6.15 (a-d) indicates the worn surfaces of dental composite filled with different wt. % of nanozirconia (0,1,2 and 3 wt. %) particulates with varying chamber temperature from 5°C to 35°C in a step of 10°C at constant loading of 40N and profile speed of 40% respectively. Dental composite filled with 2 wt. % silanized nanozirconia (NZDC-2) has shown less wear rate than dental composite without nanozirconia (NZDC-0) and 1 wt. % filled dental composite (NZDC-1). Figure 6.15(a) indicates that at 5°C chamber temperature, wear is very less which is also in line with Figure 6.11 (steady state condition). However, at this temperature, crack, voids are generated and some partially exposed filler particles can be observed on the worn surface. In Figure 6.15(b), cracks started to propagate and the propagation can be seen easily from the micrograph. Plowing grooves and slight scratching caused by sharp abrasive particles can be seen on the surface, which is perpendicular to the sliding direction. Some partially exposed filler particles can be observed on the worn surface. Figure 6.15c indicates that some surfaces are burnt due to the increase in temperature. Some pores and wear scars are also visible. The surface at this temperature of 25°C has shown more wear that the same composition surface at 15°C. This result can verified the steady state condition between chamber temperature and volumetric wear rate of dental composite as depicted in Figure 6.11. From Figure 6.15 (d), micrograph clearly indicates that the wear on the surface increases when temperature increases from 5°C to 25°C. At 25°C, more wear is found on the surface but afterward, at 35°C, wear scars on the surfaces decreased which are consistent with the steady state condition (Figure 6.11).

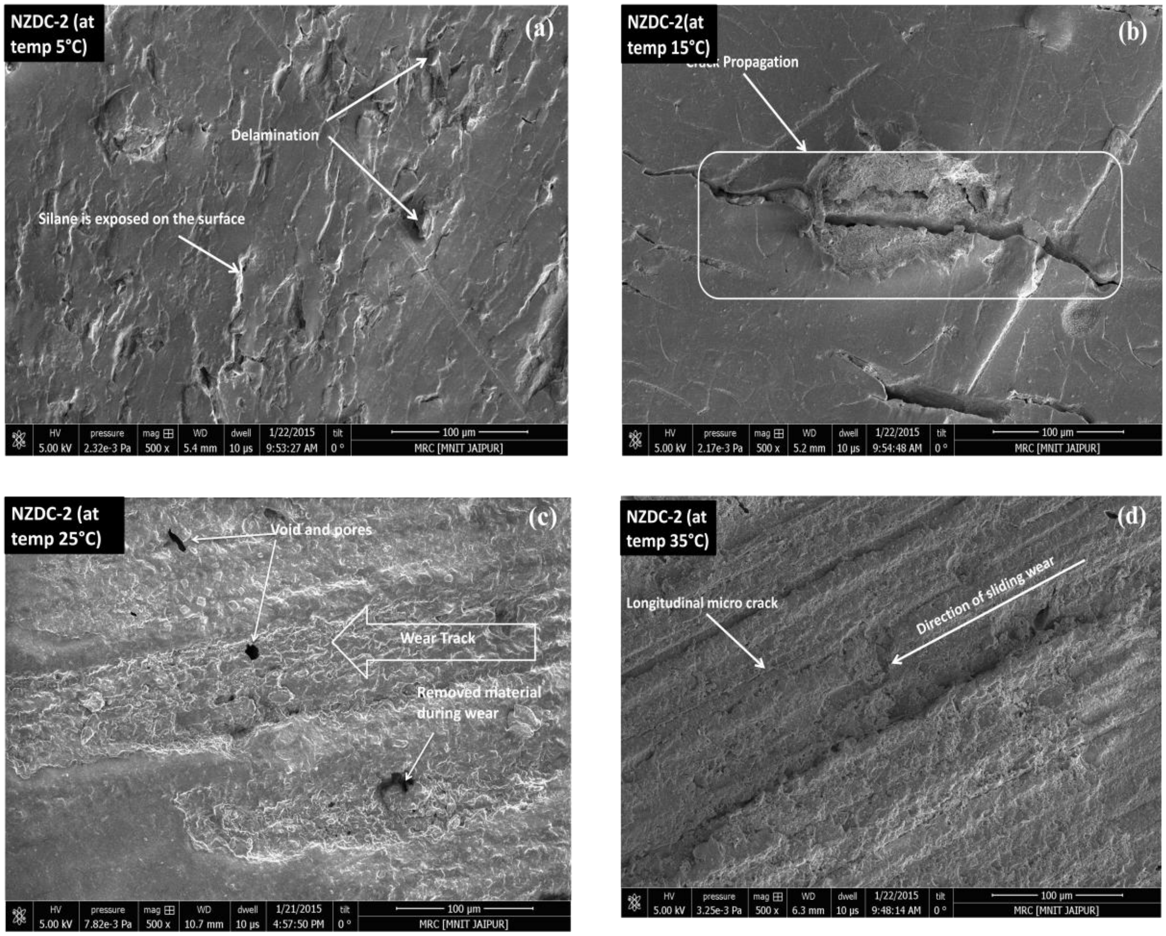


Figure 6.15 FE-SEM images of worn surfaces of composite filled with 2 wt. % nanozirconia under, chewing load 40N, profile speed 40% and varying chamber temperature a) 5°C, b) 15°C, c) 25°C and d) 35°C

6.2.3.5 Micrograph from Taguchi analysis

Figure 6.16 shows worn surfaces of dental composite filled with 3 wt. % silanized nanozirconia (NZDC-3) for the four different experimental conditions as per Taguchi orthogonal array experimental design during the experiment no 13,14,15,16 in Table 6.3. Figure 6.16 (a) indicates the micrograph for the experiment under high profile speed 80%, chewing load 40N and chamber temperature 15°C. A clear wear track direction can be seen along with more scratches around the wear track direction. Brittle crack is also very common, because of running at maximum profile speed, abraded fracture surface is also visible. Figure 6.16 (b) indicates the micrograph for the experiment under high profile speed 60%, chewing load 60N and chamber temperature 5°C respectively. In Figure 6.16 (b), plowing grooves and slight scratching caused by sharp abrasive particles can be seen on the surface, which is perpendicular to the sliding direction. Some partially exposed filler particles can also be observed on the worn surface. Figure 6.16 (c) indicates the micrograph for the experiment under profile speed 40%, chewing load 80N and chamber temperature 35°C. Due to large chewing load of 80N but low profile speed, wear track is visible, removed material can be seen. The presence of blow holes, void and pore can also be observed. Figure 6.16 (d) indicates the micrograph for the experiment no 16 in Table 6.5 under profile speed 20%, chewing load 100N and chamber temperature 25°C. In Figure 6.16 (d), presences of blow holes, void and pore, exposed wear particles can be observed. The much worn surface is indicated by dotted circle. The worn surface at this stage is due to combined effect maximum loading and minimum speed.

It can be concluded that the dental composite filled with 3 wt. % silanized nanozirconia (NZDC-3) exhibits least wear among all NZDC series composite (NZDC-0, NZDC-1, NZDC-2 and NZDC-3) despite of having maximum void content (Table 4.3 in Chapter 4). The least wear rate of NZDC-3 may conclude that wear rate depends up on number of factors such as resin chemistry, filler shape/size, composition, morphology, amount of initiators, accelerator and the quality of silanization. The scanning electron microscope image (10000X) of Figure 6.16 **(**d) is shown in Figure 12e. The presence of nanozirconia filler particle can be seen in Figure 6.16 **(**e).

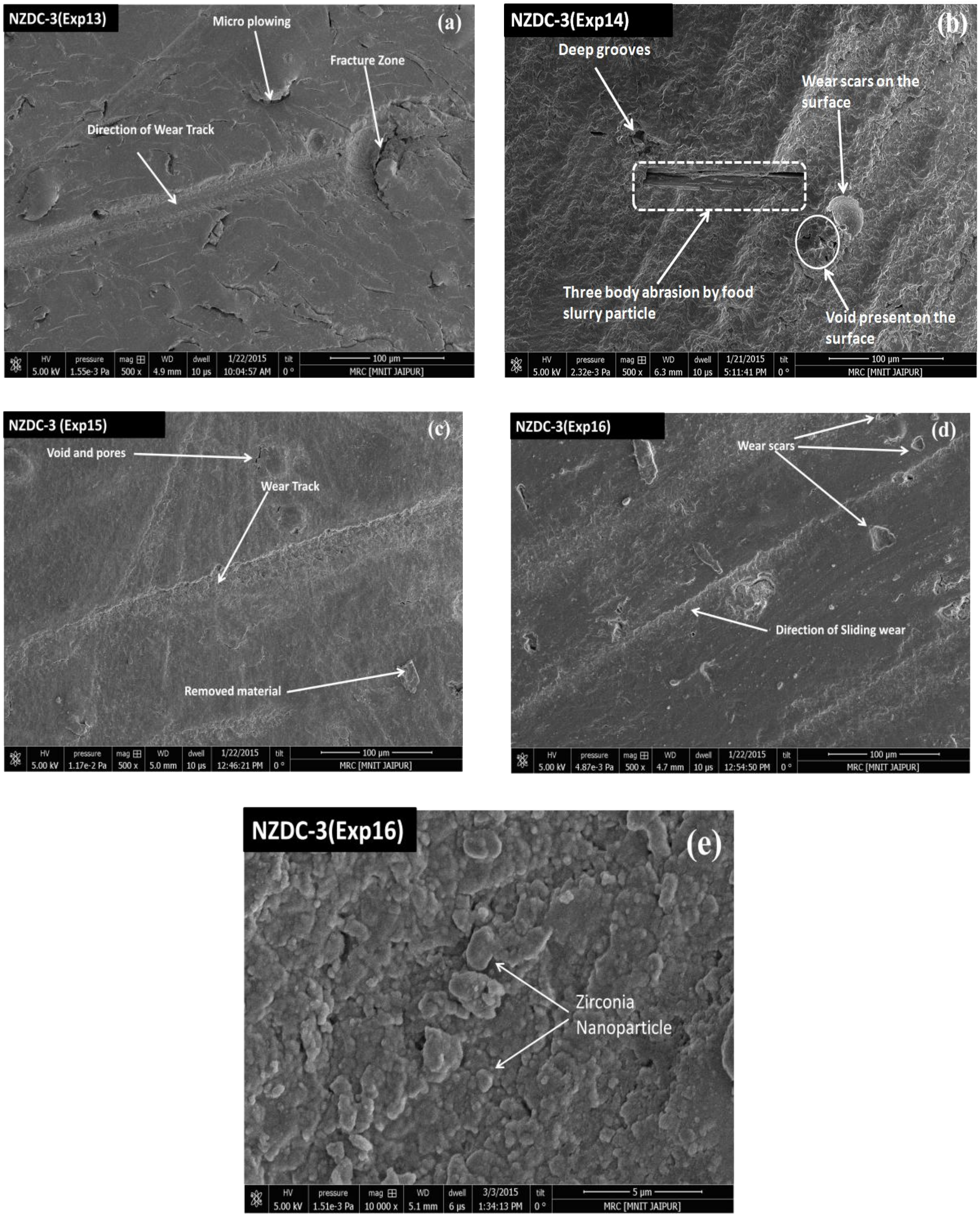


Figure 6.16 FE-SEM images of worn surfaces of composite filled with 3 wt. % nanozirconia under different working condition as in Table 6.3: a) experiment no 13, chewing load 40 N, profile speed 80, Chamber temp 15°C, b) experiment no 14, chewing load 60N, profile speed 60% , Chamber temp 5°C, c) experiment no 15 chewing load 80 N, profile speed 40,the chamber temperature 35°C, d) experiment no 16 chewing load 100 N, profile speed 20%, temperature 25°C, e) experiment no 16 at higher magnification (10000x).

6.2.4 ANOVA Analysis

Based on the results of Taguchi experimental design, statistical significance of various factors like filler contents, chewing load, profile speed, chamber temperature on volumetric wear rates of dental composite is determined with the help of Analysis of variance (ANOVA). Table 6.4 indicates the results of the ANOVA with the wear rate of dental composites taken in this investigation. The level of confidence of significance for this analysis is 5%. The last column of the Tables 6.4 indicates the level of significance of each factor. From Table 6.4, it is observed that the statistical significance of factor in the descending order follows: Chewing load (p = 0.000), filler content (p = 0.001), profile speed (p = 0.398), chamber temperature (p = 0.454). Hence, chewing load and filler content indicate great influence on volumetric wear rate of the filled composites. However, profile speed and chamber temperature indicate shows less significant contribution on volumetric wear rate of the composites.

Table 6.4 ANOVA analysis for nanozirconia filled dental composite

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Filler content (wt.%)	3	112.963	112.963	37.654	187.79	0.001
Chewing load (N)	3	158.742	158.742	52.914	263.90	0.000
Profile Speed (%)	3	0.833	0.833	0.278	1.38	0.398
Chamber Temperature (Degree-C)	3	0.695	0.695	0.232	1.16	0.454
Error	3	0.602	0.602	0.201		
Total	15	273.835				

Note: Where DF stands for Degree of freedom, Seq SS stands for Sequential sum of square, Adj SS stands for Adjacent sum of square. Adj MS stands for Adjacent sum of mean square, F stands for Variance, P stands for percentage contribution of each factor in overall performance)

Part-III

6.3 Wear assessment of dental composite reinforced with nanosilica filler

6.3.1 Steady State conditions for wear characterizations

6.3.1.1 Effect of Chewing Load on volumetric wear rate

In this steady state condition, the parameter chewing load is varied from a minimum value of 40 N to maximum value of 100 N in the step of 20N by keeping other parameters such as profile speed 40%, Profile size 100%, chamber temperature of 35°C and food slurry concentration constant. Figure 6.17 indicates the effect of change in chewing load on wear rate of dental composite filled with silane treated nanosilica filler in food slurry condition. It is revealed that the wear rate increases with the increased in chewing load for variations in the filler content. The increased in wear rate with increase in chewing load is attributed to the fact that increase in chewing load resulted in the increase the true contact area of asperities with the opposing surface which resulted into increased in wear rate of dental composite. This is in agreement with the literature [186-189] as proposed by various researchers.

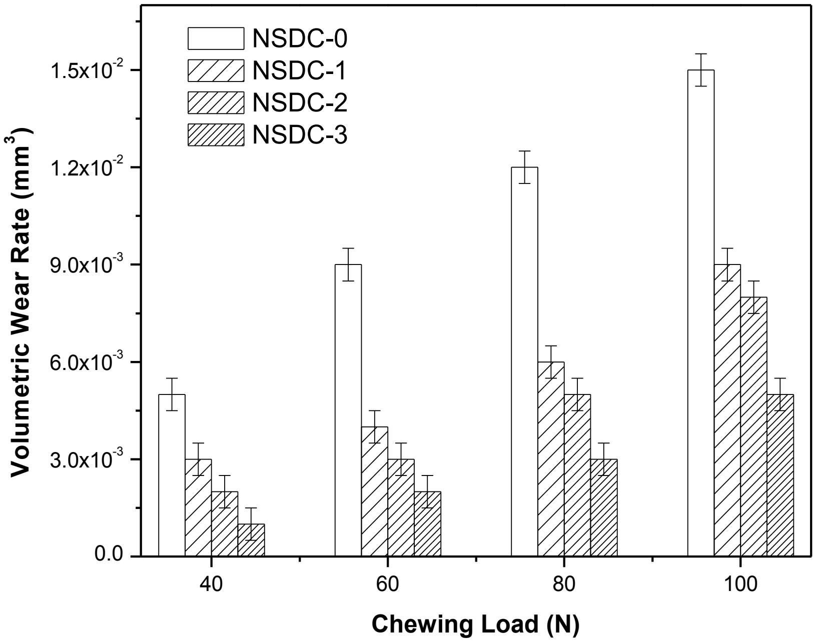


Figure 6.17 Effect of Chewing Load on volumetric wear rate of the dental composites (At constant profile speed 40%, chamber temperature: 35°C

6.3.1.2 Effect of profile speed on volumetric wear rate

Three body abrasive wear tests are conducted to find the effect of change in wear rate with the change in profile speed of the movement of dental material. Profile speeds are varied in the steps of 20% from a minimum value of 20% to a maximum value of 80% keeping other parameters i.e. chewing load as 40 N, chamber temperature 35°C and food slurry concentration remaining constant. Figure 6.18 indicates the effect of variation of profile speed on volumetric wear rate of the unfilled and particulate filled dental composites. As the speed is increased, the number of cycles is kept constant i.e. 20000 cycles, hence sliding distance is constant. Despite of constant sliding distance, volumetric wear rate is increased with the increasing in profile speed. This may be due to the fact that as the speed increases the true contact area increases the friction and thrust force. The decreased shear strength of the material and increased in true area of contact between contacting surfaces played a major role in the higher wear rate at higher sliding velocity.

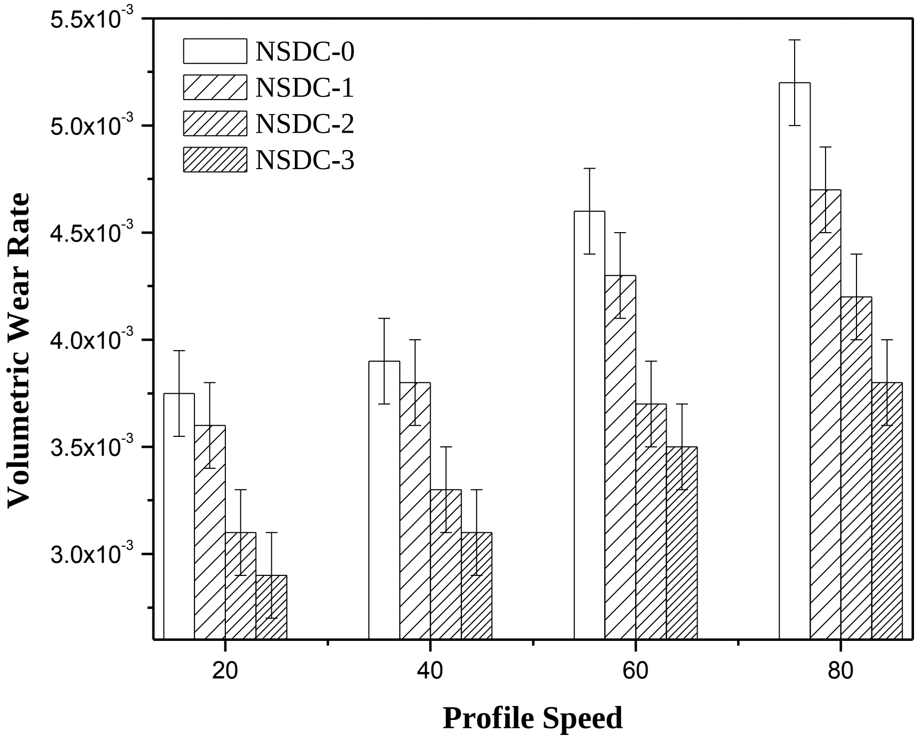


Figure 6.18 Effect of profile speed on volumetric wear rate of the dental composites (At constant Chewing Load 40 N, chamber temperature 35^{o}C)

6.3.1.3 Effect of chamber temperature on volumetric wear rate

Figure 6.19 indicates that as the temperature of chamber increases from 5°C to 15°C, the wear rate of the nanosilica filled dental composites with variation of filler content increases linearly. Further increased in temperature from 15°C to 25°C increases the wear rate in same linear pattern. However, after attaining maximum temperature 25°C, the volumetric wear rate of the dental composites is gradually decreased. The increased in wear rate with increase in temperature (5-25°C) is due to the fact that the increase in temperature increases the true contact area, friction forces and polymer chain mobility. Further increase in temperature in the range of 25-35°C results into slight decreased in the wear rate because of presence of resin matrix in the composite.

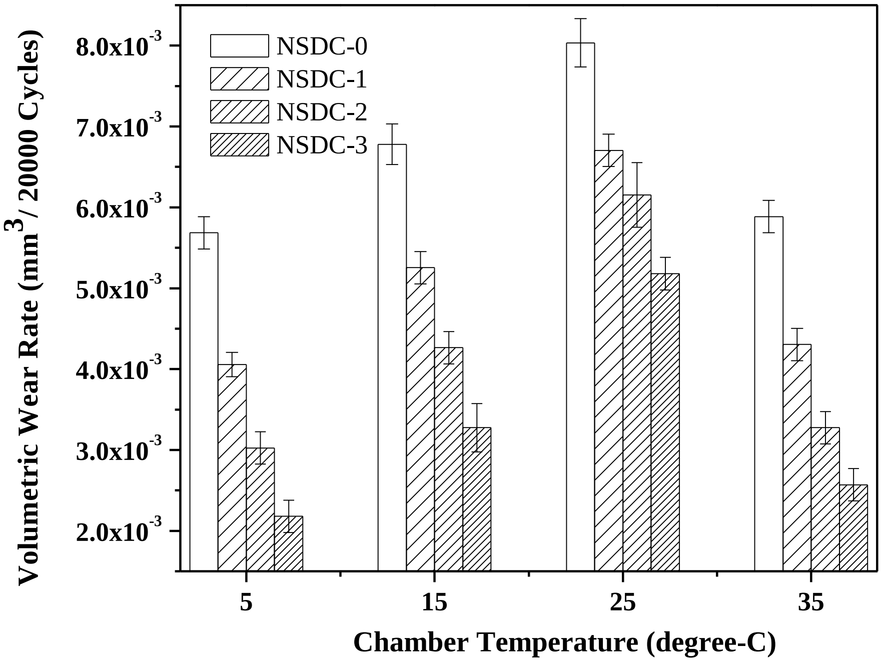


Figure 6.19**.** Effect of Chamber temperature on volumetric wear rate of the dental composites (At constant chewing load 40N, profile speed 40%

6.3.2 Wear Analysis of silane treated nanosilica filled dental composite in food slurry using Taguchi and ANOVA

In Table 6.5, seventh column represented the volumetric wear rate of dental composite filled with silane treated nanosilica in food slurry condition. Ninth column represented S/N ratio for the volumetric wear rate of dental composite filled with silane treated nanosilica. The overall mean for the S/N ratio of the specific wear rate is found to be 53.67 db for the dental composite filled with different wt.-% of silane treated nanosilica dental composite. From this analysis (Figure 6.20) it can be concluded that the factor combination of A4, B2, C1 and D2 gives minimum volumetric wear rate for dental composite filled with different wt.-% of silane treated nanosilica. It means the dental composite filled with 3 wt.-% silane treated nanosilica at chewing load of 60N and with profile speed 20% and at chamber temperature 15°C exhibited minimum wear rate.

