COMPARATIVE EVALUATION OF FLEXURAL STRENGTH OF HEAT POLYMERIZED POLYMETHYL METHACRYLATE DENTURE BASE RESIN REINFORCED WITH DIFFERENT CONCENTRATIONS OF SILANIZED TITANIUM DIOXIDE (TiO2) NANOPARTICLES - AN IN VITRO STUDY

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List of Abbreviations Used

No.	Abbreviations	Full form
1.	n	Number of specimens in each group
2.	N	Newton
3.	p value	Probability of happening of an event
4.	S.D.	Standard deviation
5.	ANOVA	Analysis of variance
6.	Mpa	Mega Pascal
7.	^{0}C	Degree Celsius
8.	^{0}	Degree
9.	mm	Millimeter
10.	M	Meter
11.	i.e.	that is
12.	PMMA	Polymethyl methacrylate
13.	µ	Micron
14.	Al_2O_3	Aluminum oxide
15.	TiO_2	Titanium dioxide

16.	ZrO_2	Zirconium oxide
17.	SiO_2	Silica
18.	Rpm	Rotations per minute
19.	mins	Minutes
20.	gms	Grams
21.	NP	Nanoparticle
22.	Wt%	Weight percent
23.	BC	Before Christ
24.	Dr	Doctor
25.	Al	Aluminum
26.	Mg	Magnesium
27.	Zr	Zirconium
28.	Vol	Volume
29.	UHMP	Ultra-High Molecular weight Polyethylene
30.	MMA	Methyl methacrylate
31.	SEM	Scanning electron microscope
32.	PE	Polyester fiber
33.	KF	Kevlar fiber
34.	GF	Glass fiber
35.	h	Hour
36.	kJ	Kilojoules
37.	TMSPM	Trimethoxysilypropylmethacrylate
38.	FS	Flexural strength
39.	DPI	Dental products of India
40.	ADA	American Dental Association
41.	Nps	Nanoparticles
42.	OPEFB (Fibers)	Oil Palm Empty Fruit Bunches (Fibers)
43.	VHN	Vickers Hardness Test

44.	Nm	Nanometre
45.	™	Trademark
46.	Pvt. Ltd.	Private Limited
47.	Fig.	Figure
48.	ISO	International Organization for Standardization
49.	pH	potential of hydrogen
50.	Psi	Pound per Square Inch
51.	W	watt
52.	KHz	kilohertz
53.	ml	Millilitre
54.	UTM	Universal Testing Machine
55.	$\bar{x}$	Mean
56.	X	The values of variable
57.	Σ	Sum of the value
58.	Min	Minimum value
59.	Max	Maximum value
60.	CI	Confidence Interval
61.	SEM (statistics)	Standard error of the mean
62.	(CV)	Coefficient of variation
63.	etc	Etcetera
64.	GPa	Giga pascal
65.	GIC	Glass Ionomer Cement
66.	et al. (Latin)	‘and others’
67.	F-value	Ratio of two variances (F- Sir Ronald Fisher)
68.	FTIR	Fourier-transform infrared (FTIR) spectroscopy

Introduction

"*Research is too see what everybody else has seen, and to think what nobody else has thought.*"

- **Albert Szent Gyorgyi**

The loss of teeth by accident or disease has plagued mankind throughout the ages. The means of replacing missing teeth structures by artificial materials continues to account for a large part of the application of material sciences.[1] The first dental prosthesis was believed to have been constructed in Egypt about 2500 BC. Dentures are believed to have surfaced as a mode of treatment for replacing missing teeth around 700 BC.[2]

During the 18th century, gold and porcelain were the material of choice for denture base materials. **Etienne Bourdet (1775)** made the first reference to the use of a gold base punctuated with small holes much like the sockets of teeth. In **1774 Alexis Duchateau**, a Parisian apothecary, dissatisfied with his own stained hippopotamus ivory denture, was inspired to attempt to use porcelain for denture fabrication.[3]

During the 19th century, Tortoise Shell, Gutta Percha, Vulcanite, Aluminum and Celluloid were used as denture base materials. Vulcanite remained the principal denture base material for the next 75 years.

In the 20th century various materials like Bakelite, Stainless steel, Cobalt Chromium, Vinyl Resin, Acrylic Resin, Polystyrene and Nylon were utilised for fabrication of dentures. [2]

The PMMA and its copolymers introduced by **Dr Walter Wright** in 1937 continues to be the most popular non-metallic material till date and is being used in 95% dentures.[4] PMMA continues to be used because of its favorable working characteristics, low cost, processing ease, accurate fit, biocompatibility, stability in the oral environment and superior aesthetics.

But it has certain drawbacks like residual monomer allergy, poor mechanical strength, low fatigue strength, brittle on impact, poor conductors of heat, low hardness, porosity, crazing, warpage, poor adhesion to metal and porcelain.[5]

Hargreaves in 1969 in a survey reported that 63% of the dentures had broken within 3 years of their delivery. Fractures in dentures result from two different types of forces, namely flexural fatigue and impact.[6]

Flexural fatigue occurs after repeated flexing of a material and is a mode of fracture whereby a structure eventually fails after being repeatedly subjected to loads that are so small that one application apparently does nothing detrimental to the component.

Impact failures usually occur out of the mouth as a result of a sudden blow to the denture or accidental dropping whilst cleaning, coughing or sneezing.[7]

Given the function of a denture base in a removable prosthesis, high flexural strength, flexural modulus and a large yield point distance would help resist torsional forces in function, leading to a longer clinical service life. There are three ways to improve the mechanical properties of PMMA: replacing PMMA with an alternative material; chemically modifying it; and reinforcing the PMMA with other materials.[5]

Improvement of mechanical properties of denture base materials were tried to be achieved by adding a polyfunctional crosslinking agent such as polyethylene glycol dimethacrylate[8] or by incorporating a rubber phase.[9]

Sehajpal and Sood added various amounts of powdered Copper, Silver and Aluminum into the PMMA resin to study the flexural strength.

Zuccari et al evaluated the improvement of the mechanical properties of PMMA by reinforcing with oxides of Al, Mg, Zr and pulverized E-glass particles.[10] Several researchers have demonstrated that PMMA can show good fatigue behavior and impact strength when it is reinforced by carbon fibers and silane-treated glass fillers. [10]

Recently, much attention has been directed towards the incorporation of inorganic nanoparticles into PMMA to improve its properties. The properties of polymer nanocomposites depend on the type of incorporating nanoparticles, their size and shape as well as the concentration and interaction with the polymer matrix.[11]

Aluminum oxide nanoparticles possesses strong ionic interatomic bonding, giving rise to its desirable material characteristics. It can exist in several crystalline phases, which all revert to the most stable hexagonal alpha phase at elevated temperatures. Alpha phase alumina is the strongest and stiffest of the oxide ceramics. It has high hardness, excellent dielectric properties, refractoriness, good thermal properties, antibacterial properties and imparts radiopacity when added to polymethyl methacrylate denture base resin.[12]

Surface modification of an inorganic particle with an organic substance is a useful way to reduce its surface energy and increase its compatibility with polymer matrix and thus improve the properties of the polymer/ inorganic particles. Treating the surface with silane coupling agent eliminates the aggregation of particles and improves its compatibility with organic polymer.[11]

Therefore, an attempt is being made to improve the mechanical properties of heat polymerized denture base resin by incorporation of non-silanized and silanized aluminum oxide nanoparticles into it.

Aims and Objectives

AIM:

To evaluate and compare the flexural strength of heat polymerized polymethyl methacrylate denture base resin reinforced with different concentrations of silanized titanium dioxide (TiO_2) nanoparticles.

OBJECTIVES:

1. To evaluate the flexural strength of heat polymerized polymethyl methacrylate denture base resin without any reinforcement of nanoparticles and heat polymerized polymethyl methacrylate denture base resin reinforced with 1wt%, 3wt% and 5wt% silanized titanium dioxide nanoparticles.
2. To compare between flexural strengths of heat polymerized polymethyl methacrylate denture base resin reinforced with 1wt%, 3wt%, 5wt% Silanized titanium dioxide nanoparticles and heat polymerized polymethyl methacrylate denture base resin.