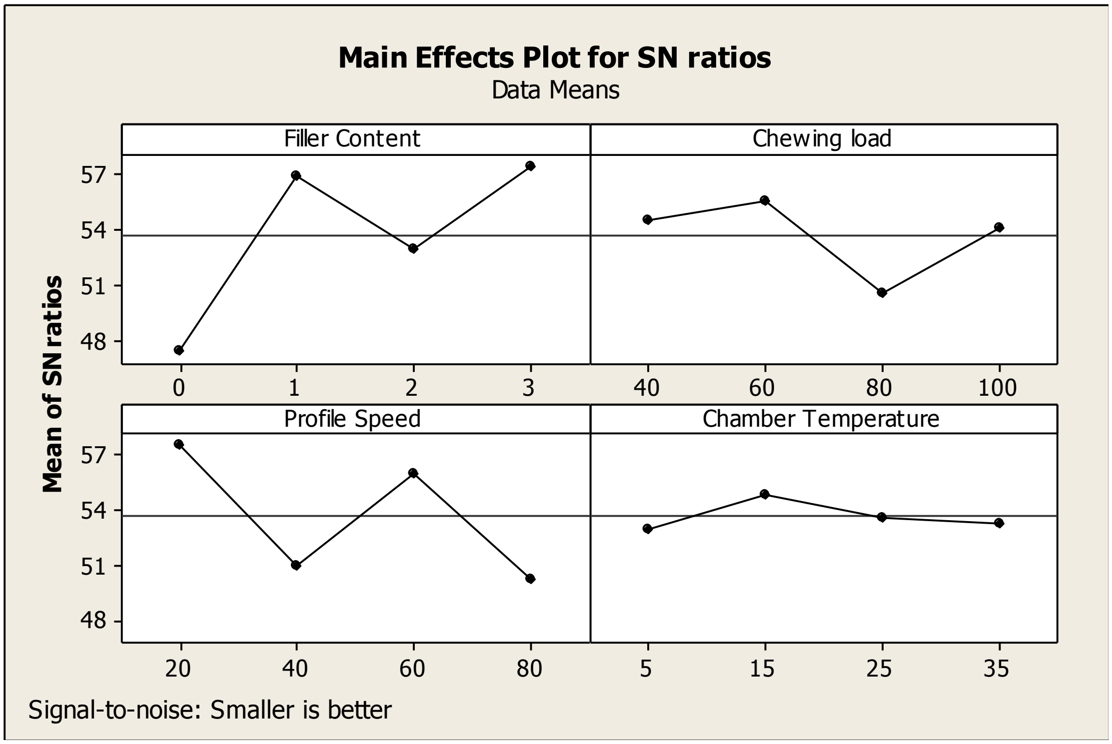


Figure 6.20 Effect of control factors on the wear rate of dental composites

Table 6.5. Taguchi experimental results for nanosilica filled dental composite

S.No	Filler content (%)	Chewing load (N)	Profile Speed (%)	Chamber Temperature (degree-C)	Volumetric Wear Rate dental composite filled with silane treated nanosilica (mm^3/ 20000 cycles) in food slurry condition	S/N ratio (dB)	Volumetric Wear Rate of silane treated nanosilica filled dental composite (mm^3/ 20000 cycles) in Citric acid condition	S/N ratio (dB)
1.	0	40	20	5	0.002546	51.88	0.003019	50.40
2.	0	60	40	15	0.0042434	47.45	0.004721	46.52
3.	0	80	60	25	0.0050921	45.86	0.005811	44.71
4.	0	100	80	35	0.0059408	44.52	0.006674	43.51
5.	1	40	40	25	0.0017055	55.36	0.001844	54.68
6.	1	60	20	35	0.0008527	61.38	0.00094	60.54
7.	1	80	80	5	0.0034109	49.34	0.004115	47.71
8.	1	100	60	15	0.0008527	61.38	0.000975	60.22
9.	2	40	60	35	0.0017053	55.36	0.001945	54.22
10.	2	60	80	25	0.002558	51.84	0.00283	50.96
11.	2	80	20	15	0.0017053	55.36	0.001877	54.53
12.	2	100	40	5	0.0034106	49.34	0.004093	47.76
13.	3	40	80	15	0.0017203	55.29	0.002053	53.75
14.	3	60	60	5	0.0008601	61.31	0.001082	59.32
15.	3	80	40	35	0.0025804	51.77	0.00292	50.69
16.	3	100	20	25	0.0008601	61.31	0.001029	59.75
Mean Volumetric Wear Rate (mm^3/ 20000 cycles)					0.002503		0.002871	

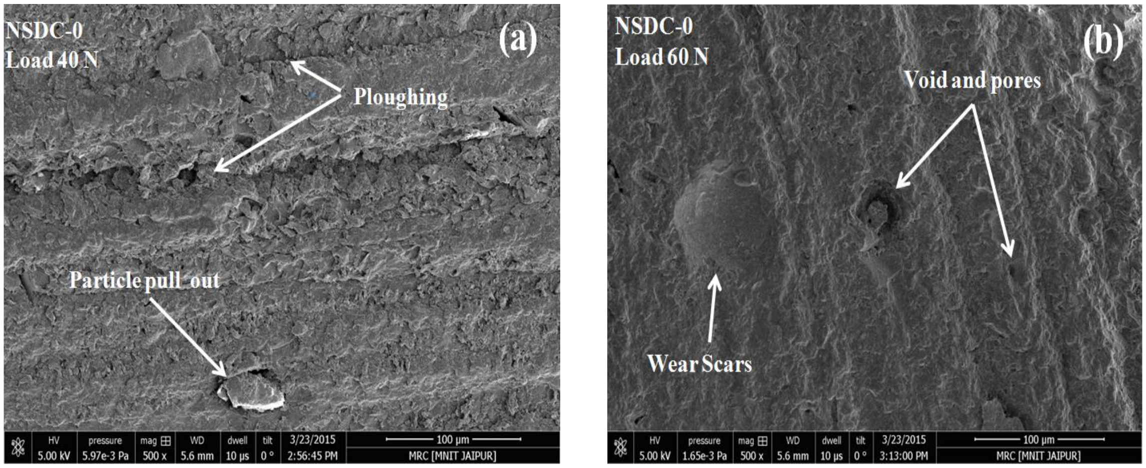
6.3.3 Surface morphology

The worn surface morphology of the nanosilica filled dental composites studied under steady state conditions using FE-SEM is presented in the Figures 6.21-6.23. All the wear analysis is conducted under limited number of cycle’s i.e. 20,000 cycles per test sample.

6.3.3.1 Micrograph for varying Chewing Load for unfilled dental composite

Figure 6.21(a-d) represented the worn surfaces of unfilled dental composite under variable chewing load i.e. 40N, 60N, 80N and 100N respectively at constant profile speed 40% and chamber temperature 35°C. Figure 6.21a indicates the SEM micrograph of the unfilled dental composites under the chewing loading of 40N, profile speed 40%, and chamber temperature 35°C respectively. From Figure 6.21a it is also observed that Ploughing and particle pull out can be seen. As the load is increased from 40N to 60N on the same unfilled composite, wear increased and void and pores are generated. Wear scars are also visible (Figure 6.21b).

With the increase in load from 60N to 80N that led to further damage the surface, formation of cracks on the composite surface as observed in Figure 6.21c. Finally, when load is increased to 100N, delamination occurred due to catastrophic failure. Severe damage on the surface is found (Figure 6.21d).



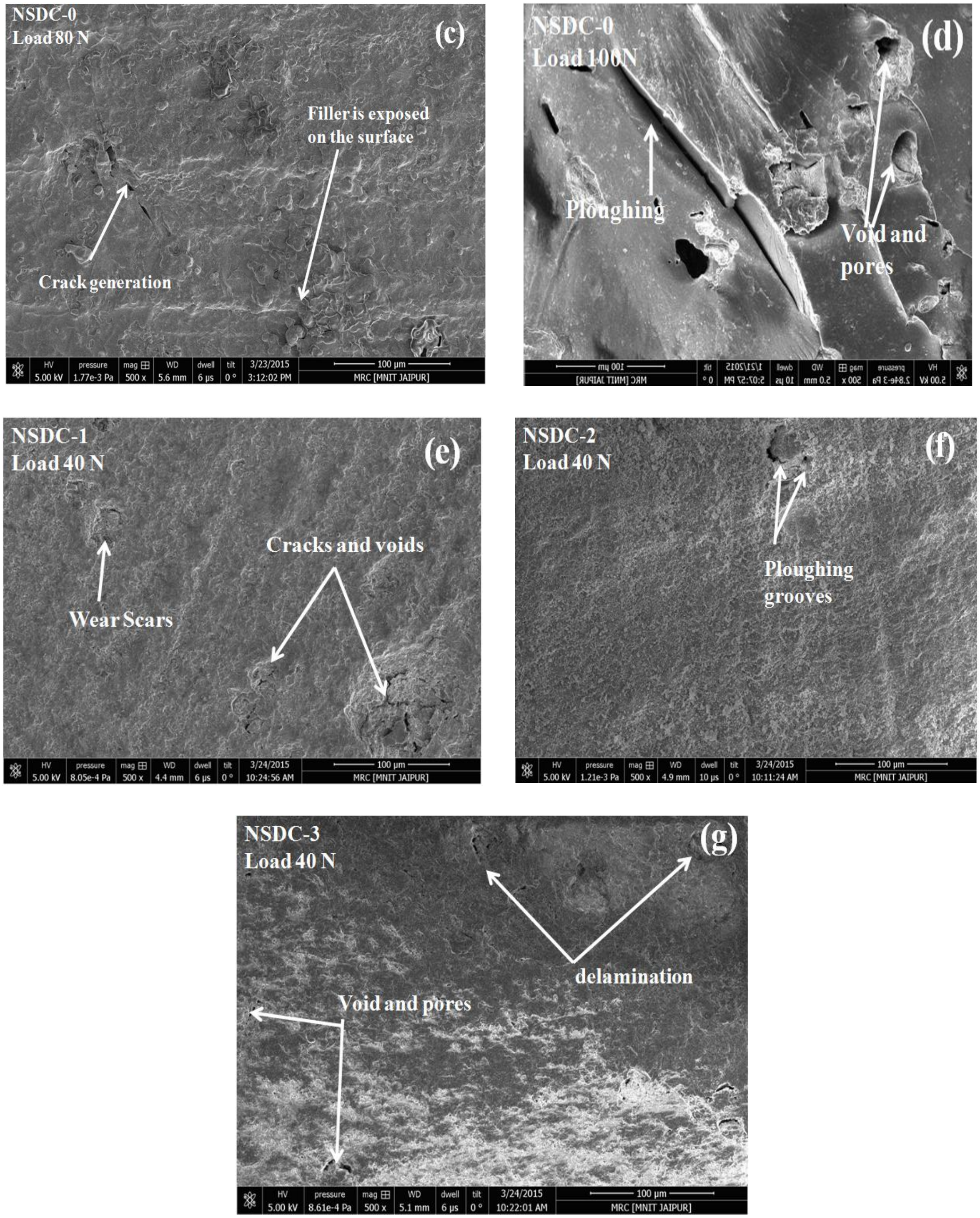


Figure 6.21 FE-SEM images of worn surfaces of composite NSDC under the profile speed 40% and temp 35 °C and varying filler content and chewing load a) 0 wt.% at 40N, b) 0 wt.% at 60N, c) 0 wt.% at 80N, d) 0 wt.% at 100N, e) 1 wt.% , 40N f) 2 wt.% , 40N g) 3 wt.% , 40N

6.3.3.2 Micrograph for different weight percentage of nanosilica at constant chewing load, speed and temperature

Figure 6.21a, Figure 6.21e, Figure 6.21f and Figure 6.21g have shown the worn surfaces morphology of different dental composites i.e NSDC-0, NSDC -1, NSDC -2 and NSDC -3 respectively after 20000 cycles of experimental run under same condition (chewing load 40N, profile speed 40%, chamber temperature 35°C), Figure 6.21e has shown less wear and fracture surface than the unfilled composite (Figure 6.21a). Wear scars and crack and void are also visible. Figure 6.21f, ploughing grooves is reported which is due to the fracture portion of surface which might be due to applying load in the cross section point of profile eight. In Figure 6.21f wear scars are less. Minimum wear can be observed in the case of Figure 9g.

6.3.3.3 Micrograph for varying profile speed

Figure 6.22 showed worn surfaces of the composite filled with 1 wt. % nanosilica (NZDC-1) under the variable profile speed of 20%, 40%, 60% and 80% at constant chewing load of 40N and chamber temperature 35°C. It can be seen that this NSDC-1 composite is shown less wear rate than the unfilled composite but still available of blow holes, scratches, wear scars and cracks in the filled composite. Figure 6.22a shows the micro graph of 1 wt. % nanosilica filled dental composite studied under constant chewing load 40N, profile speed of 20% and chamber temperature 35°C respectively. The above boundary condition the upper surface is shown initially rubbing of the resin matrix layer and then subsequently formation of micro-plowing along the sliding direction as shown in Figure 6.22a. However, with the increase in profile speed from 20% to 40% by keeping other factors remaining constant the wear rate is found to be slightly higher as shown in Figure 6.18 but when we moved towards the micrograph of Figure 6.22b the surface deformation is very less as compared with Figure 6.22a. This may be due to at higher profile speed the removal of matrix material played major role instead of matrix deformation mechanism. Again for similar composite (NSDC-1) with further increase in profile speed to 60% remaining factors remaining constant the wear rate is still increased (Figure 6.18) and lot of matrix cracks is observed on the surface of the dental composites. The formation of crack is may be due to improper binding between the matrix material and nanosilica particulates at higher profile speed (Figure 6.22c).

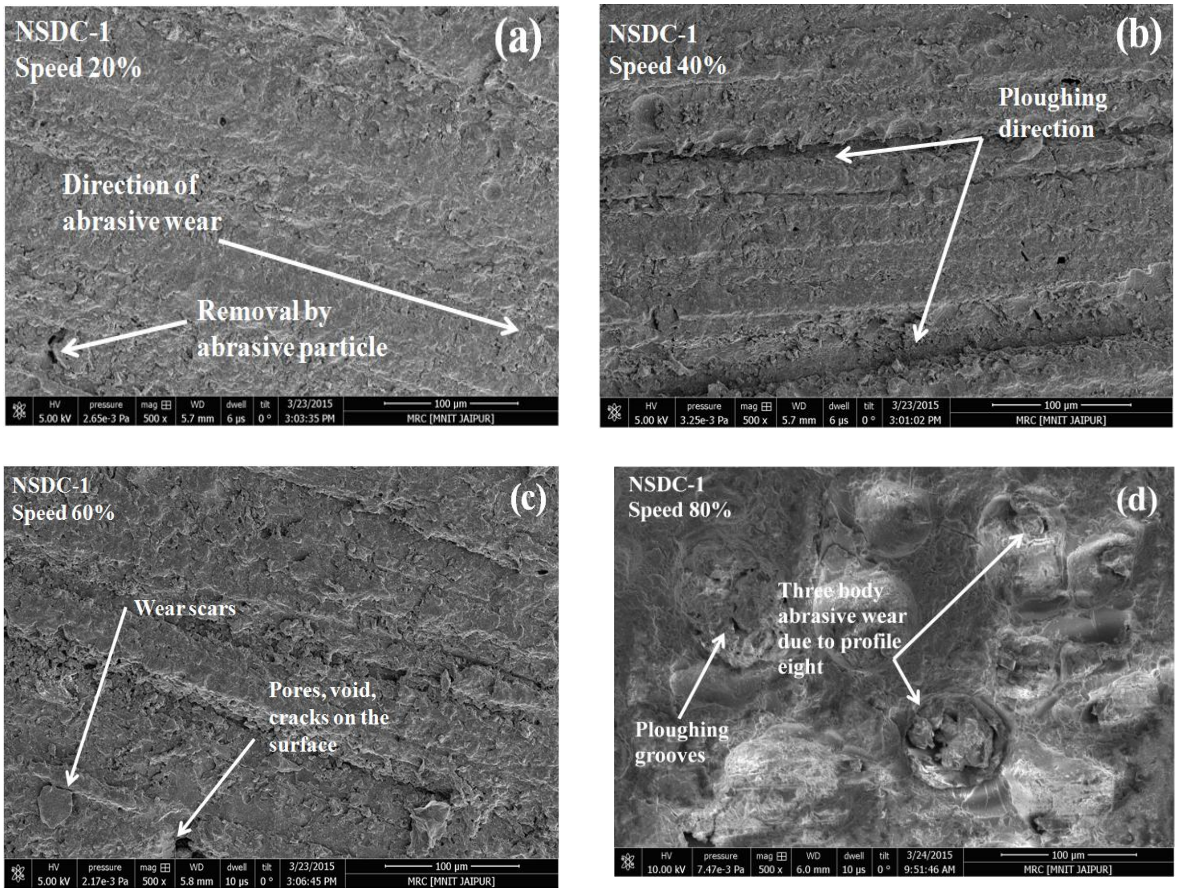


Figure 6.22 FE-SEM images of worn surfaces of composite filled with 1 wt. % nanosilica under the chewing load 40N, temp 35^0C and the varying profile speed a) 20%, b) 40%, c) 60%, d) 80%

Similarly, with the further increased in profile speed to 80% the matrix material is completely deformed with higher wear rate as observed in Figure 6.22d and Figure 6.18 (steady-state condition graph). Therefore, from the steady-state graph and their respective micro-graphs, it is clear that the profile speed has played a major role to increase the wear rate of the particulate filled dental composites.

6.3.3.4 Micrograph for varying chamber temperature

Figure 6.23 indicates the worn surfaces of dental composite filled with 2 wt. % nanosilica (NSDC-2) under varying chamber temperature from 5 to 35 in a step of 10 at constant loading of 40N and profile speed of 40%. NSDC-2 has shown less wear than unfilled and 1 wt. % filled dental composite. Crack is generated and its propagation is also visible. Some partially exposed filler particles can be seen on the worn surface. Figure 6.23a indicates that at 5°C chamber temperature, wear is very less. In Figure 6.23b, cracks are generated and plowing grooves and slight scratching caused by sharp edge abrasive particles can be observed on the surface perpendicular to the sliding direction. Some partially exposed filler particles can also be seen on the worn surface. Figure 6.23c indicates that some surfaces are burnt due to the increase in temperature. One can observe that as temperature increases from 5°C to 25°C, more wear scars are found on the surface but afterward at 35°C (Figure 6.23d), wear scars on the surfaces are decreased.

6.3.3.5 Micrograph from Taguchi analysis

Figure 6.24 shows worn surface of composite with 3 wt. % nanosilica (NSDC-3) for the four different working conditions as done during the experiment no 13,14,15,16 in Table 6.5. It can be revealed that in NSDC-3, least wear is observed and the wear track can be seen but its intensity is least among other filled and unfilled composite. However some holes and voids are visible. Figure 6.24a, a clear wear track direction can be seen along with more scratches in nearby. Brittle crack and delamination are also very common. More wear debris is also detected. In Figure 6.24b, plowing grooves and slight scratching caused by sharp abrasive particles can be seen on the surface, which is perpendicular to the sliding direction. Some filler particles on the worn surface is partially exposed. In Figure 6.24c and Figure 6.24d, presence of blow holes, void and pore can be observed. In Figure 6.24 c, the much worn surface is indicated by dotted circle. This worn is due to complicated movement at the center of eight profile motion.

NSDC-3 indicates least wear among NSDC-0, NSDC-1, NSDC-2 and NSDC-3 despite of having maximum void content (Table 4.11). The least wear rate of NSDC-3 may conclude that wear rate depends up on number of factors such as resin chemistry, filler shape/size, composition, morphology, amount of initiators, accelerator and the quality of silanization. Figure 6.24 (d) represented the worn surface during the experiment no 16 in Table 3. The figure indicates that presence of blow holes, void and pore, exposed wear particles can be observed. The scanning electron microscope image (10000X) of Figure 6.24 (d) is shown in Figure 6.24 (e). The presence of nanosilica filler particle can be seen in Figure 6.24 (e).

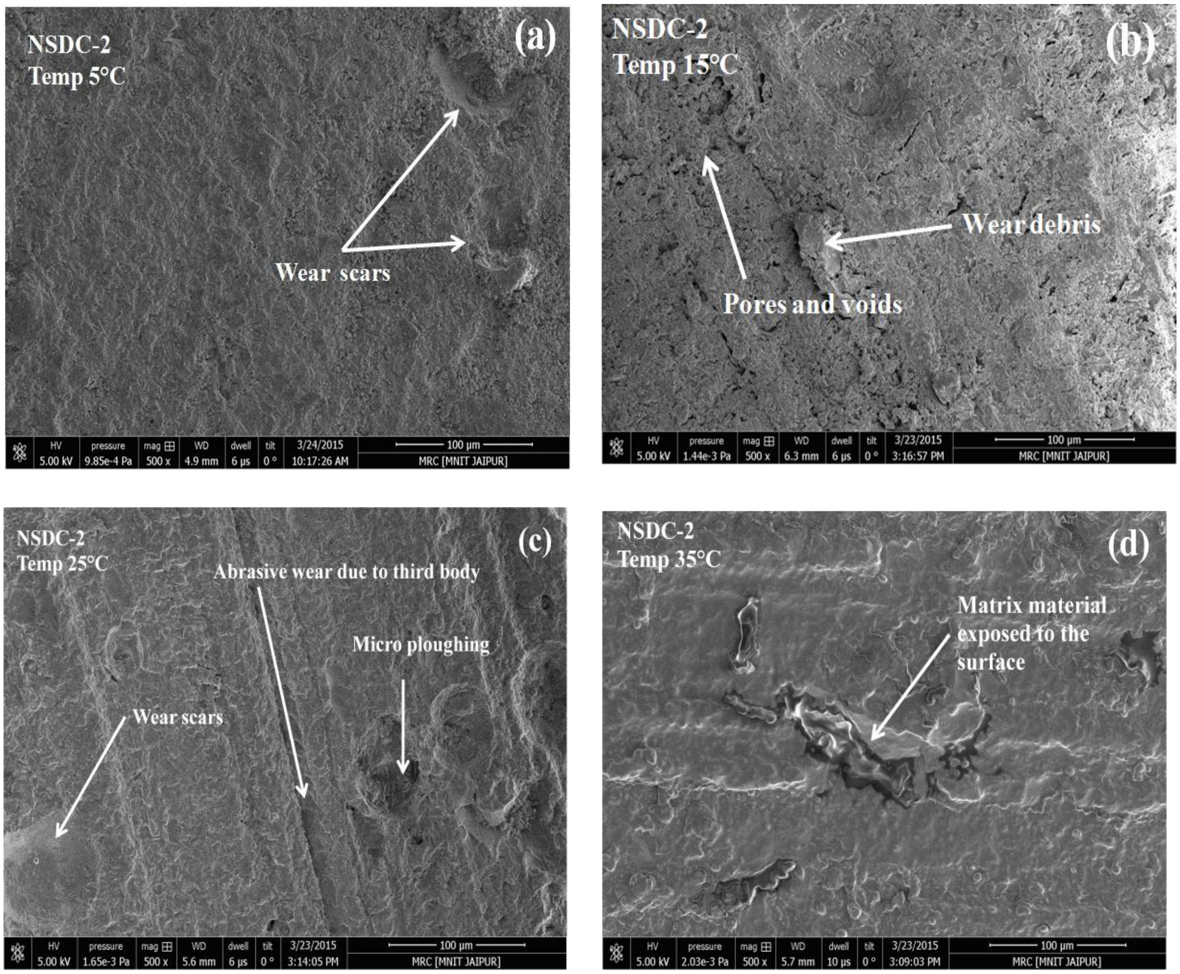
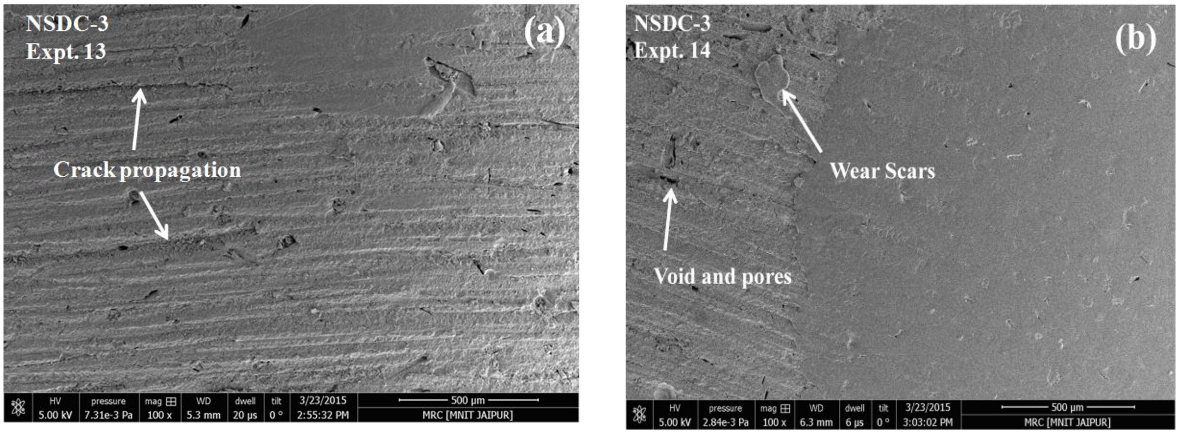


Figure 6.23. FE-SEM images of worn surfaces of composite filled with 2 wt. % nanosilica under, chewing load 40N, profile speed 40% and varying chamber temperature a) 5°C, b) 15°C, c) 25°C and d) 35°C



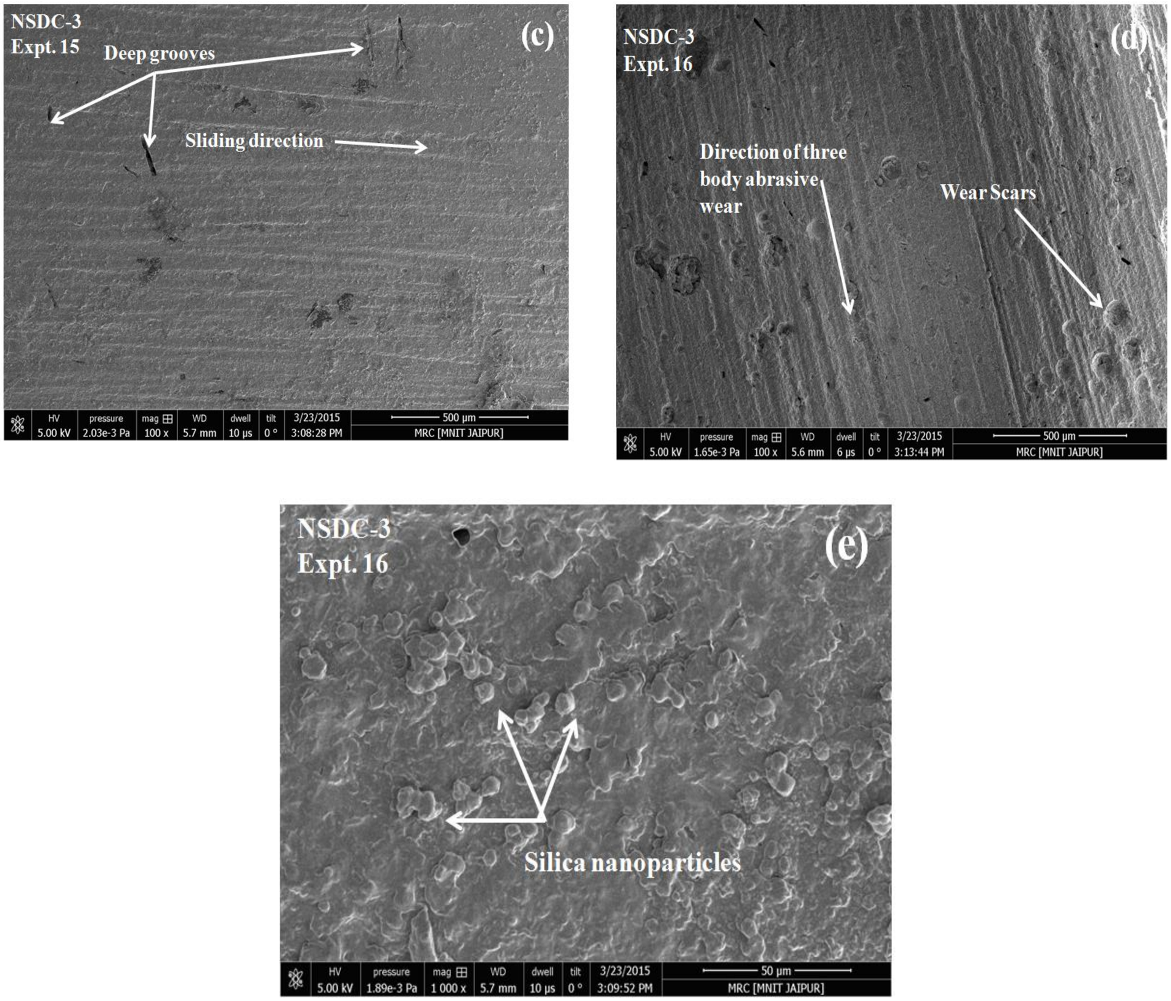


Figure 6.24 FE-SEM images of worn surfaces of composite filled with 3 wt. % nanosilica under different working condition as in Table 6.3: a) experiment no 13, chewing load 40 N, profile speed 80, Chamber temp 15°C, b) experiment no 14, chewing load 60N, profile speed 60% , Chamber temp 5°C, c) experiment no 15 chewing load 80 N, profile speed 40,the chamber temperature 35°C, d) experiment no 16 chewing load 100 N, profile speed 20%, temperature 25°C, e) experiment no 16 at higher magnification (10000x).

6.3.4 ANOVA Analysis

Based on the results of Taguchi experimental design, Statistical significance of various factors like filler contents, chewing load, profile speed, chamber temperature on volumetric wear rates of dental composite is determined with the help of Analysis of variance (ANOVA). Table 6.6 indicates the results of the ANOVA with the wear rate of dental composites taken in this investigation. The level of confidence of significance for this analysis is 5%. The last column of the table indicates the level of significance of each factor. From Table 6.6, it is observed that the statistical significance of factor in the descending order follows: filler content (p = 0.006), profile speed (p = 0.012), Chewing load (p = 0.049), chamber temperature (p = 0.273). Hence, filler content and profile speed indicate great influence on volumetric wear rate of the filled composites. However, chewing load and chamber temperature show less significant contribution on volumetric wear rate of the composites. It should be concluded that the profile speed indicated more influence than the chewing load.

Table 6.6. ANOVA analysis for NSDC series composite

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Filler content (wt.%)	3	244.854	244.854	81.618	42.70	0.006
Chewing load (N)	3	54.281	54.281	18.094	9.47	0.049
Profile Speed (%)	3	152.007	152.007	50.669	26.51	0.012
Chamber Temperature (Degree-C)	3	12.330	12.330	4.110	2.15	0.273
Error	3	5.735	5.735	1.912		
Total	15	469.206				

Note: Where DF stands for Degree of freedom, Seq SS stands for Sequential sum of square, Adj SS stands for Adjacent sum of square. Adj MS stands for Adjacent sum of mean square, F stands for Variance, P stands for percentage contribution of each factor in overall performance)

Part IV

6.4 Wear assessment of micro sized gypsum particulate filled dental composite

6.4.1 Steady State conditions for wear characterizations

6.4.1.1 Effect of Chewing Load on volumetric wear rate

Steady state abrasive wear tests are conducted to study the effect of change in wear rate with the change in chewing load. Chewing load is varied in a step of 20 N from minimum value of 40 N to maximum value of 100 N and keeping other parameters such as profile speed: 40%, Profile size 100%, chamber temperature 35°C and food slurry concentration remaining constant. Figure 6.25 shows the effect of change in chewing load with the change in wear rate of dental composites. Wear rate increases with the increased in chewing load for all dental composite filled with different wt. % of gypsum filler particle.

The increased in wear rate with increase in chewing load is attributed to the fact that, increased in chewing load increases the true contact area of asperities with the opposing surface which resulted into increase in wear of dental composite. Figure 6.25 it is also revealed that increased in filler content decreases the wear rate. This may be attributed to the fact that increased in gypsum particulate filler increases the hardness of dental composite and hence it is resulted into decreased in the wear rate.

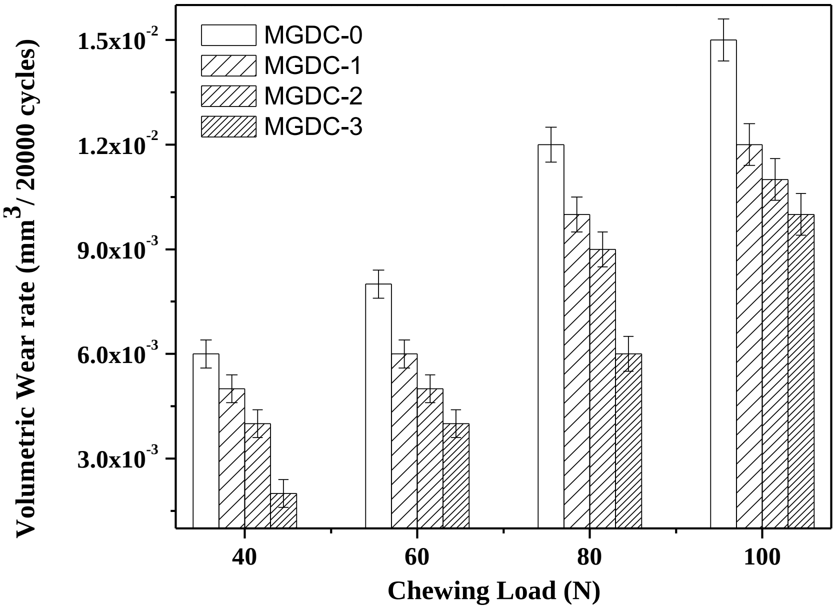


Figure 6.25. Effect of Chewing Load on volumetric wear rate of the dental composites (At constant profile speed 40%, chamber temperature: 35°C)

6.4.1.2 Effect of profile speed on volumetric wear rate

Three body abrasive wear tests are conducted to find the effect of change in wear rate with the change in profile speed of the movement of dental material. Profile speeds are varied in the steps of 20% from a minimum value of 20% to a maximum value of 80% keeping other parameters i.e. chewing load as 40 N, chamber temperature 35°C and food slurry concentration constant. Figure 6.26 represents the effect on wear rate with the change in profile speed. Wear rate decreases with increase in Gypsum content due to increase in hardness (Figure 5.18 in Chapter 5). Figure 6.26 also indicated that wear rate is increased with the increase in profile speed. The wear rate of dental composite filled with different weight percentage of Gypsum filler is slightly increased with an increased in profile speed up to 40%. Beyond 40%, the wear rate of all composite is increased with higher rate. Hence unfilled dental composite exhibits maximum wear rate. At 80% profile speed, wear by delamination is observed to occur in unfilled dental composite. This increase in wear rate of unfilled dental composite finally leads to seizure of the material, which is evident from the micrograph shown in Figure 6.30d.

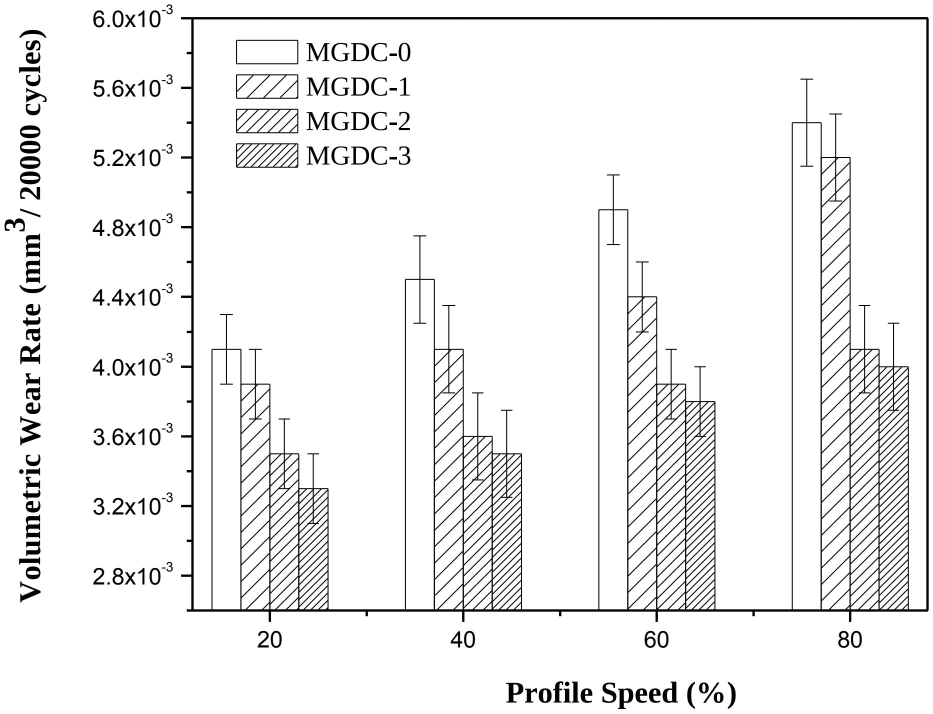


Figure 6.26 Effect of profile speed on volumetric wear rate of the dental composites (At constant Chewing Load 40 N, chamber temperature 35^{o}C)

6.4.1.3 Effect of chamber temperature on volumetric wear rate

Variation in wear rate with temperature of the gypsum particulate filled dental composites is shown in Figure 6.27. It is observed that as the temperature increased, the wear rate of dental composite also increased. However, after reaching a maximum value at 25°C, the wear rate started to decrease. The increase in wear rate with the increase in chamber temperature was due to the fact that as the temperature increased, the molecular mobility inside the polymeric matrix increased resulting into low modulus of the material. Hence, this led to increase in the wear rate. Further increased in temperature lead to decrease in wear rate was due to the fact that after a certain level decrease in modulus and softening of polymeric matrix provide more lubricating effect during wear test. Hence, wear rate was decreased.

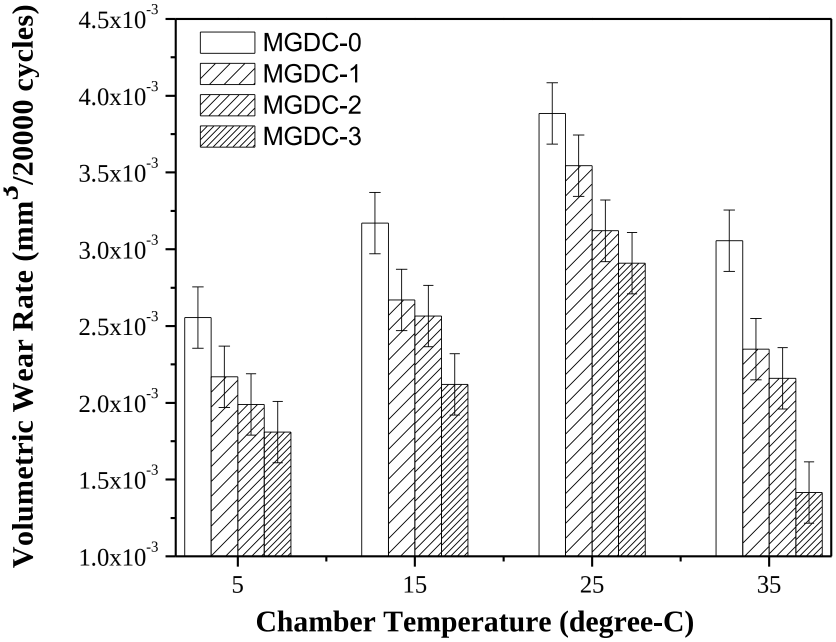


Figure 6.27 Effect of Chamber temperatures on volumetric wear rate of the dental composites (At constant chewing load 40N, profile speed 40%

6.4.2 Wear Analysis of experimental results by Taguchi method

In design of experiment, Taguchi method is applied to improve the performance output by optimizing the process parameters. In Table 6.7, seventh column represents S/N ratio of the volumetric wear rate of the composites. The overall mean for the S/N ratio of the specific wear rate is found to be 47.50 db for the dental composite filled with different wt. % of Gypsum particulates. The analysis is performed using the software MINITAB 16 to analyze the wear rate of the Gypsum particulate filled dental composites.

From this analysis (Figure 6.28) it is observed that the factor combination of A4, B1, C1 and D4 gives minimum volumetric wear rate for dental composite filled with different wt. % of Gypsum. It means the dental composite filled with 3 wt. % Gypsum at chewing load of 40N and with profile speed 20% and at chamber temperature 35 °C exhibited minimum wear rate.