Review of Literature

Polymethyl methacrylate (PMMA) acrylic resin is a preferred denture base material because of its low cost, ease of application, polish ability along with its reliance on simple processing equipment. But a major drawback of the use of PMMA as a denture base material is its low transverse and impact strength that leads to common occurrences of the fracture of prosthesis in-situ and ex-situ. Many attempts have been made in the past to improve mechanical properties of acrylic resins including its chemical modification by the addition of a rubber graft copolymer and also by the addition of various reinforcing materials like metals, metal fillers, carbon fibres, aramid fibres, glass fibres and ultra-high modulus polyethylene. [1]

Before 18th century, materials used for denture were wood, bone and ivory. **In 1678-1761**, **Pierre Fauchard** began with modern dentistry with the development of many prosthetic techniques by using human teeth or teeth made from hippopotamus or elephant ivory in the denture. He carved dentures from a single piece of ivory and bone where bone displayed better dimensional stability than wood. Although, ivory was stable in the oral environment, and offered significant esthetics, but its drawbacks were that it was not readily available, and was relatively expensive. [2] French dentist **Etienne Bourdet (1775)**, made the first reference to the use of a gold base punctuated with small holes resembling like the sockets of teeth. [2]

In **1774 Alexis Duchateau**, a Parisian apothecary, dissatisfied with his own stained hippopotamus ivory denture and inspired to use porcelain for denture fabrication. He teamed up with Parisian dentist Nicholas Dubois De Chemant.[1] Chemant's denture was popular until the introduction of individually baked porcelain teeth in **1808** by an **Italian dentist Giuseppangeio Fonzi**. In this, teeth were attached to the denture base by a small platinum hook. This pin was soldered to a gold denture base. It was one of the most important events in the history of dentistry. [2] **Loomis in 1854** fabricated the first porcelain denture with artificial teeth.

Charles H Land in 1890 made porcelain dentures with platinum bases known as continuous gum dentures. **Alexander Gutowski in 1962** from West Germany made dentures from one piece of porcelain [2]

During the latter part of the 19th century, polymers entered the field of denture base materials. **Charles Goodyear (1839)** developed the art of producing rubber and in 1851 his brother Nelson Goodyear invented a process for making hard rubber called vulcanite. Despite its displeasing appearance vulcanite dentures fitted the ridges of the patient more exactly, so that dentures could be worn with comfort.

In **1850 CF Harrington** introduce a **tortoiseshell base** that was first the thermoplastic denture base material.[2] In **1851 Edwin Truman** made a **base of Gutta percha**. However, the material was unstable and its use required complicated equipment. [2]

In **1856 Alfred A Blandy** made cheoplastic dentures by using low fusing alloy of silver, bismuth and antimony. He embedded a wax model of the denture in plaster of Paris and after melting the wax, he poured the metal compound. Although this metal denture was never accepted, molding and pouring technique was adopted for manufacturing of vulcanite dentures. [2]

Smith (1957)[7] investigated reinforcement of PMMA by mixing discrete glass fibres with the dough or by lamination with glass cloth and found that reinforcement of fibres did not improved the tensile strength. He also concluded that to strengthen polymer resins by glass fibres, the adhesion of polymer matrix and the fibres should be good because untreated fibres act as inclusion bodies and inhibits the homogenous mixture of acrylic resin and weaken the resin, in spite of strengthening it.

Grant A A and Greener E H in 1967 [14] evaluated the effect of whisker reinforcement of Polymethyl methacrylate denture base resin. Whiskers are microscopic single crystals which possess strengths of the order of 10^6 times that of the same material in bulk form. The small size of single crystal whiskers reduces the large concentration of point, line and surface defects responsible for the relatively low strengths of polycrystalline aggregates. They used the principle that relatively soft ductile matrix is fully capable of transferring an applied load to short fibres via shear forces at the interface. In this instance the fibres would be the principal load-bearing constituents. In this study Al_2O_3 whiskers were used with diameter between 0.2 to 100µ, sapphire whiskers with diameter of 1 to 10µ and the length of 75 to 125 µ, stainless steel compacted fibres and low-density fibres, boron nitride filaments and silicon carbide whiskers. The results indicated that there is an enhancement of physical properties for all whiskers types studied but addition of Al_2O_3 whiskers in concentration of 10 to 13 % are most effective in reinforcement. The bending strength for sapphire whiskers approximately doubled and 25% changes were noted in the modulus and resiliency. On the basis of the results presented, the study strongly indicates that an enhancement of flexure of denture base polymethyl methacrylate is possible through the technique of whisker reinforcement with sapphire fibres. The results of this study indicate that a systematic investigation of the entire spectrum of physical and chemical properties of sapphire whiskers-polymethyl methacrylate composites may well be in order.

Hargreaves AS in 1969 [17] conducted a survey at Dundee Dental Hospital for 6 months to study the prevalence of fractured denture. She stated that there were 113 denture repairs out of which 68% denture fractured at the end of three years, greater proportion being of partial dentures than complete dentures. 40% of dentures fractured during mastication. The survey concluded that upper denture fractured in the midline during mastication and lower denture encountered fracture after being dropped.

Schreiber CK in 1971[18] studied the effect of carbon fibres to reinforce polymethyl methacrylate by using untreated carbon fibres and untreated chopped carbon fibres. Bundles of fibres were wet with monomer and incorporated into the polymer to form a thin shit within the matrix. The results showed greatest transverse strength by the reinforcement of surface treated carbon fibres which exceeded acrylic by 50%. While adverse effects were shown by untreated carbon fibres.

In 1971, Berry HH and Funk OJ [19] constructed a strengthener which would reduce or eliminate the lower denture breakage while retaining the properties of the acrylic resin denture base. They quoted that midline fracture of lower denture is common and it might be due to difficulty in cleaning, coughing which leads to pushing out of the denture from the mouth, lack of denture base material at the midline, greater than average biting force, dropping the denture accidently. **Wasserman** suggested the advantages of inserting wire in the lingual crescent area of the acrylic resin base. Other metallic inserts as well as cast reinforcements adds strengths to the denture base. In this study vitallium was inserted in acrylic resin denture base. There was no denture breakage after the strengthener was inserted in the lower denture. The results showed that patients with chronic denture breakage problem can fracture their lower dentures on an average of three times per year. Denture flange and tooth fractures are also common among chronic denture breakers. [20]

Wylegala (1973) [21] investigated the addition of three types (untreated, untreated chopped and surface treated) of carbon fibre for the reinforcement of acrylic resin denture base material. He reported an increase in transverse strength with the addition of surface treated carbon fibre but a decrease in transverse strength with untreated fibres.

In 1981, Beyli MS, Dent M and Fraunhofer JA. [5] studied and analysed the cause of fracture of acrylic resin dentures where the ratio of fracture of upper denture to lower denture is 2:1 with the most common cause of fracture being poor fit and lack of balanced occlusion. They studied stress distribution within dentures using variety of techniques and stated that maxillary dentures are subjected to bending deformation with tensile stresses occurring at labial aspect and lingually to the incisors on the polished surface. He stated that, incisal notch represents a point of weakness which raises the stress and contributes to midline fracture of maxillary dentures resulting from cyclic deformation of the base during function. Any factor that exacerbates deformation of the base or alters its stress distribution will result in denture fracture. A survey of denture fractures, has indicated that most failures occurred when there was deep notching at the midline labial frenum. To prevent the midline fracture they suggest the use of higher strength polymers, notably impact-resistant materials, which will reduce the tendency to fracture

Carroll CE and Fraunhofer JA in 1984 [22] study was conducted to determine the effect of the use of commonly available materials to reinforce autopolymerizing acrylic resin. The acrylic resin was reinforced with flat, braided, two-strand brass wire and one of four diameters of orthodontic wires: 0.016, 0.025, 0.036, and 0.051 inch (0.41, 0.64, 0.91, and 1.30 mm). The specimens were subjected to transverse testing under three-point loading at a crosshead speed of 5mm/min. No statistically significant difference was found between the unreinforced and the unlopped 0.016-inch wire specimens, but the looped 0.016-inch specimens were stronger ($p < .05$) than the unreinforced acrylic resin. All other reinforced specimens were significantly stronger ($p < .00l$) than the unreinforced acrylic resin specimens. When stainless steel wire is used as a reinforcing system for autopolymerizing resin, greater transverse strength is obtained with the use of wires of larger dimension.