Table 6.7 Taguchi experimental results for gypsum filled dental composite

S.No	Filler content (%)	Chewing load (N)	Profile Speed (%)	Chamber Temperature (degree-C)	Volumetric Wear Rate dental composite filled with silane treated gypsum (mm^3/ 20000 cycles) in food slurry condition	S/N ratio (dB)	Volumetric Wear Rate of silane treated gypsum filled dental composite (mm^3/ 20000 cycles) in Citric acid condition	S/N ratio (dB)
1.	0	40	20	5	0.00342	49.3202	0.003879	48.2260
2.	0	60	40	15	0.005289	45.5328	0.005308	45.5021
3.	0	80	60	25	0.00684	43.2995	0.006422	43.8467
4.	0	100	80	35	0.00839	41.5246	0.007636	42.3427
5.	1	40	40	25	0.002433	52.2779	0.003177	49.9606
6.	1	60	20	35	0.00301	50.4296	0.00369	48.6605
7.	1	80	80	5	0.004866	46.2569	0.004919	46.1625
8.	1	100	60	15	0.004803	46.3696	0.005417	45.3245
9.	2	40	60	35	0.002049	53.7701	0.002888	50.7893
10.	2	60	80	25	0.003073	50.2482	0.00365	48.7530
11.	2	80	20	15	0.003458	49.2229	0.003949	48.0708
12.	2	100	40	5	0.004802	46.3710	0.005036	45.9587
13.	3	40	80	15	0.001773	55.0274	0.002699	51.3772
14.	3	60	60	5	0.002014	53.9191	0.002953	50.5953
15.	3	80	40	35	0.003223	49.8353	0.003688	48.6635
16.	3	100	20	25	0.003142	50.0572	0.003823	48.3518
Mean Volumetric Wear Rate (mm^3/ 20000 cycles)					0.00391143		0.004321	

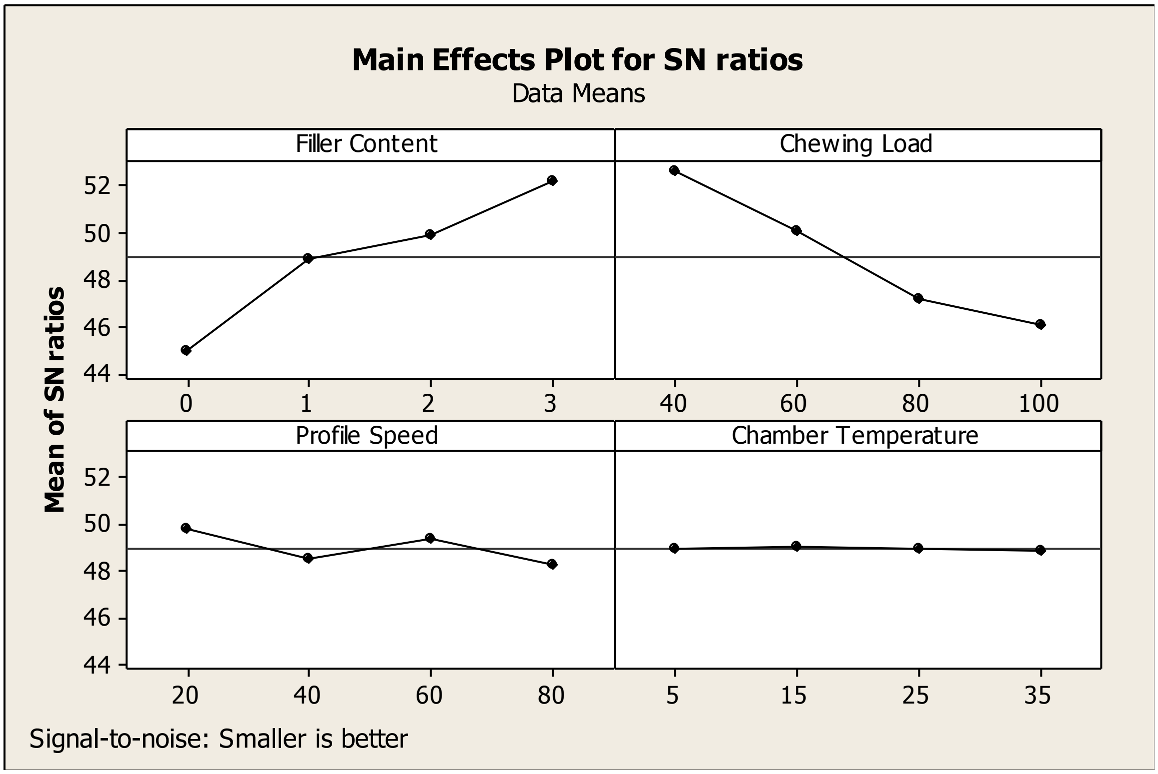


Figure 6.28 Effect of control factors on the wear rate of dental composites

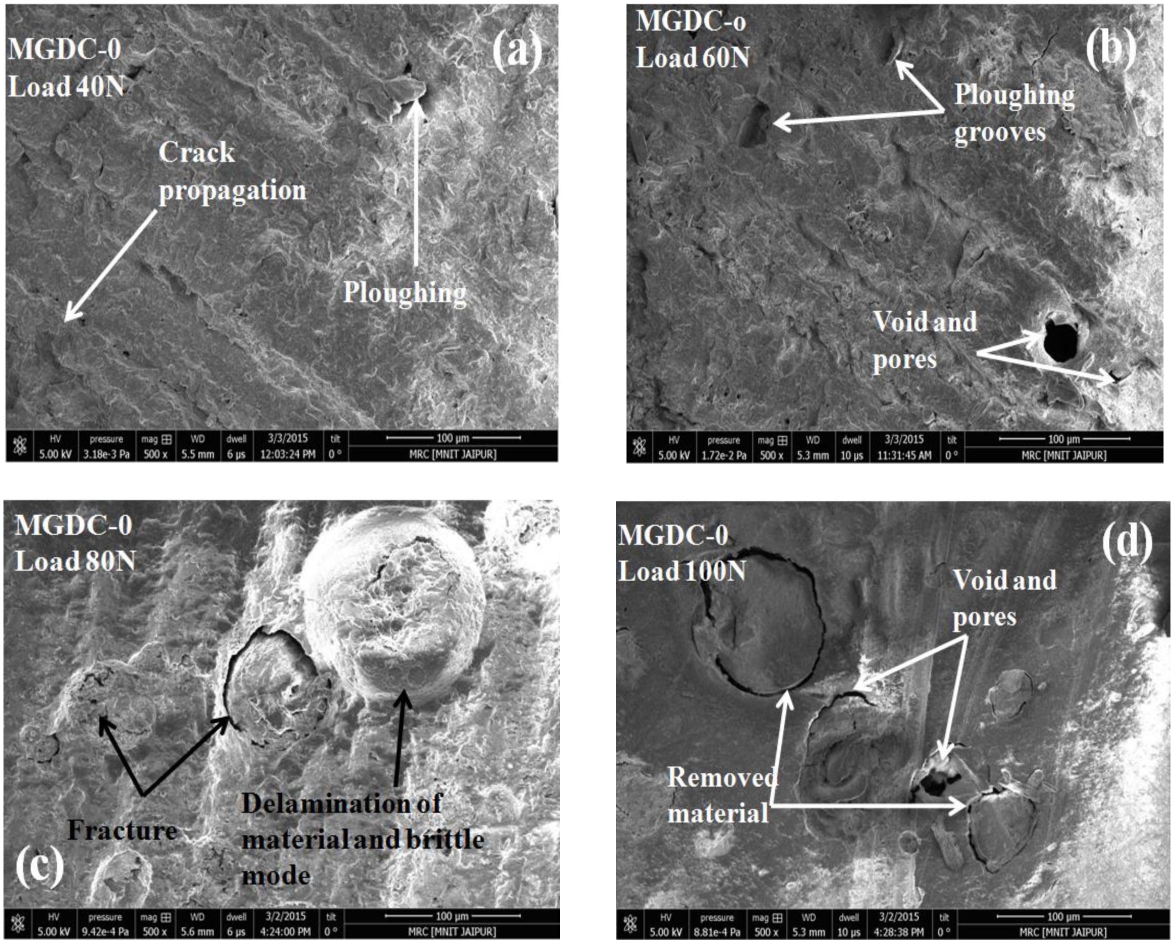
6.4.3 Surface morphology

The worn surface morphology of the Gypsum filled dental composites studied under steady state conditions using FE-SEM is presented in the Figures 6.29-6.31. All the wear analysis is conducted under limited number of cycle's i.e. 20, 000 cycles per test sample.

6.4.3.1Micrograph for varying Chewing Load for unfilled dental composite

Figure 6.29 consisted of seven micrographs to study variation in chewing load and filler content. In Figure 6.29(a-d), the effect of variation of chewing load on volumetric wear rate of unfilled dental composite is studied. Whereas, in Figures 6.29(a),(e),(f),(g), effect of variation of filler content on volumetric wear rate is studied at constant chewing load 40N. Figure 6.29 (a-d) represented the worn surfaces of unfilled dental composite under variable chewing load i.e. 40N, 60N, 80N and 100N respectively at constant profile speed 40% and chamber temperature 35°C.

Figure 6.29a indicated the SEM micrograph of the unfilled dental composites under the chewing loading of 40N, profile speed 40%, and chamber temperature: 35^{o}C respectively. Figure 6.29a showed the presence of cracks, ploughing at chewing load of 40N. When load is increased from 40N to 60N, ploughing became deeper resulting into formation of ploughing grooves as in Figure 6.29b. The depth of void and pores are also increased. Further increase of load from 60N to 80N led to formation of severe damages on the surfaces. Removed materials, void and pores can be seen Figure 6.29c. At 100N of chewing load, 40% of profile speed, and 35^{o}C of chamber temperature, delamination of material can occur (Figure 6.29d).



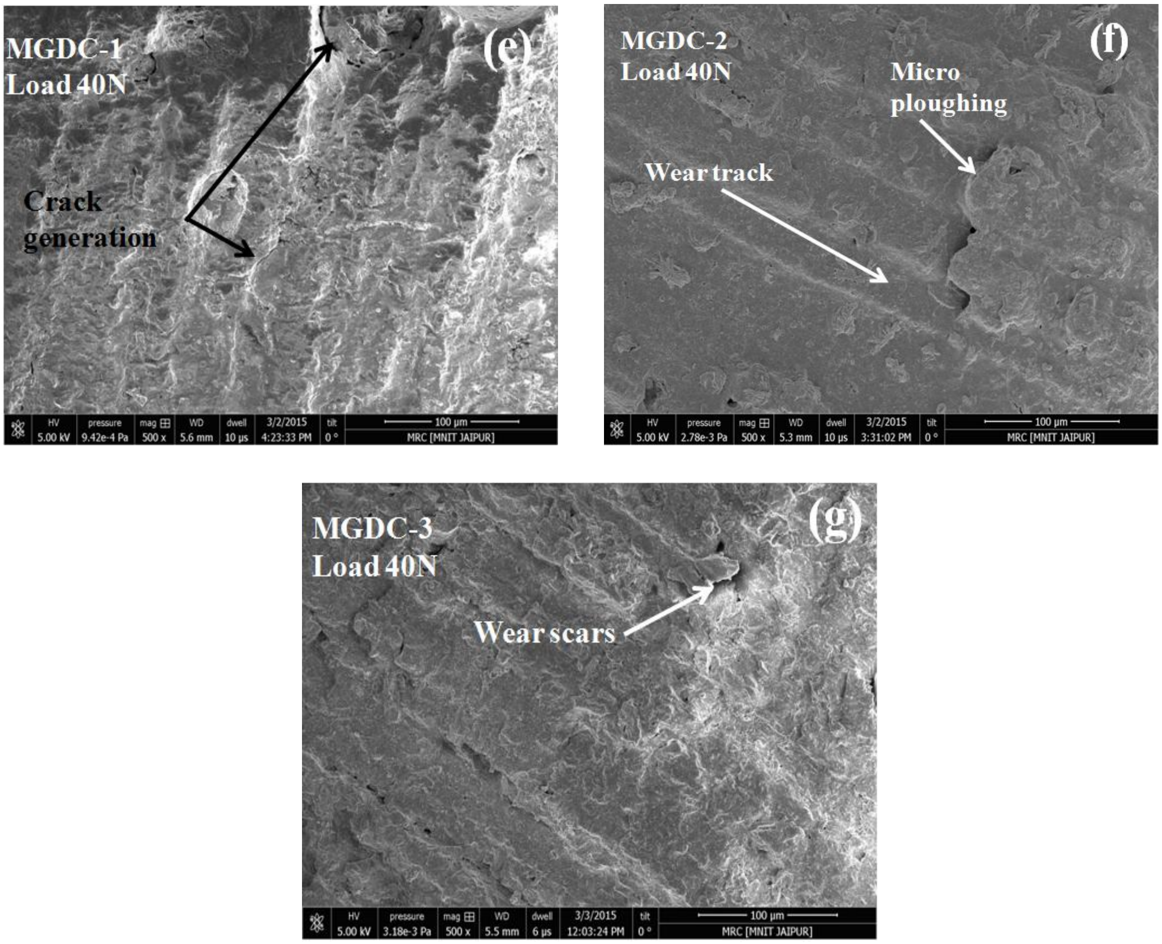


Figure 6.29. FE-SEM images of worn surfaces of composite NADC under the profile speed 40% and temp 35 °C and varying filler content and chewing load a) 0 wt.% at 40N, b) 0 wt.% at 60N, c) 0 wt.% at 80N, d) 0 wt.% at 100N, e) 1 wt.% , 40N f) 2 wt.% , 40N g) 3 wt.% , 40N

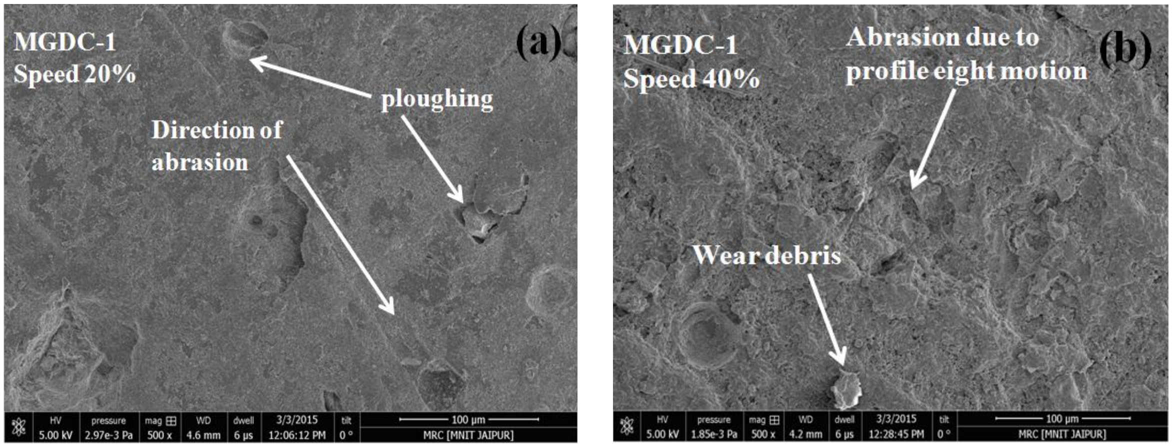
6.4.3.2 Micrograph for different weight percentage of Gypsum at constant chewing load, speed and temperature

Figure 6.29a, Figure 6.29e, Figure 6.29f and Figure 6.29g showed worn surfaces of different dental composite MGDC-0, MGDC-1, MGDC-2 and MGDC-3 respectively after 20000 cycles of experimental run under same condition (chewing load 40N, profile speed 40%, chamber temperature 35°C). Figure 6.29e showed the formation of cracks. In Figure 6.29f, micro ploughing and wear tracks are seen. Minimum wear can be observed in the case of Figure 6.29g however, wear scars are also present.

6.4.3.3 Micrograph for varying profile speed

Figure 6.30 showed worn surfaces morphology of the composite filled with 1 wt. % Gypsum (MGDC-1) under the variable profile speed of 20%, 40%, 60% and 80% at constant chewing load of 40N and chamber temperature 35°C. Figure 6.30a shows the micro graph of 1 wt. % gypsum filled dental composite studied under constant chewing load 40N, profile speed of 20% and chamber temperature 35°C respectively. The upper surface is shown initially rubbing of the resin matrix layer and then subsequently formation of micro-plowing along the direction of abrasion as shown in Figure 6.30a. However, with the increase in profile speed from 20% to 40% by keeping other two factors remaining constant the wear rate is found to be higher as shown in Figure 6.30b. Here the micrograph also indicated presence of wear debris and abraded surface due to abrasion due to profile eight motions, with the increased in speed from 40 to 60% led to interlayer debonding due to fracture Figure 6.30c.

Similarly, with the further increase in profile speed to 80% the matrix material is completely deformed with higher wear rate as observed in Figure 6.30d and Figure 6.26 (steady-state condition graph). Figure 6.30d indicated severe damage due to high profile speed which led to micro ploughing due to high shear thrust force. Therefore, it is clear from the steady-state graph and their respective micro-graphs the profile speed is played major role to increase the wear rate on the particulate filled dental composites.



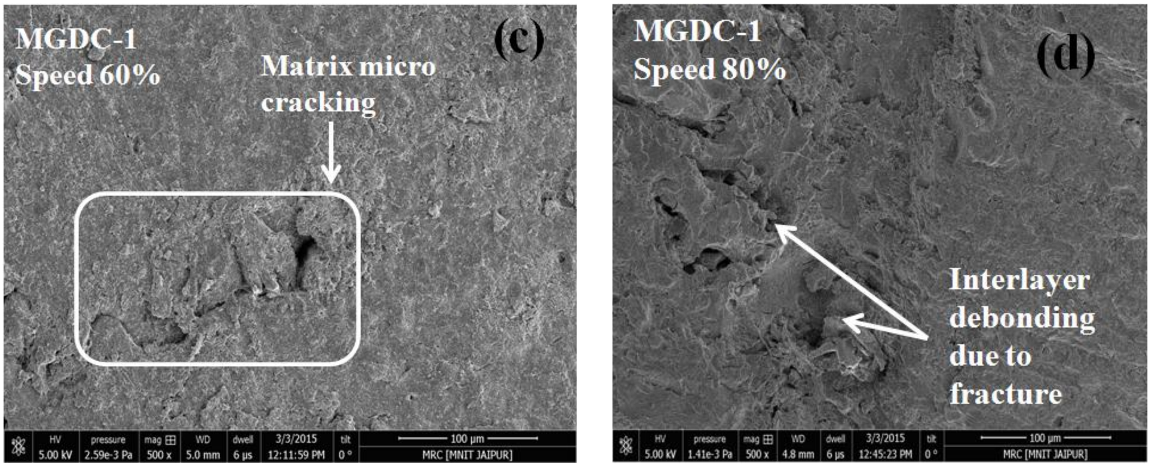
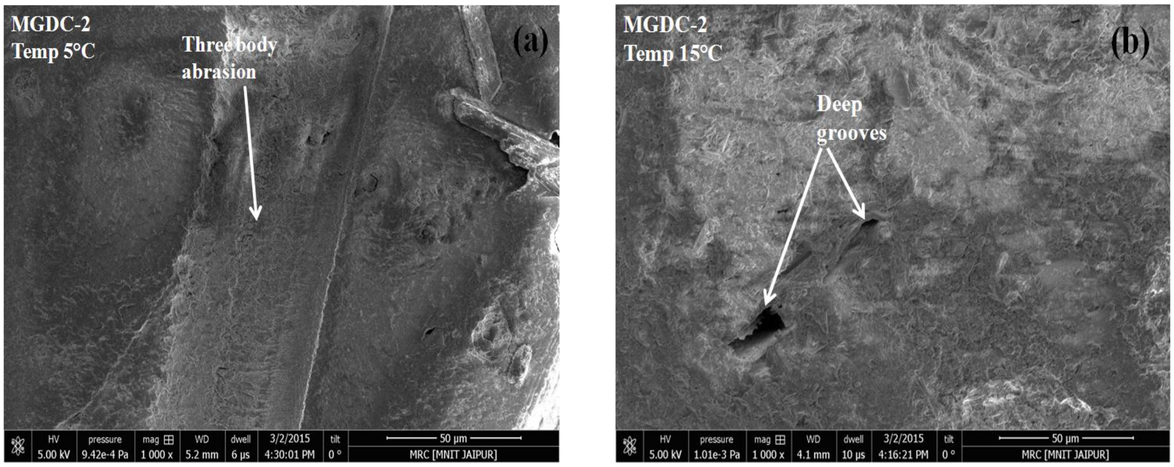


Figure 6.30 FE-SEM images of worn surfaces of composite filled with 1 wt. % gypsum under the chewing load 40N, temp 35^0C and the varying profile speed a) 20%, b) 40%, c) 60%, d) 80%

6.4.3.4 Micrograph for varying chamber temperature

Figure 6.31 showed the worn surfaces of dental composite filled with 2 wt. % Gypsum (MGDC-2) under varying chamber temperature from 5°C to 35°C in a step of 10°C at constant loading of 40N and profile speed of 40%. MGDC-2 has shown less wear than unfilled and 1 wt. % filled dental composite. Figure 6.31a indicated less wear at low temperature. However, three body abrasion directions are visible. Figure 6.31b shows that as the temperature increases from 5°C to 15°C, wear increases. Crack, void and hole are seen. Deep grooves are also visible. Further increased in temperature from 15°C to 25°C, wear attained a maximum level. Interlayer debonding occurred due to fracture Figure 6.31c. Again increase in temperature, wear rate decreased. However, void, Crack and ploughing are also seen in Figure 6.31d.



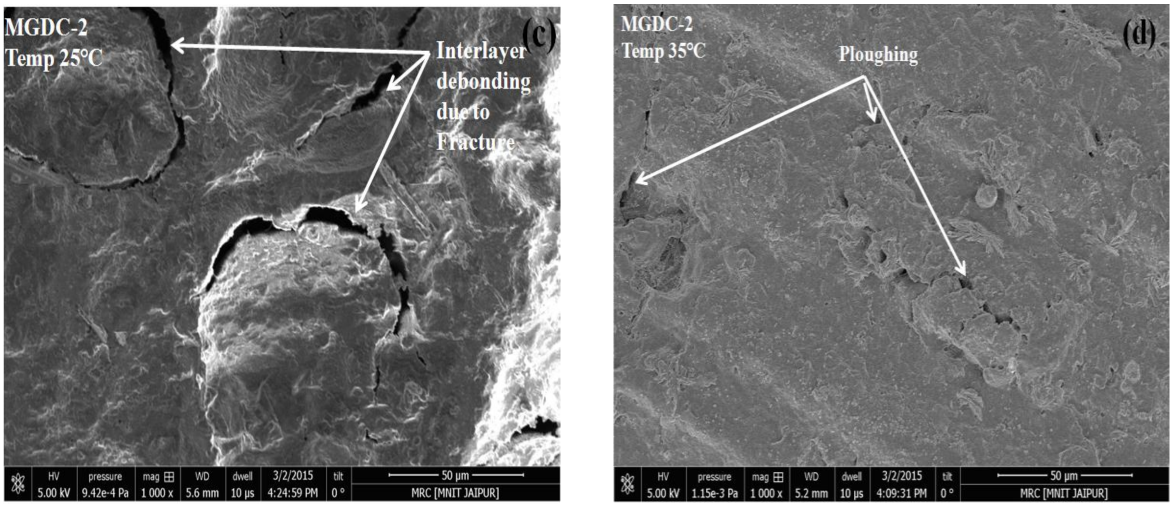


Figure 6.31 FE-SEM images of worn surfaces of composite filled with 2 wt. % gypsum under, chewing load 40N, profile speed 40% and varying chamber temperature a) 5°C, b) 15°C, c) 25°C and d) 35°C

6.4.3.5 Micrograph from Taguchi analysis

Figure 6.32 showed worn surfaces of composites filled with 3 wt. % micron sized gypsum (MGDC-3) for four different experimental conditions in Taguchi experimental design during the experiment no 13,14,15,16 in Table 6.7. It can be revealed that in MGDC-3, least wear is visible. Wear track can be seen but its intensity is least among other filled and unfilled composite. However some holes and voids are visible. Figure 6.32a showed micrograph for the worn sample under high profile speed of 80%, chewing load 40N and chamber temperature of 15°C. Due to high speed, cracks and several damages are visible. The direction of profile eight motions can be also seen. Figure 6.32b showed micrograph for the worn sample under high profile speed of 60%, chewing load 60N and chamber temperature of 5°C. High load and high speed both worked simultaneously. Wear debris are present on the worn surface. Voids and cracks are also seen. Figure 6.32(c) showed micrograph for the worn sample under high profile speed of 40%, chewing load 80N and chamber temperature of 35°C. Wear is less than the other condition as none of the two major influencing factors such as profile speed and chewing load is maximum. Figure 6.32 (e) indicated that the gypsum filler particle is exposed on the worn surface. In Figure 6.32 (b), large load and high speed is applied to the sample resulted into severe damages, removed material, voids and pores etc.

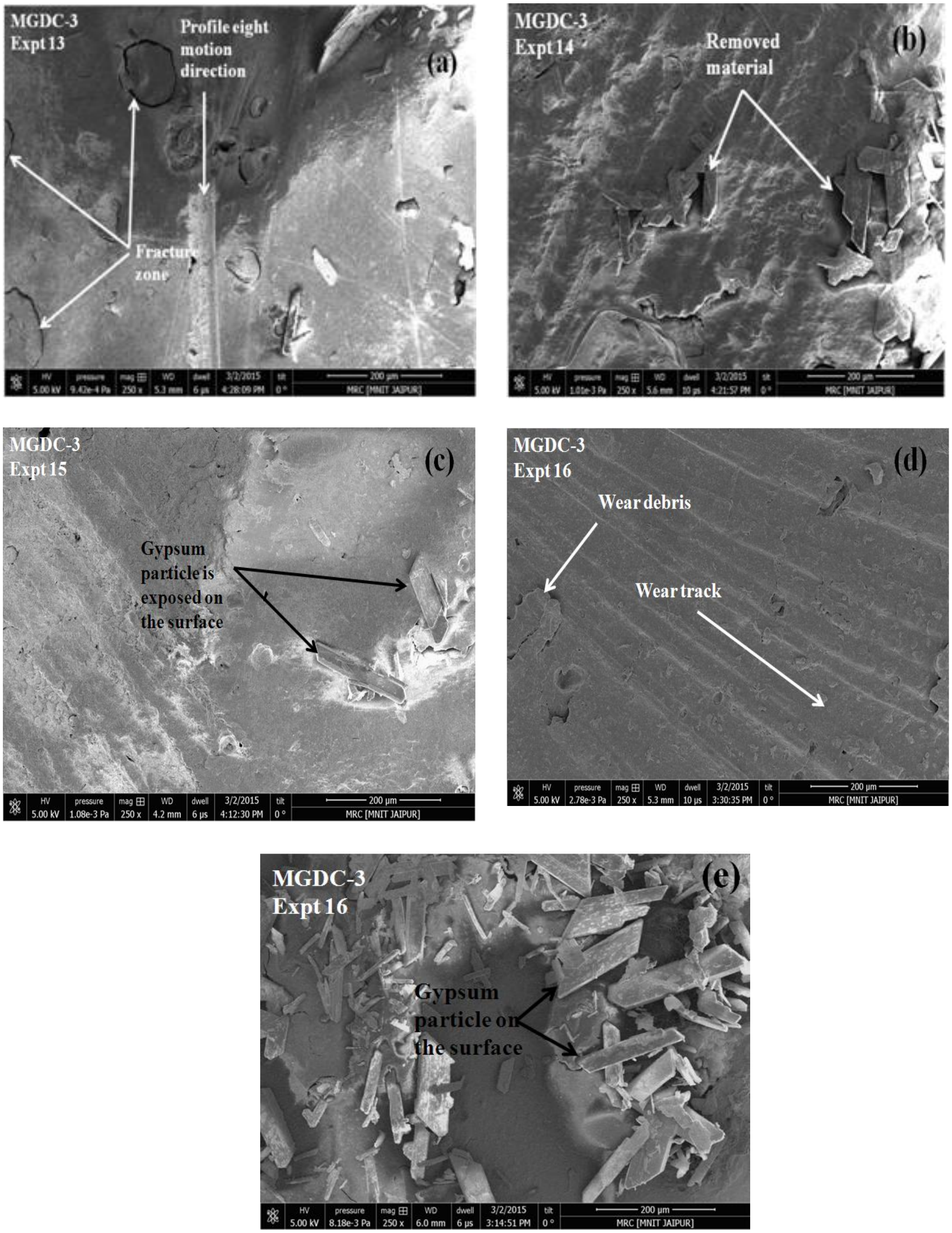


Figure 6.32 FE-SEM images of worn surfaces of composite filled with 3 wt. % gypsum under different working condition as in Table 3: a) experiment no 13, chewing load 40 N, profile speed 80, Chamber temp 15°C, b) experiment no 14, chewing load 60N, profile speed 60% , Chamber temp 5°C, c) experiment no 15 chewing load 80 N, profile speed 40,the chamber temperature 35°C, d) experiment no 16 chewing load 100 N, profile speed 20%, temperature 25°C, e) experiment no 16 at higher magnification (10000x).

Figure 6.32d showed micrograph for the worn sample under high profile speed of 20%, chewing load 100N and chamber temperature of 25°C. Both the high chewing load and chamber temperature at 25°C worked simultaneously to increase the wear rate Wear debris are present on the worn surface. Voids and cracks are also seen. The scanning electron microscope image (10000X) of Figure 6.32c is shown in Figure 6.32e. The presence of micron sized gypsum filler particle can be seen in Figure 6.32e.

6.4.4 ANOVA Analysis

Based on the results of Taguchi experimental design, Statistical significance of various factors like filler contents, chewing load, profile speed, chamber temperature on volumetric wear rates of dental composite is determined with the help of Analysis of variance (ANOVA). Tables 6.8 indicated the results of the ANOVA with the wear rate of dental composites taken in this investigation. The level of confidence of significance for this analysis is 5%. The last column of the table indicated the level of significance of each factor. From Table 6.8, it is observed that the statistical significance of factor in the descending order follows: Chewing load (p = 0.000), filler content (p = 0.000), profile speed (p = 0.031), chamber temperature (p = 0.955). Hence, chewing load and filler content indicated great influence on volumetric wear rate of the filled composites. However, profile speed and chamber temperature indicated shows less significant contribution on volumetric wear rate of the composites.

Table 6.8. ANOVA analysis for gypsum filled dental composite

Source	DF	Seq SS	Adj SS	Adj MS	F	P
Filler content (wt.%)	3	111.174	111.174	37.058	249.84	0.000
Chewing load (N)	3	103.779	103.779	34.593	233.22	0.000
Profile Speed (%)	3	5.887	5.887	1.962	13.23	0.031
Chamber Temperature (Degree-C)	3	0.044	0.044	0.015	0.10	0.955
Error	3	0.445	0.445	0.148		
Total	15	221.329				

Note: Where DF stands for Degree of freedom, Seq SS stands for Sequential sum of square, Adj SS stands for Adjacent sum of square. Adj MS stands for Adjacent sum of mean square, F stands for Variance, P stands for percentage contribution of each factor in overall performance)

6.5 Confirmation experiment of proposed composites

In any design of experiment, the confirmation experiment is required to be performed to validate the result obtained by Taguchi design of experiment.. The confirmation experiment is performed by conducting a random experiment under a new set of factor settings $A_2B_2C_3D_1$ to predict the wear rate. The estimated S/N ratio for specific wear rates can be calculated by predictive equation:

$$\eta = \eta_m + \sum_{i=1}^{n}(\bar{\eta}_i - \eta_m) \tag{6.1}$$

where η_m is the mean S/N ratio at optimal level, n is the number of parameters that affect the quality characteristics, $\bar{\eta}_1$ is the mean S/N ratio for each parameter at optimal level.

Hence for this predictive level of $A_2B_2C_3D_1$, equation becomes

$$\eta = \bar{T} + (\overline{A_2} - \bar{T}) + (\overline{B_2} - \bar{T}) + (\overline{C_3} - \bar{T}) + (\overline{D_1} - \bar{T}) \tag{6.2}$$

Where η: Predicted optimum value for dental composites, T = Overall experimental average.

A new combination of factor levels $\overline{A_2}, \overline{B_2}, \overline{C_3}$ *and* $\overline{D_1}$ is used to predict wear rate by using prediction equation (Eq. (6.1)) and the S/N ratio is found to be 47.1796dB. The resulting model indicated to predict wear rate within reasonable accuracy. An error of 4.31% for S/N ratio of wear rate is observed as shown in Table 6.9. However, the error can further be reduced if the number of measurement will be increased.

Table 6.9 Results of the confirmation experiments for wear rate

	Optimum control parameters		Error
	Prediction	Experimental	
Level	$A_2B_2C_3D_1$	$A_2B_2C_3D_1$	%
S/N ratio for wear rate (db)	47.1796	44.9644	4.70

Chapter Summary

This section concluded following observations:

- The nanofillers and microfillers are successfully modified using silane. Resin based dental composites reinforced with different (0, 1, 2, 3) wt. % of silane treated nanofiller and microfiller have been fabricated.

- A mathematical model for the estimation of volumetric wear rate during three-body abrasion has been developed. The developed theoretical model is validated by Taguchi design of experiments.
- The composite with maximum filler content i.e. composite filled with 3wt. % silanized nanozirconia, composite filled with 3 wt. % silanized nanosilica, composite filled with 3 wt. % silanized nanoalumina, composite filled with 3 wt. % silanized gypsum exhibited the maximum hardness and the best wear resistance with the smallest wear volume in the same set of composite. The worn surface of dental composite filled with maximum filler content is smoother and flatter without any voids or very less void, while larger crack propagation and marginal gap are observed for unfilled composite.
- Steady state condition tests are performed to find minimum volumetric wear rate for each factor for particular wt. % of filler content by keeping other parameters as constant. It is indicated that specific wear rate increases with increase in chamber temperature up to 25°C and then further decreases, however volumetric wear rate increases with increasing chewing load and profile speed.
- In Taguchi experimental analysis it has been revealed that the composite filled with 3 wt. % nanozirconia under the chewing load of 40N at profile speed of 20% and chamber temperature of 35°C exhibited minimum volumetric wear rate.
- The result from ANOVA analysis indicated that for all the three series silanized nanoalumina, silanized nanozirconia, silanized gypsum filled dental composite, the chewing load are more significant factor than the profile speed. Whereas in case of silanized nanosilica filled dental composite, profile speed is more significant than chewing load.
- For all series of experimental dental composite, the mean volumetric wear of dental composite in acidic medium (two body wear) is more than the same composite in food slurry (Three body) condition.

The next chapter briefly discussed the ranking of the fabricated friction composites by using Gray Relational Analysis (GRA) approach under a set of conflicting performance defining criteria.

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Chapter 7

Selection of optimal formulation by using Gray Rational optimization technique

Chapter-7

Selection of Optimal Formulation by Using Grey Relational Analysis Technique

The investigations are carried out to find the best formulation by taking both mechanical and wear properties of dental composite materials using Grey Relational Analysis (GRA). Three body abrasive wear tests are performed in a dental wear simulator machine under food slurry condition and citric acid medium. Grey relational analysis method is applied to rank the dental composites by using several performance defining attributes (PDA) including hardness, compressive strength, flexural strength, volumetric wear rate due to variation in normal load, profile speed and chamber temperature respectively.

The mechanical and wear performance of all the dental composites are carried out in similar food slurry and citric acid medium. The hardness, compressive strength, flexural strength, void content, volumetric wear rate due to variation in normal load, temperature and profile speed are measured and considered as PDC.

7.1 Effect of fillers on various PDAs

Table 7.1 indicates the detail values of PDAs while the results of sixteen investigated dental composites are given in Table 7.1 and Table 7.2. From Table 7.2, it is observed that the nano-filler has caused a distinct transition in mechanical properties. The nanofiller and microfiller improved mechanical properties significantly. This increase in mechanical properties is attributed to the presence of hard and brittle phase inorganic oxide nanoalumina, nanosilica, nanozirconia and micro sized gypsum fillers. Hence, higher degree of exfoliation and higher adhesion at the particle-matrix interface leads to higher load transfer [189-191]. Figure 7.1 clearly indicates that hardness increases with increased in filler content throughout the composite that is consistent with the direct correlation between filler content and Vickers hardness number derived by Neves et al. [153]. However, the compressive strength of dental composite has shown opposite trend for the variation of 2-3wt. % silanized nanoalumina filled dental composite. The increased in compressive strength is due to much higher increase in void content in 3wt. % nanoalumina. A similar trend is reported for the compressive strength of dental composite without nanosilica and dental composite with 1wt. % silanized nanosilica.

Table 7.1 Description of the different performance defining attributes.

Performance defining attributes (PDAs)	Feature	Test conditions	Performance implications of different PDAs
PDA-1	Hardness	ASTME 384-11e1	Higher-the-better
PDA-2	Compressive strength	ASTM D695-08	Higher-the-better
PDA-3	Flexural strength	ISO 4049	Higher-the-better
PDA-4	Void content	ASTM D2734	Lower-the-better
PDA-5	Polymerization Shrinkage	ISO 4049	Lower-the-better
PDA-6	Water Sorption	ISO 4049	Lower-the-better
PDA-7	Volumetric Wear rate (40N)	ASTM F732	Lower-the-better
PDA-8	Volumetric Wear rate (100N)	ASTM F732	Lower-the-better
PDA-9	Volumetric Wear rate (20%)	ASTM F732	Lower-the-better
PDA-10	Volumetric Wear rate (80%)	ASTM F732	Lower-the-better
PDA-11	Volumetric Wear rate (5°C)	ASTM F732	Lower-the-better
PDA-12	Volumetric Wear rate (35°C)	ASTM F732	Lower-the-better

For the flexural strength (PDA-3) and void content (PDA-4) of the nano-filled and micro-filled composite, it can be seen that the flexural strength for silanized nanoalumina filled dental composite and silanized nanosilica filled dental composite decrease as filler content increases. The decreased in the flexural properties depend upon the filler loading, and particle sizes of both the fillers are not uniform and hence, not dispersed uniformly throughout the composites. In contrast, reverse trends are also seen with dental composite filled with silanized nanozirconia and micro-sized gypsum. The increased in flexural strength with the increase in filler content is due to the addition of hard and brittle uniform shaped filler. In this study, the flexural strength of dental composite without gypsum micro particle is reached to 55.20MPa, which is within the specified limit of ISO 4049. According to ISO 4049 guidelines, the value of flexural strength should not be less than 50MPa.

The void content of the fabricated dental composites are determined by the normalization of actual density with respect to theoretical density as per ASTM D2734 standard.

Table 7.2 Experimental results of the PDAs.

Composite	PDA-1	PDA-2	PDA-3	PDA-4	PDA-5	PDA-6	PDA-7	PDA-8	PDA-9	PDA-10	PDA-11	PDA-12
NADC-0	15.00	300.00	84.50	0.12	3.95	1.25	0.0090	0.0190	0.0035	0.0051	0.0062	0.0065
NADC-1	17.50	385.00	79.00	0.18	3.22	1.58	0.0070	0.0150	0.0031	0.0045	0.0042	0.0045
NADC-2	20.00	397.00	70.50	0.27	2.51	1.82	0.0050	0.0140	0.0027	0.0035	0.0035	0.0038
NADC-3	25.00	387.00	62.50	0.78	1.75	2.50	0.0020	0.0070	0.0019	0.0025	0.0025	0.0027
NZDC-0	15.10	287.70	75.50	0.49	3.89	1.54	0.0155	0.0310	0.0031	0.0049	0.0052	0.0053
NZDC-1	22.50	309.00	80.60	0.48	2.94	2.23	0.0101	0.0291	0.0023	0.0039	0.0039	0.0041
NZDC-2	28.20	325.00	99.20	0.82	2.77	2.38	0.0096	0.0276	0.0015	0.0037	0.0026	0.0028
NZDC-3	35.60	350.00	112.50	1.15	1.47	2.50	0.0065	0.0250	0.0011	0.0029	0.0019	0.0024
NSDC-0	22.00	320.00	115.00	0.10	3.75	1.43	0.0050	0.0150	0.0038	0.0052	0.0057	0.0059
NSDC-1	24.50	290.00	80.20	0.69	2.38	1.67	0.0030	0.0090	0.0036	0.0047	0.0041	0.0043
NSDC-2	28.50	298.00	72.50	0.87	1.92	2.70	0.0020	0.0080	0.0031	0.0042	0.0030	0.0033
NSDC-3	33.60	310.00	65.50	1.20	1.53	2.86	0.0010	0.0050	0.0029	0.0038	0.0022	0.0026
MGDC-0	12.50	185.15	55.20	0.42	4.25	1.17	0.0060	0.0150	0.0041	0.0054	0.0067	0.0071
MGDC-1	16.20	199.39	65.50	0.59	3.52	1.25	0.0050	0.0120	0.0039	0.0052	0.0044	0.0047
MGDC-2	17.20	295.29	82.20	0.86	2.42	1.26	0.0040	0.0110	0.0035	0.0041	0.0040	0.0043
MGDC-3	22.50	308.59	91.50	1.16	2.02	2.77	0.0020	0.0100	0.0033	0.0040	0.0028	0.0028

The chances of agglomeration of nano-filler and micro-filler at higher concentration lead to their improper distribution in acrylate based matrix, hence void contents of the dental composites are higher as found experimentally.

The polymerization shrinkage (PDA-5) and water sorption (PDA-4) of the nano-filled and micro filled dental composites are also presented in Table 7.2. It can be seen that polymerization shrinkage decreased with the increasing in filler content in the composites. It may be attributed to the fact that increase in filler content decreased the volume of resin matrix resulting in strong coupling with the resin matrix and formation of strong and stable polymer chain with more molecular weight. The strong and stable polymer chain allows low volume shrinkage upon curing. Water sorption increases with the increased in filler content. This increase is attributed to the increase in void content. Water sorption depends upon many factors such as resin chemistry, filler size, composition, morphology, and amount of initiators and the quality of silanization.

Seventh to twelfth columns of Table 7.2 shows the influence of nano-fillers and micro-filler on the volumetric wear rate at different testing conditions viz. 40N (PDA-5) and 100N (PDA-6) of normal load, 20% (PDA-7) and 80% (PDA-8) of profile speed, 5°C (PDA-9) and 35°C (PDA-10) of temperature. As shown in Figures 4-6, the volumetric wear rate of dental composites without silanized filler is quite high and improved significantly when silanized nano-filler and micro fillers are incorporated in the composites. It is well known that wear is an intricate process, which will be affected by load, speed and temperature. The enhanced wear resistance may be attributed to the filler properties, surface-bonding strength and also to the smaller inter-particle spacing in the matrix [7]. The filler characteristics, like particle size, cannot solely influence the wear behavior directly for they act as strengthening phases; however they can also have an indirect influence on mechanical properties for influencing the surface bonding. Thus on one hand, the dental composites mechanical properties are improved by being strengthened using change in filler technology. On the other hand, wear resistance improved due to the enhancement of chemical bonding between fillers and matrix, by treating the surface of the fillers with a coupling agent such as silane.

It should be noted that the mechanical and wear performance of NADC-0, NSDC-0, NZDC-0 and MGDC-0 are the poorest among the same series of composite material. It can be seen that as the volume of silanized filler increased, the mechanical and wear characteristics of dental material increased. Hence, it can be concluded that two important factors that enhanced the mechanical and wear characteristics of dental composite are (i) the silane treatment of fillers and (ii) increase in each of the filler contents. Further, it is revealed that dental composites filled with 3 wt% silanized nanozirconia (NZDC-3) showed lowest polymerization shrinkage, highest hardness, and highest wear resistance under 20% profile speed and temperature conditions. The dental composite having 2wt. % silanized nanoalumina (NADC-2) indicates highest compressive strength. The dental composite having 3wt. % silanized nanosilica (NSDC-3) exhibits, highest wear resistance under the profile speed of 80% and normal load condition. It is clearly observed that no single alternative shows the best performance when all the PDAs are taken into account simultaneously. Hence, it is a difficult task to suggest a value of the alternative for which the dental composite will deliver the highest performance in terms of all the mentioned PDAs.

7.2 Identification of the final rank with respect to various PDAs

To find out the best formulation related to various criteria PDA-1 to PDA-10, an optimization technique GRA approach is applied. Applying Eq. 3.12 to form performance matrix for the analysis and then normalizing in the range between 0-1 by using Eq. 3.13, the normalized performance matrix is reported in Table 7.3.

After normalization, the reference sequence is defined by using Eq. (13) and a difference matrix is constructed by taking the difference between a normalized entity and its reference value as per Eq. 3.15. After difference matrix, values for grey relation coefficient are obtained according to Eq. 3.16 and provided in Table 7.4. Finally, the grey correlation degree (ϖ_i) value for each alternative is determined by using Eq. 3.17 and the results are depicted in Figure 7.1 and presented in Table 7.5.

Table 7.3 The normalized decision matrix and reference sequence.