Yazdaine N and Mahood M in 1985 [23] carried out an investigation to evaluate and compare the transverse strength of standard-sized acrylic resin specimens reinforced with varying amounts of carbon fibre in two different lay-ups. Strands and woven mat fibres were used and both fibres were silane treated to enhance the bonding ability to acrylic resin. The fibres of the woven mat were at right angles to each other and had been held together by passing a barbed wire of 1 mm diameter through them. The strands were oriented along the long axis and the woven mat fibres were arranged parallel & at right angle to the long axis. The modulus of rupture and modulus of elasticity were measured for each composite resin prepared.

This investigation has confirmed that carbon fibre acrylic resin composites are stronger and stiffer than unfilled acrylic resin. The experiments show clearly that strands are more efficient straighteners than are woven mats.

Grave, Chandler & Wolfaardt (1985) [21] compared the transverse strength of samples of cross linked acrylic resin with samples containing various percentages of aramid fibres. All of the reinforced specimens were significantly weaker. A possible explanation is the failure of adhesion between the fibre and the matrix resulting in the layers of fibre separating the matrix into layers of narrow cross-section. Contrary to this finding **Berrong, Weed & Young (1990)** reported a significant improvement of impact strength with a fibre content up to 2%. **Mullarky (1985)** also reported an increase in the strength and fatigue resistance of acrylic resin appliances reinforced with unidirectional aramid fibre.

Ruyter, Ekstrand & Bjork (1986), [21] in a search for an alternative to a gold framework on titanium implants, discussed the development of a carbon graphite fibre reinforced PMMA and compared the flexural properties in wet and dry conditions to unreinforced PMMA. Fracture stress and flexural modulus were higher for the reinforced than for the unreinforced material.

Solnit G in 1991 [24] studied the effect of methyl methacrylate reinforcement with various types of glass fibres which were silane treated and untreated. The fibres used were cloth form fibres, loose form yellow fibres and loose form white fibres. When the results were compared, samples containing silane treated loose form glass fibres strengthened the PMMA, whereas silane treated cloth form fibre weakened the PMMA when added to the monomer/polymer mixture.

Vallitu PK and Lassila VP in 1992 [25] aimed to study the effect of surface roughness of various metal wires on the fracture resistance of the acrylic resin. The metal wires used were semicircle wire (0 l-0x2-0mm), braided wire plate (0 0-8 x 2-4mm) and clasp wire (0 1-0 mm). Five roughness stages of each wire type were used and sandblasting was done with aluminium oxide (Al_2O_3) with the grain size of 50 and 250µm and the air pressure applied was 5-5 bar. The study concluded that all metal wires increased the fracture resistance of the acrylic resin significantly when compared with the control group A (P< 0-001), where semi-circular wire had the most marked effect on the fracture resistance of the resin. The braided wire plate did not have as favourable an effect as the semicircle wire. When the different methods of treating the wire surfaces were compared, it was noticed, that the sandblasting was the most effective method with all the metal wires used in this study.

Vallitu PK and Lassila VP in 1992 [26] studied the reinforcement of acrylic resin denture base material with metal or fibre strengtheners where Remanium's spring hard clasp wire (0,1-0 mm), semi-circular wire (0,1-0 x 2-0 mm and l-25x2 50mm) and braided wire plate (0, 0-8x2-4mm) were used as metal strengtheners. All metal strengtheners were divided into two major groups: glossy and sandblasted and fibres were divided into silanized and untreated groups. Sandblasting was done by using 100µm sand. The study concluded that the specimens with the metal wire strengthener were clearly stronger than the specimens in other group and the best strengthener in this study was the semicircular metal wire (0, 1-25 X 2-50 mm), which doubled the fracture resistance of specimens

Vallitu PK in 1993[12] carried out an investigation to study the effect of metal wire bonding to acrylic resin on the fracture resistance of an acrylic denture base material construction with two different bonding methods Silicoating and Eudicolle. Semicircle metal wire (1-0 X 2.0mm) were used and pressed into an aluminium mould. The metal wires were sandblasted with 250 µm grain size aluminium oxide (Al_2O_3) and the air pressure applied was 5.5 bar. The semicircle metal wires were placed in three different positions with respect to the fracture load in the test specimens. The fracture resistances of the test specimens reinforced with sandblasted metal wires were higher than the resistances of the control specimens. The bonding method of Silicoater increased the resistance significantly when compared to Eudicolle. No significant difference in fracture loads was observed when the effect of different positions of the metal strengtheners in the acrylic resin were compared.

Vallitu PK in 1993 [11] compared the effect of two different silane compounds on the adhesion between glass fibres, carbon fibres and aramid fibres reinforced with acrylic resin, where silane treated and untreated forms of each fibres were tested. 7.39% for glass fibres, 2.08% for carbon fibres and 2.30% for aramid fibres were measured by the weight percentage of the mass of the acrylic resin. The results showed that the silanized glass fibres used as reinforcement significantly increased the fracture resistance due to the good adhesion between fibres and acrylic resin. The glass fibre silanized with compound AP133 did not enhance the fracture resistance significantly, but when the fibres were treated with compound A174 the resistance was enhanced significantly. The aramid fibres treated with silane compounds AP133 or A174 increased the fracture resistance of the test specimens when compound A174 was used.

Ladizesky NH, Cheng YY and Chow TW in 1993 [27] studied the reinforcement of acrylic resin with chopped high-performance polyethylene fibre properties. The purpose of this investigation was to evaluate the mechanical properties of the new system, including the effect of notches. For straight bars the results indicated that incorporation of 2.4 vol% chopped fibres had negligible effect on the mechanical properties of the resin, whereas, the flexural modulus and impact strength were greatly enhanced when the fibre loading was increased to 37 vol%. Reinforcement with 37 vol % chopped increased the flexural modulus of the resin by over 100%, but did not have a substantial effect on the flexural strength. In summary, the incorporation of at least 30 vol % chopped HDLPE fibre greatly increased the flexural stiffness and impact strength of acrylic denture base resin, while removing the weakening effect of anatomical features such as the frenal notch

Vallitu PK in 1997 [28] studied the effect of reinforcement of ultra-high modulus polyethylene ribbon fibre on the transverse strength of denture polymethyl methacrylare and evaluated the adhesion between denture polymethyl methacrylate and UHMP. Cold gas plasma-treated woven UHMP fibre ribbon that was 4 mm in width was first wetted with methyl methacrylate (MMA) liquid and then dusted thoroughly with polymer powder. One or two layers of ribbon were placed into the silicon mould, which was filled with the mixed PMMA powder and MMA liquid. The acrylic resin was polymerized in a pneumatic curing unit with an air pressure of 0.2 MPa for 15 min at a temperature of +40°C. The bending caused a fracture on the tension side of the test specimen, but the UHMP fibre ribbon held the fractured parts together. The improvement in transverse strength of the test specimens reinforced with UHMP fibre ribbon is modest and its clinical significance is doubtful. The SEM examination of the fibre surfaces of the test specimens suggests that the fracture toughness of these specimens was actually reduced and not increased due to inadequate fibre-matrix coupling.

Stipho HD in 1998 [29] investigated the strength and deflection of repaired acrylic resin joints reinforced with 0%, 1%, 2%, 5%, 10%, and 15% of glass fibres. Results indicated that acrylic resin reinforced with 1% glass fibres showed highest mean strength before and after repair and demonstrated 48% greater strength than specimens without reinforcement. Specimens treated with 15% of glass fibres showed least deflection pattern as higher concentration inhibits the homogenous matrix of the resin. All treated and untreated acrylic resin specimens demonstrated a significant drop in fracture load and maximum deflection after repair. Reinforcement of PMMA acrylic resin with low glass fibre concentrations was found to enhance the post repair yield and the fracture strength of the resin. No significant mechanical advantages were found by the incorporation of higher than 5% glass fibre contents.