Composite	PDA-1	PDA-2	PDA-3	PDA-4	PDA-5	PDA-6	PDA-7	PDA-8	PDA-9	PDA-10	PDA-11	PDA-12
NADC-0	0.108	0.542	0.490	0.994	0.108	0.859	0.448	0.462	0.201	0.103	0.107	0.132
NADC-1	0.216	0.943	0.398	0.975	0.371	0.847	0.586	0.615	0.336	0.310	0.519	0.560
NADC-2	0.325	1.000	0.256	0.765	0.626	0.616	0.724	0.654	0.470	0.655	0.663	0.709
NADC-3	0.541	0.953	0.122	0.000	0.899	0.213	0.931	0.923	0.738	1.000	0.868	0.944
NZDC-0	0.113	0.484	0.339	0.876	0.129	0.781	0.000	0.000	0.336	0.172	0.319	0.395
NZDC-1	0.433	0.585	0.425	0.879	0.471	0.373	0.372	0.073	0.591	0.517	0.578	0.643
NZDC-2	0.680	0.660	0.736	0.771	0.532	0.284	0.405	0.131	0.862	0.597	0.858	0.934
NZDC-3	1.000	0.778	0.958	0.667	1.000	0.213	0.621	0.231	1.000	0.855	1.000	1.000
NSDC-0	0.411	0.637	1.000	1.000	0.180	0.846	0.724	0.615	0.117	0.069	0.212	0.263
NSDC-1	0.519	0.495	0.418	0.283	0.673	0.704	0.862	0.846	0.168	0.241	0.547	0.600
NSDC-2	0.693	0.533	0.289	0.095	0.838	0.095	0.931	0.885	0.336	0.414	0.760	0.822
NSDC-3	0.913	0.589	0.172	0.073	0.978	0.000	1.000	1.000	0.403	0.552	0.934	0.972
MGDC-0	0.000	0.000	0.000	0.857	0.000	1.000	0.655	0.615	0.000	0.000	0.000	0.000
MGDC-1	0.160	0.067	0.172	0.508	0.263	0.953	0.724	0.731	0.067	0.069	0.488	0.517
MGDC-2	0.203	0.520	0.452	0.422	0.658	0.947	0.793	0.769	0.201	0.448	0.565	0.597
MGDC-3	0.433	0.583	0.607	0.286	0.802	0.053	0.931	0.808	0.268	0.483	0.802	0.917
Ref. Seq	1	1	1	1	1	1	1	1	1	1	1	1

Table 7.4 Grey relation coefficient.

Composite	PDA-1	PDA-2	PDA-3	PDA-4	PDA-5	PDA-6	PDA-7	PDA-8	PDA-9	PDA-10	PDA-11	PDA-12	G.R.Coeff
NADC-0	0.335	0.495	0.468	0.986	0.334	0.761	0.448	0.454	0.360	0.333	0.334	0.341	0.471
NADC-1	0.333	0.874	0.394	0.939	0.384	0.719	0.486	0.505	0.371	0.362	0.449	0.471	0.524
NADC-2	0.355	1.000	0.355	0.636	0.523	0.517	0.598	0.542	0.436	0.543	0.549	0.585	0.553
NADC-3	0.521	0.914	0.363	0.333	0.832	0.389	0.879	0.867	0.656	1.000	0.792	0.900	0.704
NZDC-0	0.360	0.492	0.431	0.802	0.365	0.695	0.333	0.333	0.429	0.377	0.423	0.453	0.558
NZDC-1	0.450	0.527	0.446	0.793	0.467	0.425	0.425	0.333	0.531	0.490	0.524	0.565	0.500
NZDC-2	0.576	0.561	0.622	0.655	0.482	0.378	0.422	0.333	0.760	0.519	0.754	0.868	0.563
NZDC-3	1.000	0.639	0.904	0.541	1.000	0.333	0.509	0.338	1.000	0.731	1.000	1.000	0.686
NSDC-0	0.442	0.531	1.000	1.000	0.362	0.752	0.628	0.548	0.345	0.333	0.371	0.387	0.458
NSDC-1	0.464	0.452	0.417	0.367	0.560	0.584	0.751	0.730	0.333	0.354	0.479	0.510	0.498
NSDC-2	0.596	0.492	0.389	0.333	0.737	0.333	0.868	0.797	0.405	0.436	0.654	0.717	0.577
NSDC-3	0.852	0.549	0.377	0.350	0.959	0.333	1.000	1.000	0.456	0.527	0.884	0.947	0.750
MGDC-0	0.333	0.333	0.333	0.778	0.333	1.000	0.592	0.565	0.333	0.333	0.333	0.333	0.467
MGDC-1	0.357	0.338	0.366	0.492	0.393	0.910	0.634	0.639	0.338	0.339	0.482	0.497	0.482
MGDC-2	0.334	0.454	0.421	0.409	0.539	0.882	0.659	0.634	0.333	0.420	0.479	0.498	0.505
MGDC-3	0.455	0.531	0.546	0.399	0.705	0.333	0.873	0.711	0.393	0.478	0.706	0.850	0.582

It is observed that the grey correlation degree of the NZDC-3 is maximum (0.750) and hence NZDC-3 demonstrated as the most preferred dental composite material among the series. It can be further observed that grey correlation degree of the NZDC-0 is minimum (0.458) and hence NZDC-0 i.e. dental composite without silanized nanozirconia filler has demonstrated as the least preferred dental composite material. Finally, it can be concluded that the nanozirconia plays the most crucial role among all the fillers in terms of their performance among the proposed dental materials.

Table 7.5 Grey correlation degree and ranking of the dental composites

Composite designation	Grey correlation degree	Ranking
NADC-0	0.471	14
NADC-1	0.524	9
NADC-2	0.553	8
NADC-3	0.704	2
NZDC-0	0.558	16
NZDC-1	0.500	12
NZDC-2	0.563	5
NZDC-3	**0.686**	**1**
NSDC-0	0.458	7
NSDC-1	0.498	11
NSDC-2	0.577	6
NSDC-3	0.750	3
MGDC-0	0.467	15
MGDC-1	0.482	13
MGDC-2	0.505	10
MGDC-3	0.582	4

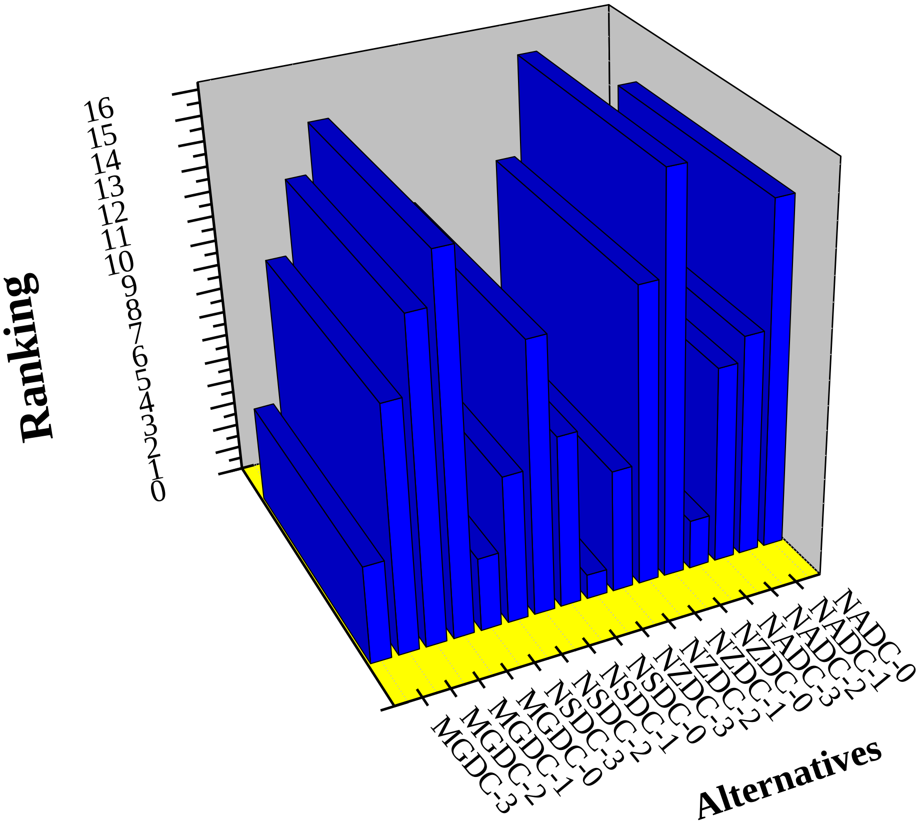

Figure 7.1-Ranking of the alternatives.

By applying GRA approach, the final ranking of dental composites formulations is obtained as NZDC-3(Rank 1) > NADC-3(Rank 2) > NSDC-3(Rank 3) > MGDC-3(Rank 4) > NZDC-2(Rank 5) > NSDC-2(Rank 6) > NSDC-0(Rank 7) > NADC-2 (Rank 8) > NADC-1(Rank 9) > MGDC-2(Rank 10) > NSDC-1(Rank 11)> NZDC-1(Rank 12)> MGDC-1(Rank 13)> NADC-0(Rank 14)> MGDC-0(Rank 15)> NZDC-0(Rank 16). The dental composite filled with 3 wt. % of silanized nanozirconia exhibited optimal physical, mechanical and wear properties.

Chapter summary

This chapter has provided:

- The optimum formulations of dental composite have been evaluated for the best combination of physical, mechanical and tribological properties. Based on these properties, twelve different criteria have been selected and various experiments have been performed.

- Among all, NZDC-3 (dental composite filled 3 wt. % silane treated nanozirconia) exhibited maximum hardness and maximum flexural strength and NADC-2 (dental composite filled 2 wt. % silane treated nanoalumina) exhibited maximum compressive strength and minimum void content among all the remaining dental composites.
- The dental composite i.e. NSDC-3 (3 wt. % nanosilica filled dental composite) shown minimum wear rate in both the loading conditions (i.e. at 40N and 100N) as well as profile speeds (20% and 80%).
- For variation in temperature, NZDC-3 (dental composite filled with 3 wt. % nanozirconia) indicates maximum wear resistance.
- By applying GRA approach, the final ranking of dental composite formulations is obtained as NZDC-3(Rank 1) > NADC-3(Rank 2) > NSDC-3(Rank 3) > MGDC-3(Rank 4) > NZDC-2(Rank 5) > NSDC-2(Rank 6) > NSDC-0(Rank 7) > NADC-2 (Rank 8) > NADC-1(Rank 9) > MGDC-2(Rank 10) > NSDC-1(Rank 11)> NZDC-1(Rank 12)> MGDC-1(Rank 13)> NADC-0(Rank 14)> MGDC-0(Rank 15)> NZDC-0(Rank 16).
- Finally, it can be concluded that the dental composite filled with 3 wt. % nanozirconia exhibits optimal properties for the physical, mechanical and wear characterization.
- GRA approach provides a strong tool to identify optimal performance of any unfilled and particulate filled dental composites to the researchers as well as dental manufactures for dental restoration applications.

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Chapter 8

Summary, Conclusions and Scope for Future Work

Chapter-8

Summary, Conclusions, and Scope for Future Work

This chapter contains the summary of the work done along with objectives, material formulations, analysis of results and conclusions based on the research work are presented in this thesis systematically followed by the scope for future work in this field.

8.1 Background to the research work

The work in this thesis is initiated with a goal to find the influence of reinforcement of silane treated/ untreated nano and micro sized filler (nanoalumina, nanosilica, nanozirconia and micro sized gypsum filler) on the performance properties of dental materials. It would lead to structure the guidelines to select the appropriate formulation to achieve the best combination of performance attributes in dental materials. Following four types of composites are developed:

Type-1: Dental composite filled with silane treated nanoalumina filler (NADC series)

Type-2: Dental composite filled with silane treated nanozirconia filler (NZDC series)

Type-3: Dental composite filled with silane treated nanosilica filler (NSDC series)

Type-4: Dental composite filled with silane treated micro-sized gypsum filler (MGDC series)

The selected four type dental composite are developed under identical processing conditions and are studied for following properties:

- Physical and chemical properties (Chapter-4)
- Mechanical and thermo-mechanical properties (Chapter-5)
- Wear properties (Chapter-6)
- Performance optimization using GRA (Chapter-7)

8.2 Summary of the research findings

The summary based on the studies conducted in this research work are presented chapter wise.

8.2.1 Summary of research finding of physical, chemical, mechanical and Thermo-mechanical characteristics of the dental composites

The studies on the evaluation of physical, chemical, mechanical and thermo-mechanical properties on the developed composites have been summarized as:

- The void content of dental composites filled with different weight percentage of silane treated nanoalumina, nanozirconia, nanosilica and micro-gypsum particles are in the range of 0.12- 0.78%, 0.42- 1.15 %, 0.11-1.20 % and 0.42- 1.16 % respectively. The void content for the dental composite with 3 wt.% of nanoalumina filled composite is much higher (around 189%) than 2wt.% nanoalumina filled dental composites. Hence, void contents remain in the range of 0.10-1.20% and found to be increased with the increasing in nanofiller and micro-filler contents.
- The incorporation of nanoalumina, nanozirconia, nanosilica and micro–sized gypsum into the dental composites lead to an enhancement in hardness. The hardness of dental composites filled with different weight percentage of silane treated nanoalumina, silane treated nanozirconia filler, silane treated silica nanofiller and silane treated gypsum micro particle are in the range of 15-25Hv, 15.10-35.6Hv, 22-33.60Hv and 12.5-22.5Hv respectively. The maximum value of hardness of dental composite (35.6Hv) is indicated by dental composite filled with 3wt. % silane treated nanozirconia filler.
- The flexural strength of dental composites filled with different weight percentage (0, 1, 2 and 3wt. %) of silane treated nanoalumina, silane treated nanozirconia filler, silane treated nanosilica and silane treated micro-gypsum particles are in the range of 62.5-84.5MPa, 75.5-112.5 MPa, 65.5-115 MPa and 55.2-91.5 MPa respectively. The flexural strength of the dental composites remains in the range of 55.20-115 MPa and found to be maximum for dental composites without nanosilica reinforcement (NSDC-0).
- The compressive strength of dental composites filled with different weight percentage of silane treated nanoalumina, nanozirconia filler, nanosilica and gypsum micro particle are in the range of 300-397MPa, 287.7-350MPa, 290-320MPa and 185.15-308.59MPa respectively. The compressive strength of the dental composites remains in the order of 185.15-397 MPa and found to be maximum for 2wt.% nanoalumina filled dental composite (NADC-2).
- The polymerization shrinkage of dental composites filled with different weight percentage of silane treated nanoalumina, nanozirconia, nanosilica and gypsum

micro particle are in the range of 1.75-3.95%, 1.47-3.89%,1.53-3.75% and 2.02-4.25% respectively. The minimum value of polymerization shrinkage of dental composite (1.47%) is observed by dental composite filled with 3wt. % silane treated nanozirconia filler. The overall polymerization shrinkage of the dental composites remains in the order of 1.47-4.25%.

- The water sorption of dental composites filled with different weight percentage of silane treated nanoalumina, nanozirconia, silica nanofiller and gypsum micro particle are in the range of 1.25-2.5 µg/mm^3, 1.43-2.86 µg/mm^3, 1.54-2.5 µg/mm^3 and 1.17-2.77 µg/mm^3 respectively. The maximum value of water sorption of dental composite (2.77 µg/mm^3) is indicated by dental composite filled with 3 wt. % silane treated micro-sized gypsum filler. The compressive strength of the dental composites remains in the order of 1.17-2.77 µg/mm^3.
- The decomposition of the dental composites is due to decomposition of organic constituents observed in simultaneous thermal analysis and thermo-gravimetric analysis respectively. The decomposition temperature les in the range of 260-350°C
- The glass transition temperature of nano particulate dental composites is increased with the increasing in nano filler content in the matrix material. Similarly, the thermal stability and degradation temperature are also improved with the increased in nano filler content. The results of glass transition temperature of dental composite using Thermo-gravimetric analysis are in agreement with the results using Dynamic mechanical analysis.
- Storage modulus (E') is in the range of 90-254 MPa at lower temperature (30°C) and remains higher for 1wt.% nanosilica filled dental composite (i.e. NSDC-1). However, at higher temperature (i.e 225°C) the storage modulus lies in the range of 40-60 MPa.

8.2.2 Summary of research findings of wear characteristics of the dental composites

This section provides the detailed material formulations as far as particulate filled dental composites for wear analysis in different oral environment. These studies are targeted to evaluate the potential of a material under food slurry and citric acid condition. These experiments are performed initially under steady state condition in order to obtain factor settings and then Taguchi orthogonal array design is implemented to get optimal correlation between the control factors and the performance output. Finally, Analysis of variance (ANOVA) has been applied to find the significance of factors in the wear analysis of dental composite.

8.2.2.1 Summary of research findings of dental composite filled with silane treated nanoalumina filler

The research findings of NADC-series dental composites are summarized as:

- Steady state condition tests indicate that the wear rate increases with increased in chamber temperature up to 25°C and then further decreases. However, volumetric wear rate increases with the increased in chewing load and profile speed.
- The result from ANOVA analysis indicated that profile speed, chewing load and filler content are most significant whereas the chamber temperature is the least significant factor affecting wear rate of dental material. It is also concluded that the chewing load is more significant than profile speed.
- The total mean wear rate in food slurry by silane treated nanoalumina filled dental composite is less that the total mean wear rate by the same composite in citric acid.

Thus, dental composite filled with 3 wt.-% silane treated nanoalumina at chewing load of 40N and with profile speed 20% and at chamber temperature 15°C exhibits minimum wear rate.

8.2.2.2 Summary of research findings of dental composite filled with silane treated nanozirconia filler

The research findings of NZDC-series dental composites are summarized as:

- Steady state condition tests indicate that the wear rate increases with the increased in chamber temperature up to 25 °C and then further decreases. However, volumetric wear rate increases with increased in chewing load and profile speed.
- The result from ANOVA analysis indicates that in case of silane treated nanozirconia filled dental composite, the filler content and chewing load are the most significant factors. Whereas, profile speed and chamber temperature are the least significant factors.

- The total mean wear rate in food slurry by each of silane treated nanozirconia filled dental composite is less that the total mean wear rate by the same composite in citric acid.
- In each of the medium food slurry and citric acid, the mean wear rate of silane treated nanozirconia filled dental composite was the least among all experimental composites. Hence, nanozirconia based dental composite can be preferred over other dental composites for dental application.

8.2.2.3 Summary of research findings of dental composite filled with silane treated nanosilica filler

The research findings of NSDC-series dental composites are summarized as:

- Steady state condition tests indicate that the wear rate increases with the increased in chamber temperature up to 25 °C and then further decreases. However, the volumetric wear rate increases with the increased in chewing load and profile speed.
- The result from ANOVA analysis indicates that in the case of silane treated nanosilica filled dental composite, the profile speed is more significant than chewing load which is the reverse trend as compared with other silane treated filled and unfilled composites.
- The total mean wear rate in food slurry by each of silane treated nanosilica and silane treated nanoalumina filled dental composite is less that the total mean wear rate by the same composite in citric acid.
- In each of the food slurry and citric acid medium, the mean wear rate of silane treated nanosilica filled dental composite is less than that of silane treated nanoalumina filled dental composite.

Thus, dental composite filled with 3 wt.-% silane treated nanosilica at chewing load of 60N and with profile speed 20% and at chamber temperature 15°C exhibits minimum wear rate.

8.2.2.4 Summary of research findings of dental composite filled with silane treated micro sized gypsum filler

The research findings of MGDC-series dental composites are summarized as:

- Steady state condition tests indicate that the wear rate increases with increased in chamber temperature up to 25 °C and then further decreases. However, volumetric wear rate increases with increasing in chewing load and profile speed.
- The result from ANOVA analysis indicate that in case of silane treated micron size gypsum filled dental composite, chewing load and filler content are the most significant factor. Whereas, profile speed and chamber temperature are the least significant factor.
- The total mean wear rate in food slurry by each of silane treated micron size gypsum filled dental composite is less that the total mean wear rate by the same composite in citric acid.

8.2.3 Summary of findings of GRA method

The selection of dental materials is a multiple criteria decision making problem. In this thesis, an optimization technique Gray Relational Analysis (GRA) approach was applied to find out the best formulation related to various characterizations. The overall performances order based on GRA method are

- The criteria PDA-1 to PDA-10 include hardness, compressive strength, flexural strength, void content, polymerization shrinkage, water sorption, different volumetric wear rate against the variation of load, speed and temperature.
- Based on final optimization by Gray Rational Optimization approach, rankings of dental composites are:
  In NADC series dental composites: NADC-3>NADC-2>NNDC-1>NADC-0.
  In NZDC series dental composites: NZDC-3>NZDC-2>NZDC-1>NZDC-0.
  In NSDC series dental composites: NSDC-3>NSDC-2>NSDC-0>NSDC-0.
  In MGDC series dental composites: MGDC-3>MGDC-2>MGDC-1>MGDC-0.
  Overall the ranking order was: NZDC-3(Rank 1) > NADC-3(Rank 2) > NSDC-3(Rank 3) > MGDC-3(Rank 4) > NZDC-2(Rank 5) > NSDC-2(Rank 6) > NSDC-0(Rank 7) > NADC-2 (Rank 8) > NADC-1(Rank 9) > MGDC-2(Rank 10) > NSDC-1(Rank 11)> NZDC-1(Rank 12)> MGDC-1(Rank 13)> NADC-0(Rank 14)> MGDC-0(Rank 15)> NZDC-0(Rank 16).

Thus, it is concluded that the dental composite filled with 3 wt.-% silane treated nanozirconia indicated the optimal performance among all other experimental dental composites considered in this study.

8.3 Conclusions of the research work

Following salient conclusions are drawn based on the studies on the evaluation of physical, chemical, mechanical, thermo-mechanical and wear behavior of these experimental dental composites.

1. The physical, chemical and mechanical properties have been found to be well within the ISO 4049 standard.
2. The nanofillers (nanoalumina, nanosilica, and nanozirconia) and micro-filler (gypsum) are successfully treated with silane c-MPS. The treated and untreated filler are subsequently characterized by using FTIR spectroscopy and Transmission Electron Microscope.
3. Resin based dental composites reinforced with different wt. % of silane treated nanofillers (nanoalumina, nanosilica, and nanozirconia) and micro-sized gypsum fillers have been fabricated.
4. The inclusion of nanofillers and micro-filler contents lead to increase in the density and void content of the dental composites.
5. The inclusion of nanofillers and micro-filler contents lead to increase in the depth of cure and decrease in polymerization shrinkage of dental composite.
6. The magnitude of mechanical properties indicates appreciably high in all dental composites which may be attributed to the presence of hard and brittle phase inorganic oxide nanoalumina, nanosilica, nanozirconia and micro sized gypsum filler because of higher degree of exfoliation and higher adhesion at the particle-matrix interface leads to higher load transfer
7. The flexural strength for silane treated nanoalumina filled dental composite and silane treated nanosilica filled dental composite silica are decreased as filler content increased. In contrast, reverse trends are seen with dental composite filled with silane treated nanozirconia and micro-sized gypsum.
8. The glass transition temperature is increased with increase in nano filler content and micro filler content in the composites. Addition of fillers also leads to

improvement in thermal stability and degradation temperature dental composite materials.

9. The volumetric wear rate of dental composite without silane treated filler is quite high and decreases significantly when silane treated nano-filler and micro fillers were incorporated in the composites.
10. The mean volumetric wear rate of experimental dental composite in citric acid is more than in food slurry medium.
11. The silanized nanozirconia filled dental composited indicates the least wear rate in both the acidic and food slurry medium. Hence, it may be used for dental application.
12. The ranking of dental composites is: NZDC-3(Rank 1) > NADC-3(Rank 2) > NSDC-3(Rank 3) > MGDC-3(Rank 4) > NZDC-2(Rank 5) > NSDC-2(Rank 6) > NSDC-0(Rank 7) > NADC-2 (Rank 8) > NADC-1(Rank 9) > MGDC-2(Rank 10) > NSDC-1(Rank 11)> NZDC-1(Rank 12)> MGDC-1(Rank 13)> NADC-0(Rank 14)> MGDC-0(Rank 15)> NZDC-0(Rank 16). (Dental composite filled with 3 wt.-% nanozirconia) shows the optimal performance among all other experimental dental composites considered in this study.

8.4 Scope for future work

Because of time limit, the research work accomplished in this project is still in initial stage. Following aspects could not be addressed in this thesis work and hence should be taken up in the future work.

1. The studies are mainly focused on wear performance of nano particulate filled dental composites. However, few more parameters can be introduced in future scope such as effect of change in pH of the lubricating medium, position of teeth for which it is used, size/ shape of abrasive particle in the food slurry.
2. The applying loads in the dental application are varied from 30 to 120N. But in this research, the applied chewing load has varied from 40-100N, therefore future study can focus on wear due to excess loading on dental material.
3. The friction and wear study of dental material in the different working condition such as cold drink, citric acid, artificial saliva etc will be done as future scope.

4. There is strong need to research on the dental wear for the patient suffering from Xerotima, Thegosis and Bruxism.

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References

References

[1] W. Hoffmann-Axthelm. History of Dentistry, Chicago, Quintessence Publishing, 1981.

[2] C. E. Black, B. M. Black. From Pioneer to Scientist. St. Paul, MN, Bruce Publishing, 1940.

[3] M. L. Logan, "artificial tooth crown." US310294A issued april 6, 1885**.**

[4] W.D. Cook, D. R. Beech, M. J. Tyas. Structure and properties of methacrylate based dental restorative materials. Biomaterials 6(6) (1985)362-368

[5] R. L. Bowen. A method of preparing a monomer having phenoxy and methacrylate groups linked by hydroxyl glycerol groups. US patent no 3179623, 1965.

[6] U. Palotie, M. M. W. Vehkalahti Reasons for replacement and the age of failed restorations in posterior teeth of young Finnish adults. Acta. Odontol. Scand. 60(6)(2002)325-329.

[7] C. Y. K. Lung, Z. Sarfraz, A. Habib, A. S. Khan, J. P. Matinlinna, Effect of silanization of hydroxyapatite fillers on physical and mechanical properties of a bis-GMA based resin composite, J. Mech. Behav. Biomed. 54(2016)283-294.

[8] S. R. Kumar, A. Patnaik, I. K. Bhat,. Novel dental composite material reinforced with silane functionalized micro-sized Gypsum filler particles. Polym Composite DOI: 10.1002/pc.23599 (2015).

[9] K. H. Kim, J. L. Ong, O. Okuno, The effect of filler loading and morphology on the mechanical properties of contemporary composites, J. Prosthet. Dent. 87(2002)642–9.

[10] M. Braem, W. Finger, V. E. V. Doren, P. Lambrechts, G. Vanherle, Mechanical properties and filler fraction of dental composites, Dent. Mater. 5(1989)346-348.

[11] M. Atai, D. C. Watts, A new kinetic model for the photo polymerization shrinkage–strain of Dental composites and resin-monomers, Dent. Mater. 22 (2006)785–791.

[12] S. O. Alsharif, H. B. M. Akil, N. A. A. El-Aziz, Z. A. B Ahmad, Effect of alumina particles loading on the mechanical properties of light-cured dental resin composites, Mater. Design 54 (2014) 430–435.

[13] J. Li, H. Li, A. S. L. Fok, A mathematical analysis of shrinkage stress development in dental composite restorations during resin polymerization, Dent. Mater. 24(2008)953-931.

[14] V. S. Nagarajan, S. Jahanmir, V. P. Thompson, In vitro contact wear of dental composites Dent. Mater. 20 (2004) 63–71.

[15] S. Benazzi, O. Kullmer, I. R. Grosse, G. W. Weber, Using occlusal wear information and finite element analysis to investigate stress distributions in human molars, J. Anat. 219(3) (2011) 259–272.

[16] J. Li, H. Li, A. S. L. Fok, D. C. Watts, Numerical evaluation of bulk material properties of dental composites using two-phase finite element models, Dent. Mater. 28(2012)996–1003.

[17] A.J. Gwinnett, Structure and composition of enamel, Oper. Dent. 5(Suppl), (1992) 10-17.

[18] M. S. Lamkin, F.G. Oppenheim. Structural features of salivary function. Crit. Rev. Oral. Biol. Med. 4(3-4) (1993)251-59.

[19] M. Hannig, The protective nature of the salivary pellicle. Int. Dent. J. 52(2002) 417–423.

[20] S. Hooper, R. G. Newcombe, R. Faller, R. Eversole, M. Addy, N. X. West, The protective effects of toothpaste against erosion by orange juice: studies in situ and in vitro, J. Dent. 35(2007) 476–481.

[21] R. Cheng, H. Yang, M. Shao, T. Hu, X. Zhou, Dental erosion and severe tooth decay related to soft drinks: a case report and literature review, J. Zhejiang. Univ. Sci. B. 10(5)(2009)395-399.

[22] R. Lewis, R S Dwyer-Joyce, Wear of human teeth: a tribological perspective. J. Eng. Tribol 219 (2005)1–18.

[23] D. T. Zero, A. Lussi, Erosion-chemical and biological factors of importance to the dental practitioner. Int. Dent. J. 55(2005)285-290.

[24] T. Piangprach, C. Hengtrakool, B. Kukiattrakoon, U Kedjarune-Leggat, The effect of salivary factors on dental erosion in various age groups and tooth surfaces. J Am Dent Assoc, 140(2009)1137-1143.

[25] T. Jaeggi T, A. Lussi, Prevalence, incidence and distribution of erosion, Monogr Oral Sci 20 (2006)44-65.

[26] E. Bashir, F. Lagerlo, Effect of citric acid clearance on the saturation with respect to hydroxyapatite in saliva. Caries Res 30 (1996)213-217.

[27] V. K. Jarvinen, I. I. Rytomaa, O. P. Heinonen, Risk factors in dental erosion. J. Dent. Res. 70 (1991)942-947.

[28] M. Hannig, M. Fiebiger, M. Güntzer, A. Döbert, R. Zimehl, Y. Nekrashevych, Protective effect of the in situ formed short-term salivary pellicle. Arch. Oral. Biol. 49 (2004)903–910.

[29] A. V. Amerongen, J. G. M. Bolscher, E. C. I. Veerman, Salivary proteins: protective and diagnostic value in cariology? Caries. Res. 38(2004)247–253.

[30] J.R. Holum, Fundamentals of General, Organic and Biological Chemistry, 2nd ed., Wiley (1982).

[31] L. H. Mair, T. A. Stolarski, R. W. Vowles, C. H. Lloyd, Wear: mechanisms, manifestations and measurement. Report of a workshop. J. Dent. 24(1996)141–148.

[32] T. Imfeld, Dental erosion, definition, classification and links. Eur. J. Oral. Sci. 104(1996)151–155.

[33] M. Eisenburger, M. Addy, Erosion and attrition of human enamel in vitro. Part I: interaction effects. J Dent 20 (2002) 341–347.

[34] D. W. Bartlett, L. Blunt, B. G. N. Smith, Measurement of tooth wear in patients with palatal erosion. Br. Dent. J. 182(1997)179–184.

[35] M. E. Barbour, J. S. Rees, The laboratory assessment of enamel erosion: a review. J. Dent. 32(2004) 591–602.

[36] B. T. Amaechi, S. M. Higham, Dental erosion: possible approaches to prevention and control. J. Dent. 33 (2005)243–252.

[37] N. X. West, J. A. Hughes, M. Addy, The effect of pH on the erosion of dentine and enamel by dietary acids in vitro. J. Oral. Rehabil. 28(2001)860–864.

[38] J. O. Grippo, J. V Masi, Role of biodental engineering factors (BEF) in the etiology of root caries. J. Esthet. Restor. Dent. 3(1991)71–76.

[39] D. Palamara, J.E.A. Palamara, M.J. Tyas, M. Pintado, H.H. Messer, Effect of stress on acid dissolution of enamel, Dent. Mater. 17(2001)109–115.

[40] M. Eisenburger, R. P. Shellis, M. Addy, Comparative study of wear of enamel induced by alternating and simultaneous combinations of abrasion and erosion in vitro. Caries. Res. 37(2003)450–455.

[41] J. A. Hughes, N. X. West, D. M. Parker, M. H. van den Braak, M. Addy, Effects of pH and concentration of citric, malic and lactic acids on enamel, in vitro. J. Dent. 28(2000)47–152.

[42] W. P. Holbrook, I. B. Árnadóttir, E. J. Kay, Prevention. Part 3: prevention of tooth wear, Br. Dent. J. 195(2) (2003)75–81.

[43] A. Mulic, A. B. Tveit, D. Songe, H. Sivertsen, A. B. Skaare, Dental erosive wear and salivary flow rate in physically active young adults, BMC Oral Health 12(2012)1-8.

[44] B. Suh, L. Feng, Y. Wang , C. Cripe, F. Cincione , W. de Rjik, The effect of pulse delay curing technique on residual strain in composites, Compend. Cont. Ed. 20(1999)4-12.

[45] A. Peutzfeld. Resin composites in dentistry: the monomer systems. Eur. J. Oral. Sci. 105(1997)97-116.

[46] J. Manhart, K.H. Kunzelmann, H. Chen, Mechanical properties and wear behavior of light-cured packable composite resins, Dent. Mater. 16(2000)33–40.

[47] R. Hickel, W. Dasch, R. Janda, M. Tyas, K. Anusavice. New direct filling materials. Int Dent J. 48(1998)3-16.

[48] E. C. Combe, F. J. T Burke. Contemporary resin-based composite materials for direct placement restorations: packables, flowables, and others. Dent Up. 27(2000)326-336.

[49] H.F. Albers. Tooth-Colored Restoratives. 8th ed. Santa Rosa; (1996)5b-2.

[50] Y. Hosoya, Five-year color changes of light-cured resin composites: influence of light-curing times. *Dent Mat.* 15(1999)353-362.

[51] D. Dietschi, G. Campanile, J. Holz, Comparison of the color stability of ten new-generation composites: An in vitro study. Dent. Mat. 10(1994)353-362.

[52] J. W. Stansbury. Curing dental resins and composites by photopolymerization. J. Esthet. Dent. 12 (2000)300-308.

[53] H. F. Albers. Resin polymerization, ADEPT Report, 6(3)(2000).

[54] J. Ferracane, E. Greener, The effect of resin formulation on the degree of conversion and the mechanical properties of dental restorative resins. J. Biomed. Mater. Res. 20(1986)121-131.

[55] J. Rees, P. Jacobsen, The polymerization shrinkage of resin composites, Dent. Mater. 77(1989)41-44.

[56] A. Puckett, R. Smith, Method to measure the polymerization shrinkage of light-cured composites, J. Prosth. Dent. 68(1992)56-58.

[57] J. Lai, A. Johnson, Measuring polymerization shrinkage of photoactivated restorative materials by a water-filled dilatometer. Dent. Mater. 9 (1993)139-143.

[58] J. Ferracane, Materials in Dentistry: Materials and Applications, 2nd ed. Baltimore, Lippincott, 2001.

[59] S. R. Kumar, A. Patnaik, I. K. Bhat, Analysis of polymerization shrinkage and thermo-mechanical characterizations of resin-based dental composite reinforced with silane modified nanosilica filler particle. Proc. Inst. Mech. Eng. L. J. Mater. Des. Appl. 2015. DOI: 10.1177/1464420715581003.

[60] S. R. Kumar, A. Patnaik, I. K. Bhat, Physical and thermo-mechanical characterizations of resin-based dental composite reinforced with silane-modified nanoalumina filler particle, Proc. Inst. Mech. Eng. L. J. Mater. Des. Appl. 2015. DOI: 10.1177/1464420715581004.

[61] L.H. Mair, T.A. Strlarski, R.W. Vowles, C.H. Lloyd, Wear: mechanisms, manifestations and measurement. Report of a workshop, J. Dent. 24(1996)141–148.

[62] Y. Li, M. L. Swartz, R.W. Phillips, B.K. Moore, T.A. Roberts, Effect of filler content and size on properties of composites, J. Dent. Res. 64(1985)1396–1401.

[63] B. A. Venhoven, A. J. D. Gee, A. Werner, C. L. Davidson. Influence of filler parameters on the mechanical coherence of dental restorative resin composites. Biomaterials. 17 (1996)735–740.

[64] Y. Tamura, K. Kakuta, H. Ogura, Wear and mechanical properties of composite resins consisting of different filler particles, Odontology, 101(2013) 156–169.

[65] J. D. Satterthwaite, A. Maisuria, K. Vogel, D. C. Watts, Effect of resin-composite filler particle size and shape on shrinkage-stress, dental materials 28(2012)609–614.

[66] A. A. Korichi, M. Mouzali, D. C. Watts, Effects of monomer ratios and highly radiopaque fillers on degree of conversion and shrinkage-strain of dental resin Composites , dental materials 25(2009)1411–1418.

[67] K. Fujita, T. Ikemi, N. Nishiyama, Effects of particle size of silica filler on polymerization conversion in a light-curing resin composite, Dent. Mater. 27(2011)1079–1085.

[68] M. Zhang, J. P. Matinlinna, E-Glass Fiber Reinforced Composites in Dental Applications, Silicon 4 (2012)73–78.

[69] L. Feng, B. I. Suh, A. C. Shortal, Formation of gaps at the filler–resin interface induced by polymerization contraction stress Gaps at the interface, Dent. Mater. 26(2010) 719–729.

[70] Y. K. Lim, Y. K. Lee, B. S. Lim, S. H. Rhee, H. C. Yang, Influence of filler distribution on the color parameters of experimental resin composites, Dent. Mater. 24(2008)67–73.

[71] S. H. Kasraei, M. Atai, Z. Khamverdi, S. Khalegh Nejad, Effect of Nanofiller Addition to an Experimental Dentin Adhesive on Microtensile Bond Strength to Human Dentin, Journal of Dentistry, Tehran University of Medical Sciences, Tehran, Iran 6(2)(2009)1-5.

[72] F. Goncalves, C.L.N. Azevedo, J. L. Ferracane, R. R. Braga, BisGMA/TEGDMA ratio and filler content effects on shrinkage stress, Dent. Mater. 27(2011)520–526.

[73] A. Karmaker, A. Prasad, N. K. Sarkar, Characterization of adsorbed silane on fillers used in dental composite restoratives and its effect on composite properties, J. Mater. Sci: Mater. Med. 18(2007)1157–1162.

[74] L. L. Valente, S. L. Peralta, F. A. Ogliari, L. M. Cavalcante, R. R. Moraes, Comparative evaluation of dental resin composites based on micron- and submicron-sized monomodal glass filler particles, Dent. Mater. 29(2013)1182–1187.

[75] V. S. Nagarajan, B. J. Hockey, S. Jahanmir, Contact wear mechanisms of a dental composite with high filler content, J. Mater. Sci. 35 (2000) 487– 496.

[76] L. Shajiiff, J. P. Santerre, Effect of filler content on the profile of released biodegradation products in microfilled bis-GMA/TEGDMA dental composite resins, Biomaterials 20 (1999) 1897-1908.

[77] D. J. Callaghan, A. Vaziri, H. N. Hashemi, Effect of fiber volume fraction and length on the wear characteristics of glass fiber-reinforced dental composites, Dent. Mater. 22(2006)84–93.

[78] F. Foroutan, J. Javadpour, A. khavandi, M. Atai and H. R. Rezaie, Mechanical properties of dental composite materials reinforced with micro and nano-size Al_2O_3 filler Particles, Iranian Journal of Materials Science & Engineering 2 (8) (2011) 25-33.

[79] L. Wang, Mechanical properties of dental Restorative materials: relative Contribution of laboratory tests, J. Appl. Oral. Sci. 11(3)(2003)162-167.

[80] M. S. Al-Haik, S. Trinkle, D. Garcia, F. Yang, Investigation of the nanomechanical and tribological properties of dental materials, Int. J. Theoretical and Applied Multiscale Mechanics, 1(1)(2009)1-15.

[81] D. Khvostenkoa, J.C. Mitchellb, T.J. Hiltonc, J.L. Ferracanec, J.J. Kruzica, Mechanical performance of novel bioactive glass containing dental restorative composites, Dent. Mater. 29(2013)1139–1148.

[82] S. El-Safty, R. Akhtarc, N. Silikas a, D.C. Wattsa, Nanomechanical properties of dental resin-composites, Dent. Mater. 28(2012) 1292–1300.

[83] S.P. Samuel, S. Li, I. Mukherjee, Mechanical properties of experimental dental composites containing a combination of mesoporous and nonporous spherical silica as fillers, Dent. mater. 25(2009)296–301.

[84] M. Atai, M. Nekoomanesh, S.A. Hashemi, S. Amani, Physical and mechanical properties of an experimental dental composite based on a new monomer, Dent. Mater. 20(2004) 663–668.

[85] M. Michalek, J. Sedlacek, M. Parchoviansky, M. Michalkova, D. Galusek, Mechanical properties and electrical conductivity of alumina/MWCNT and alumina/zirconia/MWCNT composites, Ceram. Int. 40(2014)1289–1295.

[86] S. Thomaidis, A. Kakaboura, W. D. Mueller, S. Zinelis, Mechanical properties of contemporary composite resins and their interrelations, dental materials 29(2013) e132–e141.

[87] R. W. Arcis, A. L. Macipe, M. Toledano, E. Osorio, R.R. Clemente, J. Murtra, M. A. Fanovich, C. D. Pascual, Mechanical properties of visible light cured resin reinforced with hydroxyapatite for dental restoration, Dent. Mater. 18(2002)49–57.

[88] W. H. Mormann, B. Stawarczyk, A. Ender, B. Sener, T. Attin, A. Mehl, Wear characteristics of current aesthetic dental restorative CAD/CAM materials : Two-body wear, gloss retention, roughness and Martens hardness J. Mech. Behav. Biomed. 20(2013)113–125.

[89] K. Okadaa, S. Tosaki, K. Hirota, W.R. Hume, Surface hardness change of restorative filling materials stored in saliva, Dent. Mater.17 (2001) 34-39.

[90] K. E. Frauscher, N. Ilie, Depth of cure and mechanical properties of nano-hybrid resin-based composites with novel and conventional matrix formulation, Clin. Oral. Invest. 16(2012)1425–1434.

[91] M. Mass, A scanning electron-microscope study of in vitro abrasion of mammalian tooth enamel under compressive loads. Arch. Oral. Biol. 39(1)(1994)1–11.

[92] M. Eisenburger, M. Addy, Erosion and attrition of human enamel in vitro, Part II: influence of time and loading. J. Dent. 30(2002)349–352.

[93] T. Imfeld, Dental erosion: definition, classification and links. Eur. J. Oral. Sci. 104(1996)151–155.

[94] Z. R. Zhou, H. Y. Yu, J. Zheng, L. Qian, Y. Yan, Dental Biotribology, Springer-Verlag New York Inc.(2013).

[95] E Sajewicz, A comparative study of tribological behaviour of dental composites and tooth enamel: an energy approach, P. I. Mech. Eng. J-J. Eng. 224(6)(2010)559-568.

[96] J. L. Ferracane; Is the wear of dental composites still a clinical concern? Is there still a need for in vitro wear simulating devices, Dent. Mater. 22(2006)689–692.

[97] K. J. Soderholm, N. D. Richards. Wear resistance of composites: a solved problem? Gen. Dent. 46(1998) 256–263.

[98] E. Sajewicz, Z. Kulesza, A new tribometer for friction and wear studies of dental materials and hard tooth tissues, Tribology International 40 (2007) 885–895.

[99] W. Wang, A. T. DiBenedetto, A. J. Goldbergh, Abrasive wear testing of dental restorative materials, Wear 219(1998)213-219.

[100] J.A. Arsecularatne, M. Hoffman, Ceramic-like wear behaviour of human dental enamel, J. Mech. Behav. Biomed. 8(2012)47–57.

[101] M. Scherge, S. Sarembe, A. Kiesow, M. Petzold, Dental tribology at the micro scale, Wear 297 (2013) 1040–1044.

[102] M. D. Ramalho, C. Bragade, P. V. Antunes , Effects of temperature on mechanical and tribological properties of dental restorative composite materials, Tribology International 63(2013)186–195.

[103] J. Zheng, F. Xiao, L. Zheng, L. M. Qian, Z. R. Zhou, Erosion behaviors of human tooth enamel at different depth, Tribology International 43 (2010) 1262–1267.