Jagger DC and Harrison A in 1999 [21, 30] studied the transverse strength of reinforcement of acrylic resin with chopped polymethyl methacrylate fibres. 0.75 mm in diameter and 5 mm in length of polymethyl methacrylate fibres were added to the denture base material in 0%, 5%, 15%, 20% & 25% by weight. The study concluded that randomly arranged chopped polymethyl methacrylate fibres have no advantage on acrylic resin when compared to unmodified polymer in terms of strength and chopped polymethyl methacrylate cannot be mentioned as reinforcing agent for denture base material.

Jagger DC, Harrison A and Jandt KD in 1999 [21] reviewed the attempts made to improve the mechanical properties of denture base materials in last few years and found that developments of these materials possess a balance of impact resistance and flexural properties, however, most are not acceptable due to their processing characteristics. They concluded that most popular material to fabricate a denture, having a high impact strength, is a rubber modified acrylic polymer with handling characteristics similar to conventional poly (methyl methacrylate). The flexural properties of these materials, however, are relatively poor and long-term failure due to fatigue can be a problem.

Vallitu PK in 1999 [31] aimed to study the effect of acrylic resin reinforced with unidirectional and woven glass fibres on flexural properties. The Stick (S) and Stick Net (SN) reinforcements composed of silanized

Eglass fibers were preimpregnated with porous polymer. The S reinforcement was made from continuous unidirectional glass fibers with a diameter of 12 µm and SN reinforcement was a weave with fiber thickness of 5 µm. Thickness of preimpregnated woven SN reinforcement was 0.06 mm. Results showed that transverse strength of heat polymerizing acrylic resin polymer was 76 MPa and S reinforcement increased it to 341 MPa. They concluded that Novel glass fiber reinforcements may considerably enhance flexural properties of multiphase dental polymers, which is due to proper impregnation of fibers with polymer matrix.

Chen SY, Liang WM and Yen PS in 2001,[32] investigated the mechanical properties of acrylic resin reinforced with Polyester fiber (PE), Kevlar fiber (KF), and Glass fiber (GF) in the concentration of 1%, 2% and 3% by weight. The fibres were cut into 2mm, 4mm and 6mm in length and incorporated in the resin mixture cured at 70°C in a water bath for 13 h, then at 90°C for 1 h. The results showed that the impact strength tended to be enhanced with fiber length and concentration, particularly PE at 3%and 6 mm length, which was significantly stronger than other specimens. Bending strength did not change significantly with the various formulations when compared to a control without fiber.

Foo SH et al in 2001 [33] investigated the effect of polyaramaid fibres on the transverse strength of intact and repaired heat-polymerized denture base acrylic resins where Acron MC, Lucitone 199, and Microlon were used. The treatment groups were intact heat-polymerized PMMA control, PMMA with unreinforced repair, PMMA with polyaramid reinforced repair, intact polyaramid reinforced heat-polymerized PMMA control, polyaramid reinforced PMMA with unreinforced repair, and polyaramid reinforced PMMA with polyaramid reinforced repair. The highest mean strength at fracture was recorded with intact polyaramid reinforced heat polymerized PMMA controls for all resins. Polyaramid fibers did not significantly increase strength to reinforce PMMA repairs.

Jacob John, Shivaputrappa A. Gangadhar, Shah (2001)[33] studied and compared the flexural strength of conventional PMMA resin reinforced with glass, aramid and nylon fibers in loose form. They concluded that glass and aramid fibers appeared to be suitable for long-term use in complete dentures and distal extension partial denture bases, which are considered prone to fracture. Glass fiber reinforcement may also help prevent fracture in provisional fixed partial dentures by strengthening them at the connector sites

T Kanie et al in 2003 [34] studied the flexural properties of denture base polymers reinforced with glass cloth–urethane polymer composite. The silanized glass cloth was sandwiched between two pieces of polyethylene film and pressed to form a sheet of 0.3 mm in thickness, which was light-cured and prepared using four different surface conditions: with or without the polyethylene film and with or without a bonding agent. The results showed that baseline flexural strengths of the self-, heat-, and light-curing resins were 76.2, 68.6, and 55.6 MPa, respectively, and these values were increased to 271.7, 216.4, and 266.5 MPa by the reinforcement sheet.

Arundhati R and Patil NP in 2006 [35] carried out to evaluate and compare the transverse and impact strength of a new high - impact denture base resin and it was compared with DPI-TUFF, Lucitone 199 and DPI heat cure denture base resins. They concluded that DPI-TUFF high impact denture base resin appeared superior to other resins, with mean transverse strength of 115.0 MPa and impact strength of 18.95 kJ/m· The dry strength of the samples of the materials tested show that it is greater than after immersion of the samples in water at 37ºC for a week. The long curing cycle shows considerably higher values of transverse and impact strength as compared to short curing cycle.

Barbosa D B, Souza R F de, Pero A C, Marra J and Compagnoni M A in 2007, [36] studied the effect of different polymerization cycles on the flexural strength of acrylic resin. A conventional heat polymerized, a microwave-polymerized and a autopolymerizing acrylic resins were used. The microwave-polymerized groups showed the highest means ($p<0.05$) for flexural strength (MPa), and there were no significant differences among them. The heat-polymerized group (T) showed the lowest flexural strength means and differ significantly from all groups.

Ellakwa et al in 2008 [37] investigated the effect of Aluminium Oxide addition on the flexural strength and thermal diffusivity of heat-polymerized acrylic resin. Concentration of 5%, 10%, 15%, and 20% of aluminium oxide was used by weight and specimens were prepared. Results were analysed and presented that the mean flexural strength values of the heat-polymerized acrylic resin were (in MPa) 99.45, 119.92, 121.19, 130.08, and 127.60. The flexural strength increased significantly by incorporation of 10% Al_2O_3. Thermal diffusivities of the composites were found to be significantly higher than the unmodified acrylic resin. Thermal diffusivity was found to increase in proportion to the weight percentage of alumina filler, which suggested that the proper distribution of alumina powders through the insulating polymer matrix might form a pathway for heat conduction.

Ayad NM, Badawi MF and Fatah AA in 2008, [38] studied and evaluated the effect of reinforcement of high-impact acrylic resin (Metrocryl HI) with zirconia powder on physical and mechanical properties. 5% and 15% of zirconia powder was used by weight and specimens were fabricated and subjected to transverse strength test. The results showed that addition of zirconia significantly increased the transverse strength of high impact acrylic resin. Increase in transverse strength was directly proportional to the concentration of zirconia powder.

Ihab NS, Moudhaffar M in 2011, evaluated the effect of addition of modified nano-zirconium oxide (ZrO2) on some properties of heat cured acrylic denture base material. (ZrO2) nanofillers were incorporated into (PMMA) denture base by free radical bulk polymerization. (PMMA) nanoparticales were coated with a layer of trimethoxysilypropylmethacrylate (TMSPM) before dispersed and sonicated in monomer (MMA) in different percentages 2%, 3%, 5% and 7% by weight. Then mixed with acrylic powder as general conventional method. The result showed that the maximum increase in impact strength, transverse strength and radio-opacity was observed in denture base nano composite containing 5wt% of nano-ZrO_2.

Yadav et al in 2012, [39] studied the effect of reinforcement of silane treated silver and aluminium microparticles on strength and thermal conductivity of polymethyl methacrylate. The study was carried out in two parts where in Part 1 the effect of addition of 10%, 20% and 30% of metal fillers by weight was carried out on the tensile, compressive, and flexural strength of PMMA. In part II, 10 edentulous patients were clinically evaluated by providing two sets of complete dentures, one without reinforcement and one with 20% aluminium particle filled on the palatal portion of the upper denture. The results showed mean tensile and flexural strength values among control and other groups were found to have statistically significant differences. All 10 participants reported higher perception of hot and cold sensations in dentures with a metalized palatal portion. They concluded that compressive strength increased progressively on increasing the filler concentration for both silver- and aluminium-filled PMMA. Silane-treated metalized PMMA showed reduction in tensile and flexural strength at 30% concentration. Metalized dentures led to an appreciable increase in thermal perception by the participants of this study.

M Vojdani et al in 2012 [40] studied the effect of aluminium oxide reinforcement on the flexural strength, surface hardness and roughness of heat polymerized acrylic resin. 0.5%, 1%, 2.5% and 5% of aluminium oxide was measured and flexural strength was assessed with a three-point bending test using a universal testing machine. The results showed 2.5% of Al_2O_3 significantly increased the flexural strength compared to the control group. The Vickers hardness significantly increased after incorporation of 2.5 and 5% Al_2O_3. No significant difference was detected in surface roughness levels between the reinforced and control groups.

Asar NV et al in 2013 [41] carried out an investigation to evaluate the influence of various metal oxides on mechanical and physical properties of heat-cured polymethyl methacrylate denture base resins. 1% TiO_2 and 1% ZrO_2, 2% Al_2O_3, 2% TiO_2, and 2% ZrO_2 by volume were used. Results showed that impact strength and fracture toughness values were significantly higher. Modification of heat-cured acrylic resin with metal oxides, especially with ZrO_2, may be useful in preventing denture fractures and undesirable physical changes resulting from oral fluids clinically.

Ahmad Sodagar et al in 2013, evaluated the effects of TiO2 and SiO2 nanoparticles on flexural strength (Fs) of poly (methyl methacrylate) acrylic resins. Acrylic resin containing nanoTiO2, SiO2 and TiO2 with SiO2 in two concentration of 1% and 0.5%, in addition to a control group. To prepare nano AR, nanoparticles were added to the monomer. They concluded that incorporation of TiO2 and SiO2 nanoparticles into acrylic resins can adversely affect the flexural strength of the final products, and this effect is directly correlated with the concentration of nanoparticles.

Jasim BS and Ismail IJ in 2014 [10] study was to evaluate the effect of addition of surface treated Aluminium oxide nano fillers on some properties of heat cured (PMMA) where silanized (Al_2O_3) nanoparticles was added to PMMA powder by weight in three different percentages 1wt%, 2wt% and 3wt% and mixed by probe ultrasonication machine. A highly significant increase in transverse strength was observed with the addition of (Al_2O_3) nanoparticles to (PMMA) at the percentage of 1wt%, the value was 117.72 Mpa and significant increase at 2wt%; while a significant reduction occurred in transverse strength at the percentage of 3% the value was 90.110 Mpa. They concluded that addition of Al_2O_3 nanoparticles to acrylic resin improves the thermal properties and transverse strength of acrylic resin at the same time this addition decreases water sorption and solubility.

Girish Nazirkar et al in 2014, evaluated and compared the effect of different concentration of TiO2 NP on the flexural strength of PMMA resins. Specimens made from heat polymerizing resin (DPI) without NP were used as a control group (Group A). The two experimental groups, (Group B and Group C) had 0.5 and 1 % concentration of TiO2 NP respectively. They concluded that the maximum mean flexural strength (90.65 MPa) belonged to the control group; and acrylic resin with 1 % TiO2 NP demonstrated the minimum mean flexural strength (76.38 MPa). Addition of TiO2 NP into acrylic resin can adversely affect the flexural strength of the final product and is directly proportional to the concentration of NP.

Ibrahim M Hamouda, Mohammed M Beyari in 2014, evaluated the effect of addition of glass fibers and titanium dioxide nanoparticles to the conventional acrylic resin. The conventional acrylic resin was modified using 5% glass fibers and 5% titanium dioxide nanoparticles. They concluded that the specimens modified with glass-fibers showed improved flexural strength and toughness similar to that of the high impact acrylic resin. Specimens modified with titanium dioxide nanoparticles exhibited reduction in the flexural properties and toughness. No significant changes were observed in the flexural modulus.

Harini P, Kasim Mohamed, Padmanabhan TV in 2014, evaluated whether the incorporation of titanium dioxide nanoparticles in polymethylmethacrylate (PMMA) increases the flexural strength and to compare the different concentrations of titanium dioxide nanoparticles and its relation to flexural strength. A (CONTROL) with no titanium dioxide (TiO2) nanoparticles, B with 0.5 gms of TiO2 nanoparticles, C with 1 gm of TiO2 nanoparticles and D with 2.5 gms of TiO2 nanoparticles added. The concentrations of titanium dioxide in each group were 1 wt%, 2 wt% and 5 wt%. The result showed highest mean flexural strength is observed in Group D, while the lowest is seen in Group A. The results concluded that polymethylmethacrylate reinforced with different concentrations of titanium dioxide nanoparticles showed superior flexural strength than those of normal PMMA.

Alwan SA and Alameer SS in 2015 [16] conducted a study the effect of addition of 3% weight of treated (silanized) Titanium oxide Nano filler on some physical and mechanical properties of heat cured acrylic denture base material. They concluded that addition of Titanium dioxide Nano particle to heat cure acrylic resin improve the impact strength, transverse strength and surface hardness of heat cure acrylic resin and at the same time this addition decreases water sorption and solubility.

Asopa V et al (2015) [42] and compared the transverse strength, impact strength; surface hardness and water sorption of 10% and 20% zirconia (ZrO_2) reinforced high impact acrylic resin with that of high impact acrylic resin. They concluded that the addition of zirconium oxide as a filler in the high impact acrylic resin increases their transverse strength. Impact strength and surface hardness of the zirconia reinforced specimens were found to have relatively lesser values as compared to the control specimens. Water sorption of the zirconia reinforced specimens was found to increase but was within the limit of ADA Specifications No. 12.

Sama A. Alwan, Shatha S. Alameer in 2015, evaluate the effect of addition of 3% wt of treated (silanized) Titanium oxide Nano filler on some physical and mechanical properties of heat cured acrylic denture base material. They stated that the addition of TiO2 Nano particles to heat cure acrylic resin improve the impact strength, transverse strength and surface hardness of heat cure acrylic resin at the same time this addition decrease water sorption and solubility. On the other hand there was an increase in surface roughness with the addition of 3% wt of silanized TiO2 Nano particles.

Mohamed Ashour Ahmed et al in 2016, evaluated the effect of different concentrations of titanium dioxide nanoparticles (Nps) on the properties of two types of heat polymerized acrylic resin. The tested parameters were flexural strength, impact strength, and microhardness. The two types of acrylic resin used in this study were conventional unmodified (Implacryl, Vertex) and high impact heat polymerized acrylic resin (Vertex-Dental, Netherlands). The result stated that flexural strength considerably decreased by increasing TiO2 concentration in both types of acrylic resin. Impact strength of the conventional acrylic resin modified by 1% of additives significantly increased. The microhardness is significantly increased by addition of 5% of TiO2 Nps. The Incorporation of TiO2 nanoparticles into acrylic resins can adversely affect its flexural strength. Meanwhile, the impact strength can be modified by small percentage of additives (abt. 1%). This effect is directly correlated with the concentration of nanoparticles. On the other hand, concentrations of TiO2 Nps (abt. 5%) positively affect the microhardness of both types of acrylic resin.

Gad et al in 2017 [15] reviewed the enhancement of acrylic denture base resin during the past few decades by giving specific attention to the effect of fiber, filler, and nanofiller addition on poly(methyl methacrylate) (PMMA) properties. He concluded that

- Glass fiber reinforcement significantly increases the mechanical properties of PMMA. Natural fibers (OPEFB) and vegetable fiber can be used, but further investigations are needed.
- Obvious enhancement in the properties of denture base resin material properties was found with the addition of NPs and nanotubes, depending on the application and manipulation.
- Silane coupling agents play a central role in improving bonding between fillers and the resin matrix, and they subsequently improved the resin's properties. The newest reinforcement system is a hybrid one.
- Hybrid fiber, hybrid fillers, or hybrid fiber and filler may considerably enhance the properties of PMMA.

Arora et al in 2017 [43] evaluated the flexural strength, hardness, and impact strength of heat-cured high-impact denture base resins with different polymer/monomer ratios. The samples were divided into five groups based on different powder/liquid ratios (g/ml) with. The polymer/monomer ratio in Group 1 (Ratio - 2.2:1) was the manufacturer's recommended ratio and was used as control. In Group 2, the ratio was 2.7:1, in Group 3, the ratio was 3.2:1, in Group 4, the ratio was 1.9:1, and Group 5 the ratio was 1.6:1. The results showed that the flexural strength values and VHN (Vickers Hardness Test) values showed a similar trend. The values decreased significantly as the ratio was increased or decreased from the control group. He concluded that for reinforcing resins or high impact resins, the manufacturer's recommended polymer/monomer mixing ratio should be used to obtain the appropriate strength of the material.