[104] J. Zheng, F.Xiao, L.M.Qian, Z.R.Zhou, Erosion behavior of human tooth enamel in citric acid solution, Tribology International 42(2009)1558–1564.

[105] G. Guo, Y. Fan, J.F. Zhang, Novel Dental Composites Reinforced with Zirconia-Silica Ceramic Nanofibers. Dent. Mater. 28(4) (2012)360–368.

[106] S. Beigi, H. Yeganeh, M. Atai, Evaluation of fracture toughness and mechanical properties of ternary thiol–ene–methacrylate systems as resin matrix for dental restorative composites, dental materials 29(2013)777–787.

[107] T. Singh, A. Patnaik, B. K. Satapathy. Development and optimization of hybrid friction materials consisting of nanoclay and carbon nanotubes by using analytical hierarchy process (AHP) and technique for order preference by similarity to ideal solution (TOPSIS) under fuzzy atmosphere. *Walailak.* J. Sci. & *Tech*. 10(4)(2013)343-362.

[108] X. Y. You, J. X. You, H. C. Liu, L. Zhen, Group multi-criteria supplier selection using an extended VIKOR method with interval 2-tuple linguistic information. Expert Systems with Applications Volume 42, Issue 4, March 2015, Pages 1906–1916.

[109] T. Singh, A. Patnaik, B.K. Satapathy, M. Kumar. Performance analysis of organic friction composite materials based on carbon nanotubes-organic-inorganic fibrous reinforcement using hybrid AHP-FTOPSIS approach. Composites: Mechanics, Computations, Applications. An International Journal 3(3) (2012)189-214.

[110] T.Y. Chen. An ELECTRE-based outranking method for multiple criteria group decision making using interval type-2 fuzzy sets. Inform. Sciences. 263(2014)1–21.

[111] J.L. Deng, Introduction to grey system theory, J. Grey. Syst. 1(1) (1989)1-24.

[112] T. Singh, A. Patnaik, B. Gangil, R. Chauhan. Optimization of tribo-performance of brake friction materials: Effect of nano filler. Wear (10-16)(2015)324-325.

[113] *J.W.K. Chan, T.K.L. Tong,* Multi-criteria material selections and end-of-life product strategy: Grey relational analysis approach, Mater. Design 28(5)(2007)1539-1546.

[114] R.K. Pandey, S.S. Panda, Optimization of multiple quality characteristics in bone drilling using grey relational analysis. J. Orthop. 12(1)(2015)39-45.

[115] B.D. Agarwal, L.J. Broutman, Analysis and performance of fiber composites. 2nd ed. John Wiley and Sons, Inc. New York, (1990).

[116] ISO 4049. Dentistry–polymer-based restorative materials. International Organization for Standardization, Geneva (Switzerland) (2009).

[117] M. Atai, D. C. Watts, A new kinetic model for the photopolymerization shrinkage-strain of dental composites and resins. Dent Mater 22(2006)1–7.

[118] ASTM D792-13, Standard Test Methods for Density and Specific Gravity (Relative Density) of Plastics by Displacement, ASTM International, West Conshohocken, PA, 2013.

[119] ASTM D695-08, Standard Test Method for Compressive Properties of Rigid Plastics, ASTM International, West Conshohocken, PA (2008).

[120] N. Finlay, S. Hahnel, A. H. Dowling, G. J. P. Fleming, The in vitro wear behavior of experimental resin-based composites derived from a commercial formulation, Dent. Mater. 29(2013)365–374.

[121] C.P. Tripp, M.L. Hair, Reaction of Chloromethysilanes with Silica: A Low-Frequency Infrared Study. Langmuir 7(5)(1991)923-927.

[122] L. A. S. A Prado, M. Sriyai, M. Ghislandi, Surface Modification of Alumina Nanoparticles with Silane Coupling Agents. J. Braz. Chem. Soc. 21(12)(2010)2238-2245.

[123] M. Wang, S. Deb, W. Bonfield, Chemically coupled hydroxyapatite-polyethylene composites: processing and characterization, Mater. Lett. 44(2000)119–124.

[124] A. R. Ramos, J. Arguello, H. A. Magosso, Al_2O_3 coated with 3-*n*-propyl-1-azonia-4-azabicyclo octane silsesquioxane chloride and its use for immobilization of cobalt(II) tetrasulfonated phthalocyanine in oxalic acid electro oxidation. J. Braz. Chem. Soc. 4(19)(2008)755-761.

[125] K. H. Chung. The relationship between composition and properties of posterior resin composites. J. Dent. Res. 69(1990)852-856.

[126] S. H. Germain, M. L. Swartz, R.W. Phillips, B. K. Moore, T. A. Roberts. Properties of microfilled composite resin as influenced by filler content. J. Dent. Res. 64 (1985)155-60.

[127] H. F. Albers. Resin in tooth colored restoratives. Principle and technique. BC Decker Inc.; 9th edition Santa Rosa, California, (2002).

[128] I. C. Nagas, F. Egilmez, G. Ergun, The Effect of Irradiation Distance on Microhardness of Resin Composites Cured with Different Light Curing Units, Eur. J. Dent. 4(2010)440–446.

[129] International Organization for Standardization. BS EN ISO 4049:2000 polymer-based filling, restorative and luting materials. Brussels; 2000.

[130] M.A. Rodrıguez, M.J. Liso, F. Rubio, J. Rubio, J.L. Oteo, Study of the reaction of γ – methacryloxypropyltrimethoxysilane (γ – MPS) with slate surfaces, Mater. Sci. 34(1999)3867-3873.

[131] R.W. Mills, K. D. Jandt, S. H. Ashworth, Light emitting diode (LED) and halogen curing - composite depth of cure, Brit. Dent. J. 186(1999)388 – 391.

[132] J. L. Ferracane, Correlation between hardness and degree of conversion during setting reaction of unfilled dental restorative resins, Dent. Mater. 1(1985)11-14.

[133] Y. Bin, W. Xin, X. Weiyi. Enhanced thermal and mechanical properties of functionalized graphene/thiol-ene systems by photo polymerization technology. Chem. Eng. J. 228(2013)318–326.

[134] M. Pantoja, B. Díaz-Benito, F. Velasco, J. Abenojar, J.C. de-Real, Analysis of hydrolysis process of γ methacryloxypropyl trimethoxy silane and its influence on the formation of silane coatings on 6063 aluminum alloy, Appl. Surf. Sci. 255(12)(2009)6386-6390.

[135] A. Y. Fadeev, R. Helmy, S. Marcinko, Self-assembled monolayers of organosilicon hydrides supported on titanium, zirconium, and hafnium dioxides, Langmuir 18(2002)7521–7529.

[136] S. Gharazi, A. E. Langroudi, A. Rahimi, The influence of silica synthesis on the morphology of hydrophilic nanocomposite coating, Scientia. Iranica. F. 18(3)(2011)785–789.

[137] F.A. Rueggeberg, W.F. Caughman, J. Curtis, Factors affecting cure at depths within light activated resin composites. Am. J. Dent. 6(1993)91-95.

[138] P. Koran, R. Kurschner, Effect of sequential versus continuous irradiation of a photoactivated resin composite on shrinkage, viscosity, adhesion, and degree of polymerization, Am. J. Dent. 11(1998)17-22.

[139] M. Xanthos, Functional fillers for plastics, Wiley-VCH Verlag Gmbh &Co. KGaA, (2009).

[140] J. Abenojar, M. A. Martínez, F. Velasco, Effect of Boron Carbide Filler on the Curing and Mechanical Properties of an Epoxy Resin. J Adhesion, 85(4-5) (2009)216-238.

[141] K. Masouras, N. Silikas, D.C. Watts, Correlation of filler content and elastic properties of resin-composites. Dent. Mater. 24(2008)932–939.

[142] J. R. M. D. Almeida, B. H. P. Manfredini, Hardness evaluation of epoxy resin filled with mineral waste. J. Appl. Polym. Sci. 84(2001)2178–2184.

[143] A. Misra, P. Spencer, O. Marangos, Micromechanical analysis of dentin/adhesive interface by the finite element method. J. Biomed. Mater. Res. B. 70(1)(2004)56–65.

[144] G. Agrawal, A Patnaik, R.K. Sharma, Thermo-Mechanical Properties and Abrasive Wear Behavior of Silicon Carbide Filled Woven Glass Fiber Composites, Silicon. 6(2014)155-168.

[145] I. Sideridou, D.S. Achilias, E. Kyrikou. Thermal expansion characteristics of light-cured dental resins and resin composites. Biomaterials 25(2004)3087-3097.

[146] S.L. Wendt, The effect of heat used as a secondary cure upon the physical properties of three composite resins. I. Diametral tensile strength, compressive strength, and marginal dimensional stability. Quintessence. Int. 18(1987)265-271.

[147] I.L. Santana, E. Lodovici, J.R. Matos, Effect of experimental heat treatment on mechanical properties of resin composites. Braz. Dent. J. 20(2009)205-210.

[148] C.L. Miyazaki, I.S. Medeiros, I.L. Santana, Heat treatment of a direct composite resin: influence on flexural strength. Braz. Oral. Res. 23(2009)241-247.

[149] J.F. Mc-Cabe, R.W. Wassell. Hardness of model dental composites the effect of filler volume fraction and silanation. J. Mater. Sci. Mater. Med. 10(1999)291-294.

[150] J. Abenojar, J. C. del Real-Romero, M. A. Martínez, M. Cano, Effect of Silane Treatment on SiC Particles Used as Reinforcement in Epoxy Resins, J. Adhesion. 85(6) (2009)287-301.

[151] G. L. Adabo, C. A. S. Cruz, R. G. Fonseca, L. G. Vaz, The volumetric fraction of inorganic particles and the flexural strength of composites for posterior teeth, J. Dent. 31(5) (2003)353-359.

[152] E. C. Vouvoudi, I. D. Sideridou, Dynamic mechanical properties of dental nanofilled light-cured resin composites: Effect of food-simulating liquids, J. Mech. Behav. Biomed. 10(2012)87–96.

[153] Neves AD, Discacciati JAC, Orefice RL, W.C. Jansen. Correlation between degree of conversion, microhardness and inorganic content in composites, Pesqui. Odontol. Bras. 16(2002)349–354.

[154] M. El-Nawawy1, L. Koraitim, O. Abouelatta, Depth of Cure and Microhardness of Nanofilled, Packable and Hybrid Dental Composite Resins. American Journal of Biomedical Engineering 2(6)(2012)241-250.

[155] M. M. Pereira, R. L. Oréfice, H. S. Mansur, Preparation and biocompatibility of poly (methyl methacrylate) reinforced with bioactive particles. Mater. Res-Ibero-Am. J. 6(2003) 311–315.

[156] M. Willis, I. Masters. The effect of filler loading and process route on the three point bend performance of waste based composites. Compos. Struct. 62(2003)475–479.

[157] J. John, S.A. Gangadhar, I. Shah. Flexural strength of heat-polymerized polymethyl methacrylate denture resin reinforced with glass, aramid, or nylon fibers. J Prosthet. Dent. 86(2001)424–427.

[158] E.G. Mota, A.Weiss, A.M. Spohr, H.M.S. Oshima, and L.M.N. Carvalho. *Revista* Odonto. Ciência. 26(2010)151-155.

[159] B. Gangil, A patnaik, A Kumar, and M. Kumar, Investigations on mechanical and sliding wear behaviour of short fibre-reinforced vinylester-based homogenous and their functionally graded composites, Proc. Inst. Mech. Eng. L. J. Mater. Des. Appl. 226(2012)300-315.

[160] P. Hvizdos, V. Puchy, A. Duszova, J. Dusza, Tribological behavior of carbon nanofiber–zirconia composite, Scripta. Materialia. 63 (2010) 254–257.

[161] A. J. D. Gee, P. Pallav, C. L. Davidson Effect of abrasion medium on wear of stress-bearing composites and amalgam in vitro. J. Dent. Res 65(1986) 654–658.

[162] N. E. Waters, Some mechanical and physical properties of teeth, Symp. Soc. Exp. Biol. 34(1980)99-135.

[163] J.F.V. Vincent, D. Currey (eds) Mechanical properties of biological material. Cambridge University Press, Cambridge, 99–135 (1980).

[164] C. Hagberg Assessment of bite force: a review. J. Craniomandib. Disord. 1(1987) 162–169.

[165] M. A. Chowdhury, M. M Helali, The Effect of Frequency of Vibration and Humidity on the Wear rate, Wear, 262(2007)198-203.

[166] J.A. Kaidonis, L.C. Richards, G.C. Townsend, G.D. Tansley Wear of human enamel: a quantitative in vitro assessment, J. Dent. Res. 77(12)(1998) 1983–1990.

[167] S. Biswas, A. Satapathy, Tribo-performance analysis of red mud filled glass-epoxy composites using Taguchi experimental design, Mater. Design. 30(2009)2841–2853.

[168] M. A. Martinez, A. Martin, J. Llorca, Wear of Al-Si alloys and Al-Si/SiC composites at ambient and elevated temperatures, Scripta. Metall. Mater.28(1993)207-12.

[169] A. Martin, M. A. Martinez, J. Llorca, Wear of SiC-reinforced Al-matrix composites in the temperature range 20-200℃, Wear 193 (1996)169-179.

[170] D. J. Lloyd, F.R. Brotzen, Particle reinforced aluminium and Mg matrix composites, Int. Mater. Rev. 39(1994)1-39.

[171] P. K. Rohatgi, Y. Riu, S. Ray, Friction, Lubrication and Wear Technology, ASM Handbook. ASM International, Metals Park, OH, (1992)801-811.

[172] M. K. Surappa, P. K.Rohatgi, Preparation and properties of cast aluminium-ceramic particle composites, J. Mater. Sci., 1981, 16(4)(1981)983-993.

[173] M. Roy, B. Venkataraman, V.V. Bhanuprasad, Y.R. Mahajan, G. Sundararajan, The effect of particulate reinforcement on the sliding wear behaviour of aluminium matrix composites, Metall. Trans. 23A(1992)2833-2847.

[174] C. G. Cordovilla, J. Narciso, E. Louis, Abrasive wear resistance of aluminium alloy/ceramic particulate composites, Wear 192 (1996) 170-177.

[175] J. Zheng, Z.R. Zhou, Friction and wear behavior of human teeth under various wear conditions, Tribology International 40 (2007) 278–284.

[176] H. Pihtili, N. Tosun, Investigation of the wear behavior of a glass fiber-reinforced composite and plain polyester resin. Composites Science and Technology 62(2002)367-370.

[177] H. Pihtili, N. Tosun. Effect of load and speed on the wear behavior of woven glass fabrics and aramid fiber-reinforced composites. Wear 252(2002)979-984.

[178] E. Santner, H. Czichos. Tribology of polymers. Tribology International 22(2)(1989)103–109.

[179] Tevruz, T. Tribological behaviours of bronze-filled polytetrafluoroethylene dry journal bearings. Wear 230(1999)61–69.

[180] T. Tevruz, Tribological behaviours of carbon-filled polytetrafluoroethylene dry journal bearings. Wear 221(1998)61–68.

[181] J. C. Anderson, The wear and friction of commercial polymers and composites. In: Friction and wear and polymer composites. Friedrich K, editor. Composite materials series, vol. 1. Amsterdam: Elsevier (1986)329–362.

[182] B. H. Stuart, Tribological studies of poly(ether ether ketone) blends. Tribology International 31(11)(1998)647–651.

[183] H. Unal, A. Mimaroglu, Influence of test conditions on the tribological properties of polymers. Industrial Lubrication and Tribology 55(4)(2003)178–183.

[184] H. Unal, A. Mimaroglu, Friction and wear behavior of unfilled engineering thermoplastics. Material Design; 24(2003)183–187.

[185] V. Vishwanath, A. P. Varma, C. V. S. Kumeswara Rao. Wear studies on both polyester and phenolic reinforced glass fibre composites. Comp. Sci. Tech. 44(1991)77-86.

[186] H. Unal, A. Mimaroglu, U. Kadıoglu, H. Ekiz. Wear behavior of pure polytetrafluoroethylene (PTFE) and its composites. Mater. Des. 25(2004)239-245.

[187] B. Suresha, Siddaramaiah, Kishorec, S. Seetharamud, P. S. Kumarand. Investigations on the influence of graphite filler on dry sliding wear and abrasive wear behaviour of carbon fabric reinforcedepoxy composites. Wear 267 (2011) 1405-1414.

[188] B. N. Raju, R. K, Prasad. Wear studies on polyester resin filled with ZnO nano particles. ARPN J Eng Appl Sci; 6(2011)75-82.

[189] O. Kim, W. J. Shim, Studies on the preparation and mechanical properties of esthetic polymeric dental restoratives using silane treated silica microfiller via freeze-drying, Polym. Composite 22(5)(2004)650-659.

[190] M. Hosseinalipour, J. Javadpour, H. Rezaie, T. Dadras, A. N. Hayati, Investigation of mechanical properties of experimental Bis-GMA/TEGDMA dental composite resins containing various mass fractions of silica nanoparticles, J. Prosthodont 19(2010)112-117.

[191] J.L. Drummond, Nanoindentation of dental composites. J. Biomed. Mater. Res. Part. B. Appl. Biomater., 78(2006)27-34.

List of Publications Out of This Research Work

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Science Citation Indexed International Journal

1. **Shiv Ranjan Kumar**, Amar Patnaik**,** I K Bhat. Analysis of polymerization shrinkage and thermo-mechanical characterizations of resin-based dental composite reinforced with silane modified nanosilica filler particle. **Journal of Materials: Design and Applications**, 230 (2016) 492-503. **SCI Indexed I.F = 0.746**
2. **Shiv Ranjan Kumar**, Amar Patnaik**,** I K Bhat. Physical and thermo-mechanical characterizations of resin-based dental composite reinforced with silane-modified nanoalumina filler particle, **Journal of Materials: Design and Applications** 230 (2016) 504-514. **SCI Indexed I.F = 0.746.**
3. **Shiv Ranjan Kumar**, I K Bhat, Amar Patnaik.(2015) Novel dental composite material reinforced with silane functionalized micro-sized Gypsum filler particles, **Polymer Composites** DOI: 10.1002/pc.23599 **SCI Indexed I.F = 1.65.**
4. **Shiv Ranjan Kumar**, Amar Patnaik, I K Bhat. (2015). Optimum selection of nano and micro sized filler for the best combination of physical, mechanical and wear properties of Dental composites, Journal **of Materials: Design and Applications** DOI: 10.1177/1464420716629825 **SCI Indexed I.F = 0.746.**
5. **Shiv Ranjan Kumar**, AmarPatnaik, I K Bhat. (2015). In vitro wear behavior of dental composite filled with silane treated nanozirconia filler, **Journal of Engineering Tribology** DOI: 10.1177/1350650116641329 **SCI Indexed I.F = 0.91.**
6. **Shiv Ranjan Kumar**, Amar Patnaik**,** I K Bhat. (2016), The in vitro wear behavior of dental composite filled with nanosilica filler, **Journal of Material Engineering and Performance** (*Under review*). I.F = 1.27.
7. **Shiv Ranjan Kumar**, Amar Patnaik**,** I K Bhat. (2016), **Two-body and three-body abrasive wear of silane treated nanoalumina filled dental composite, Journal of Mechanical Behavior of Biomedical Materials** (*Under review*). I.F = 3.8.
8. Anoj Meena, Harlal Singh Mali, Amar Patnaik**, Shiv Ranjan Kumar**. (2016), Effect of adding nanoalumina and marble dust powder on the physical, mechanical and thermo-mechanical characterization of dental composite, **Polymer Composites** (*Under review*). I.F = 1.672.

Book Chapter

1. IK Bhat, Amar Patnaik, **Shiv Ranjan Kumar**. 2015. Investigation of wear characteristics of dental composite reinforced with rice husk derived nanosilica filler Particles, Volume7, Nanocomposite: Fundamental and Science, Handbook of composite from renewable materials and agricultural sources" being published by prestigious Wiley Scrivener publisher (*In press*).

National and International Conferences

1. **Shiv Ranjan Kumar,** I.K. Bhat, Amar Patnaik. Evaluation of Mechanical Properties of resin based dental composite materials reinforced with silane treated nano- size Al2O3 filler particles. **NIT-MTMI** International conference on Emerging Paradigms and Practices in Global Technology, Management & Business Issues, NIT Hamirpur, 22-24th Dec., 2014.
2. **Shiv Ranjan Kumar,** Amar Patnaik, I.K. Bhat, Water Sorption and Solubility Behaviour of Dental Composites reinforced with Nanotitania Filler, Emerging and Futuristic Trends in Engineering & Technology, held at Maharaja Agrasen University Baddi May 8-9, 2015.
3. **Shiv Ranjan Kumar,** Amar Patnaik, I.K. Bhat, Analysis of Polymerization Shrinkage and Water Sorption of Silane Modified Nanoalumina Particle Reinforced Dental Composite, National Conference on Futuristic in Mechanical Engineering (FME-2015), held at Madam Mohan Malviya University Gorakhpur Nov. 6-7, 2015.

Patent filed

1. **Shiv Ranjan Kumar,** Dr. Amar Patnaik, Prof. I.K Bhat. Development of polymeric dental material reinforced with new filler gypsum, Patent application number **1321/DEL/2015A (Under Examination).**
2. Shiv Ranjan Kumar, Dr. Amar Patnaik, Prof. I.K Bhat. Development and characterization of self healing and antibacterial dental material, Patent application number **201611002648 A.**

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He has published five research papers in Science Citation Indexed Journals, filed two patents (one is under examination), authored one book chapter, and presented three research papers in International Conferences to his credit. Since 2013, he has been engaged in his Doctoral Research in the area of Development and characterization of polymeric Dental materials at M.N.I.T, Jaipur under the Institute Research Fellowship scheme by Ministry of Human Resource Development, Government of India.

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