Ali Mohammad Ali Aljafery in 2018, evaluated the flexural resistance and impact resistance of high-impact acrylic resin with addition of TiO2-Al2O3 nanoparticles. Titanium oxide and aluminum oxide nanoparticle mixture was added to the liquid (monomer) of acrylic resin (high-impact) with sonication at 3 wt% (TiO2:Al2O3 ratio1:1) which was then blended with polymer (powder) of acrylic resin using conventional procedure to form nanocomposite. The result stated that the flexural strength and the impact strength increased with high significance upon the addition of 3 wt% nanoparticle mixture. The incorporation of nanoparticle mixture to acrylic resin (high-impact) material resulted in better flexural resistance and impact resistance of high-impact acrylic resin.

Ali Alrahlah et al in 2018, evaluated a polymethylmethacrylate denture base material modified with TiO2 nanoparticles in terms of nanomechanical, creep-recovery, and relaxation and the effects of addition TiO2 nanoparticles on the thermal and antimicrobial adhesion behaviors. The nanomechanical test results of the PMMA and PMMA/TiO2 nanocomposites indicated that the hardness and modulus in the nanoscale range improved due to TiO2 addition. At a 1200-nm penetration depth, the modulus increased by 10%, 16%, and 29% and hardness increased by 18%, 24%, and 35% with the addition of 1 wt. %, 2 wt. %, and 3 wt. % TiO2, respectively. The creep-recovery and relaxation behaviors of PMMA were significantly improved due to the addition of TiO2. The improvement in the nanohardness, modulus, creep recovery, and relaxation behavior of PMMA due to the addition of TiO2 nanoparticles indicated the role of the nanoparticles in increasing the PMMA matrix stiffness by reducing its mobility and free volume. TiO2 nanoparticles also improved the antimicrobial behaviour of PMMA by significantly reducing bacterial adherence with increasing TiO2 ratio.

Hawraa Khalid Aziz in 2018, investigated the addition of TiO2 nano practical on impact strength, thermal conductivity and color stability of acrylic resin cured by microwave in comparison to the conventional cured of heat-polymerized acrylic resin. He concluded that the microwave curing of acrylic resin had no change in the color stability and thermal conductivity in comparison to the water bath, but the impact strength was decreased. The addition of 3% TiO2 improved the impact and the color stability, but the thermal conductivity did not change.

Materials and Method

In 1937 Dr. Walter Wright introduced polymethyl methacrylate (PMMA), Since the introduction it has been most widely used for the fabrication of complete dentures. In spite of certain drawbacks like poor mechanical strength, low fatigue strength, brittleness, poor thermal conductor and low hardness, it has been the material of choice because of its favorable working characteristics, processing ease, accurate fit, biocompatibility, stability in the oral environment, superior esthetics, and use with inexpensive equipment.[7,57] Flexural failure of denture base resins is considered the primary mode of clinical failure.[41] Hence the ultimate flexural strength of a material reflects its potential to resist catastrophic failure under a flexural load. High flexural strength is crucial to the long term success of dentures.

Modifications in the composition of conventional acrylic resin denture base material can be done to achieve this purpose.[1]

This *in-vitro* study was done to evaluate and compare the flexural strength of heat polymerized acrylic resin denture base material reinforced with 1wt%, 3wt% and 5wt% silanized titanium dioxide nanoparticles.

Material and methods are divided under the following heads:

I. Materials
II. Armamentarium and equipment
III. Method

I. Materials: (COLOR PLATE I)

SR. NO.	MATERIALS	MANUFACTURER	BATCH NO.
1	Heat polymerized acrylic resin (Fig.1)	DPI Heat Cure™, (Dental products of India Ltd)	10111
2	Die stone (Fig.2)	Ultrarock; Kalabhai Karson Pvt Ltd, India	170201
3	Titanium dioxide nanoparticles.(Fig.3)	Aldrich	SHBG2374V
4	Silane coupling agent (3-methacryloxypropyltrimethoxy silane) (Fig.4)	Aldrich	SHBG2374V
5	Toluene (Fig.5)	MERCK	ID21F62193
6	Cold mould seal (separating medium) (Fig. 1)	DPI	8117

II. Armamentarium and equipment (COLOR PLATE II & III)

a) High accuracy balance (Fig.6)
b) Ultrasonicator (Fig.7)
c) Magnetic stirrer (Fig.8)
d) Vacuum rotary evaporator (Fig.9)
e) Glass Beaker (Fig.10)
f) Sterile Syringe (Fig.10)
g) Mixing spatula (Fig.10)
h) Petroleum jelly (Fig.10/15)
i) Para-film (Fig.11)
j) FTIR spectrometer (Fig.12)
k) Brass metal dies (Fig.13)
l) Varsity flasks and clamps (Fig14)
m) Rubber bowls and plaster spatula (Fig.14)
n) Camel hair brush (Fig. 15)
o) Porcelain jar(Fig. 15)
p) Hydraulic bench press (Sirio dental hydraulic press 400) (Fig.16)
q) Acrylizer with thermostat (Fig. 17)
r) Vernier calliper (Fig.18)
s) Sand paper (No. 120) (Fig.15)
t) Universal testing machine (Fig19)
u) Distilled water (Fig.20)

III. Methodology

The basic methodology consisted of-

a) Die preparation

b) FTIR Testing of Non-silanized TiO_2 nanoparticle specimens.

c) Silanization of titanium dioxide nanoparticles

d) FTIR Testing of silanized TiO_2 nanoparticle specimens.

e) Preparation of gypsum mould for fabrication of specimens.

f) Preparation of heat polymerized acrylic resin denture base specimens **(Group A)**

g) Preparation of heat polymerized acrylic resin denture base specimens reinforced with 1wt% silanized titanium dioxide nanoparticles. **(Group B)**

h) Preparation of heat polymerized acrylic resin denture base specimens reinforced with 3wt% silanized titanium dioxide nanoparticles. **(Group C)**

i) Preparation of heat polymerized acrylic resin denture base specimens reinforced with 5wt% silanized titanium dioxide nanoparticles. **(Group D)**

j) Testing of specimens for flexural strength.

A total of 60 specimens were prepared with each group having 15 specimens. The specimens were divided under the following groups:-

Group A	The control group; heat polymerized polymethyl methacrylate denture base resin without reinforcement. (n=15)
Group B	Heat polymerized polymethyl methacrylate denture base resin reinforced with 1wt% silanized titanium dioxide nanoparticles (n=15)
Group C	Heat polymerized polymethyl methacrylate denture base resin reinforced with 3wt% silanized titanium dioxide nanoparticles (n=15)
Group D	Heat polymerized polymethyl methacrylate denture base resin reinforced with 5wt% silanized titanium dioxide nanoparticles (n=15)

a) Die preparation:

Metal dies were fabricated to prepare mould for the fabrication of heat polymerized acrylic resin specimens. Three brass metal dies of dimension 65 mm in length, 10 mm in width, and 3 mm in height were fabricated. (ISO 1567 standard) [42,57]

These fabricated metal dies had two threaded holes through top and bottom surfaces. These holes were of 5 mm in diameter and 3 mm in depth. Screws were used to engage these threaded holes to facilitate easy removal of dies from the stone mold. (PLATE III, Fig.15)

b) FTIR Testing of Non-silanized TiO_2 nanoparticle specimens.

Before silanization of TiO_2 nanoparticles FTIR analysis of non-silanized TiO_2 nanoparticles was done using FTIR spectrometer (model- SHIMIDZU, IR- AFF INITY-1) to obtained the characteristic vibrations of functional groups in Nano-TiO_2 as shown in **Fig. 21**

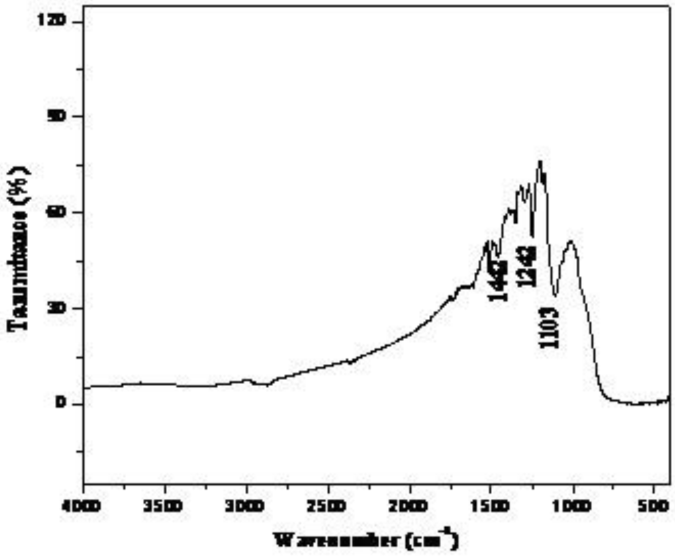

Figure 21 **IR Spectra of nano TiO2 before Silanization**

c) Silanization of titanium dioxide nanoparticles:

100 ml of ethanol aqueous solution (70 vol %) was prepared using 99.8 vol% ethanol and de-ionized water (30 % vol), and adjusted to pH of 4.5 using pH meter through titrating with 99.9% acetic acid. To it 0.1125ml of silane coupling (5% wt to nano filler) [11] agent (3-methacryloxy propyl trimethoxy silane) was added to ethanol aqueous solution, and stirred using magnetic stirrer. After this 5g of titanium dioxide nanoparticles were added into the silane solutions and the mixture was stirred with magnetic stirrer for 20 minutes followed by sonication of the mixture with

probe sonication apparatus for 30 minutes. The solution was left to dry at room temperature for 14 days. [14]

d) FTIR testing of Silanized TiO_2 nanoparticle specimens.

After silanization of TiO_2 nanoparticles FTIR analysis of silanized TiO_2 nanoparticles was done using FTIR spectrometer (model-SHIMIDZU, IR- AFF INITY-1) to obtained the characteristic vibrations of functional groups in modified Nano-TiO2 and to clarify the interaction of Nano-TiO_2 with silane coupling agent (TMSPM) as shown in **Fig. 22**

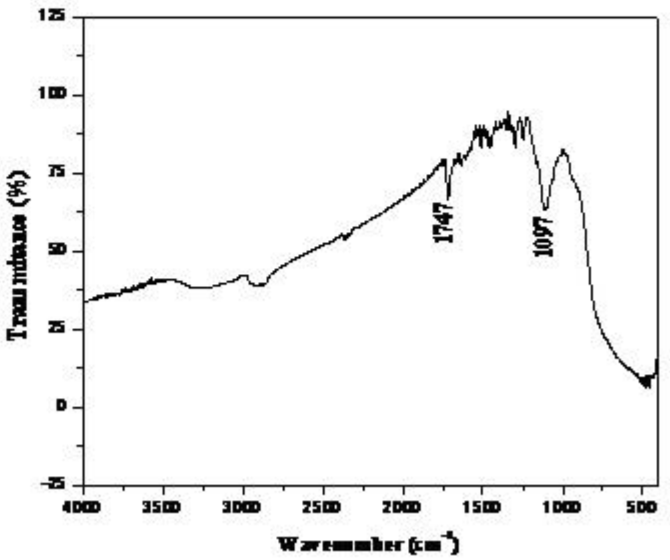

Fig. 22: IR Spectra of nano TiO2 after Silanization

e) Preparation of gypsum mould for fabrication of specimens

Gypsum moulds were prepared with preformed brass metal dies. The threaded holes on the dies were blocked with carding wax before investing them. A thin layer of petroleum jelly was applied on three metal dies which was invested in the lower half of the varsity flask. Investment material (die stone) was used for base flasking taking care to embed half the thickness of the metal die in it.[36] After the investment material had set, a thin layer of petroleum jelly was applied to the metal dies and to the investment material and then the counter flasking was done. The flasks were closed to ensure metal to metal contact between the base of the flask and its counterpart. After the investment material had set (1 hour)[3] the flasks were opened and the carding wax within the holes was removed. The dies were engaged with a screw and gently teased out.

The moulds formed were then immersed in hot water to remove any traces of petroleum jelly, wax and also to facilitate application of separating medium. These mould cavities thus obtained were used for the fabrication of heat polymerized acrylic resin denture base material specimens (PMMA). (PLATE ~~IV~~, Fig.23)

f) Preparation of heat polymerized acrylic resin denture base specimens (Control Group A)

15 samples were prepared using conventional heat polymerized denture base material (PMMA)

As per manufacturer’s recommendation, monomer and polymer were mixed in ratio of 1: 2.5 by weight[59]. An electronic balance of high accuracy was used to weigh the materials. 7.5 gm of polymer powder and 3 ml of monomer was used for preparing 3 specimens. Packing was carried out at dough stage, following which trial closure was performed. Final closure was done under a hydraulic bench press at a pressure of 3000 psi for 3 mins (according to the manufacturer). The flask was clamped and maintained under pressure for 1 hour.[60] It was then immersed in water in an acrylizer at room temperature. The temperature was raised slowly up to 74^0C and was held for 2 hours. The temperature was then raised to 100^0C and was maintained for 1 hour,[61] after completion of this short curing cycle, the flask was removed from the water bath and allowed to bench cool at room temperature prior to deflasking.[60]

The polymerized specimens were carefully removed from the mould. Specimens with defects were discarded. Finishing of the specimens was done using sand paper (No. 120). The finished specimens were stored in distilled water for 1 week at room temperature.[1,42] (PLATE V, Fig.25)

g) Preparation of heat polymerized acrylic resin denture base specimens reinforced with 1wt% silanized titanium dioxide nanoparticles (Group B)

15 samples were prepared using conventional heat polymerized denture base material (PMMA) reinforced with 1wt% silanized titanium dioxide nanoparticles

As per group A, same proportion of monomer and polymer was maintained by taking 0.075 gm of 1wt% silanized titanium dioxide nanoparticles, 7.425 gm of polymer powder and 3 ml of monomer for fabrication of 3 specimens. For complete homogenous dispersion, 1wt% silanized titanium dioxide nanoparticles was added to the monomer.[11,49] An electronic balance of high accuracy was used to weigh the materials.

1wt% silanized titanium dioxide nanoparticles was well dispersed in monomer by using an ultra-sonicator. The ultra-sonication was done at 120 W, 60 KHz for 3 minutes. This allowed the homogenous dispersion of silanized titanium dioxide nanoparticles in the monomer.[11,49] (PLATE IV, Fig.24)

Immediately to this suspension, polymer powder was added gradually to reduce the possibility of particle aggregation and phase separation. Mixing was done according to manufacturer's instructions. Packing, curing, deflasking and finishing was done in the same manner as that for fabrication of heat polymerized acrylic resin denture base (Control group A). Specimens with defects were discarded. The finished specimens were stored in distilled water for 1 week at room temperature.[1,42] (PLATE V, Fig.25)

h) Preparation of heat polymerized acrylic resin denture base specimens reinforced with 3wt% silanized titanium dioxide nanoparticles (Group C)

15 samples were prepared using conventional heat polymerized denture base material (PMMA) reinforced with 3wt% silanized titanium dioxide nanoparticles.

For complete homogenous dispersion, 3wt% silanized titanium dioxide nanoparticles was added to the monomer. [10,58] 7.275 gm of polymer powder, 3 ml of monomer and 0.225 gm of 3wt% silanized titanium dioxide nanoparticles was taken for fabrication of 3 specimens. The finished specimens were stored in distilled water for 1 week at room temperature. (PLATE V, Fig.25)

i) Preparation of heat polymerized acrylic resin denture base specimens reinforced with 5wt% silanized titanium dioxide nanoparticles. (GROUP D)

15 samples were prepared using conventional heat polymerized denture base material (PMMA) reinforced with 5wt% silanized titanium dioxide nanoparticles.

For complete homogenous dispersion, 5wt% silanized titanium dioxide nanoparticles was added to the monomer. [10,58] 7.125 gm of polymer powder, 3 ml of monomer and 0.375 gm of 5wt% silanized titanium dioxide nanoparticles was taken for fabrication of 3 specimens.

The finished specimens were stored in distilled water for 1 week at room temperature. (PLATE V, Fig.25)

j) **Testing of specimens** (PLATE IV, Fig.26)

Testing of specimens was carried out at metallurgical laboratory. The specimens for each group were tested for flexural strength. The flexural three-point bending test is useful in comparing the flexural strength of denture base materials as it simulates the type of stress that is applied to the denture during mastication.

Flexural strength was tested with universal testing machine (Star Testing System, India) at a 0.5 mm/minute crosshead speed.[1] The specimens were supported on the jig separated at a distance of 50 mm. Load was applied at the center of the specimen. Stress- strain curves were recorded on a chart throughout the flexural tests. The maximum load during fracture was determined from the chart and recorded as fracture load in N (Newton) and the flexural strength was calculated in MPa.

Fig 27 showing fractured samples after testing.

Flexural strength (FS) was calculated using the formula.[42]

$$FS = {}^{3PI}\!/_{2bd^2}$$

Where, FS = flexural strength (N/mm^2),

P = load at fracture (N),

I = distance between the supporting wedges (mm),

b = width of the specimen (mm) &

d = thickness of the specimen (mm).

PLATE I

Fig. 1 Heat cure poly – methylmethacrylate & cold mold seal

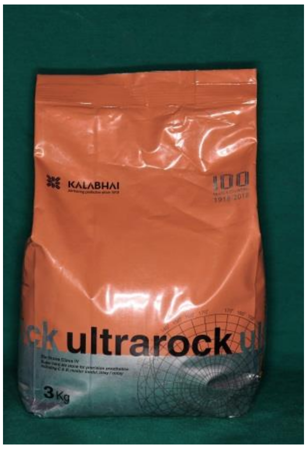

Fig. 2 Die Stone

Fig. 3 Titanium dioxide Nanoparticles

Fig. 4. Silane coupling agent

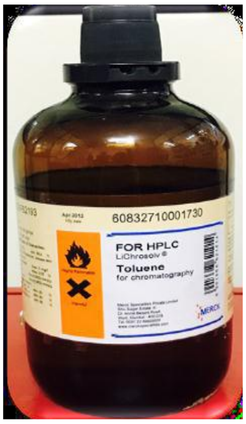

Fig. 5 Toulene

Fig. 6 High accuracy balance

Fig. 7 Ultrasonicator

Fig. 8 Magnetic stirrer

Fig. 9 Vacuum rotary Evaporator

PLATE II

Fig. 10 Glass beaker, Sterile syringe Mixing spatula, Vaseline

Fig. 11 Para film

Fig.12 FTIR spectrometer

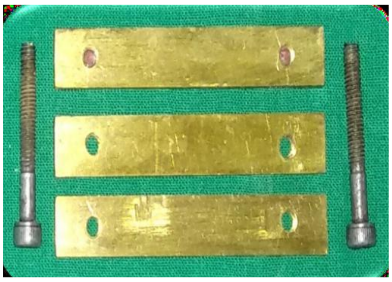

Fig. 13 Brass metal dies

Fig.14 Varsity flask & clamp Rubber bowl, Spatula

Fig. 15 Camel hair brush, Porcelain jar, sandpaper

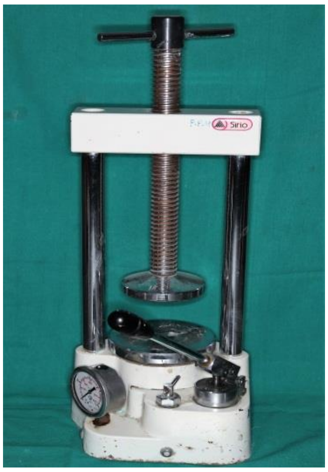

Fig. 16 Hydrollic press

Fig. 17 Acrylizer with Thermostat

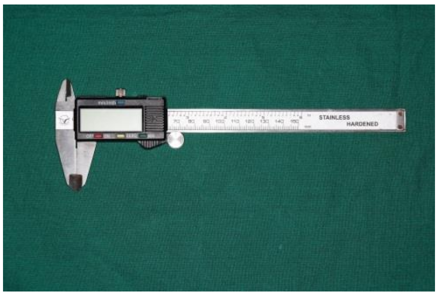

Fig. 18 Vernier calliper

PLATE III

Fig. 19 Universal Testing Machine

Fig. 20 Distilled water

Fig. 23 Preparation of Gypsum mold

Fig. 24 Silanization process

PLATE IV

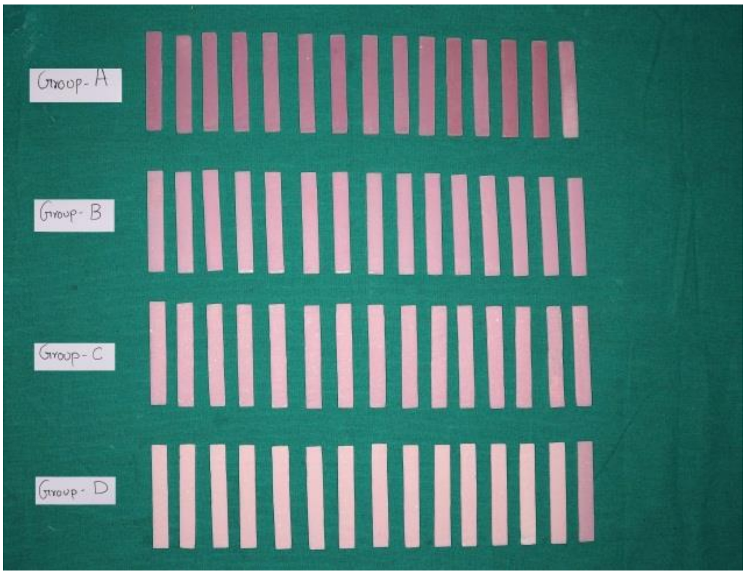

Fig. 25 Samples of Group A, Group B, Group C, Group D before testing

Fig. 26 Testing of samples

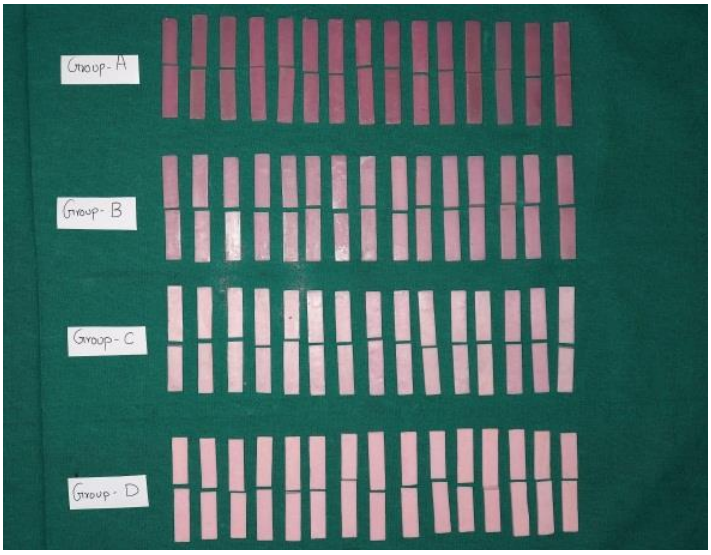

Fig. 27 Samples of Group A, Group B, Group C, Group D after testing

Results

"Success is the result of perfection, hard work, learning from failure, loyalty, and persistence." *-Colin Powell*

In this study, flexural strength of heat polymerized polymethyl methacrylate acrylic resin specimen reinforced with 1 wt% silanized titanium dioxide nanoparticles, 3 wt% silanized titanium dioxide nanoparticles and 5 wt% silanized Titanium dioxide nanoparticles was evaluated and compared with the non-reinforced heat polymerized polymethyl methacrylate denture base resin specimens.

60 samples were prepared in total and were divided into four groups, including 15 samples in each group.

DISTRIBUTUON OF SAMPLES INTO GROUPS

Sr. No	Groups code	Group	n= no. of Samples
1.	**A**	The control group; heat polymerized polymethyl methacrylate denture base material without reinforcement. (n=15)	n=15
2.	**B**	Heat polymerized polymethyl methacrylate denture base material reinforced with 1 wt% silanized Titanium dioxide nanoparticles. (n=15)	n=15
3.	**C**	Heat polymerized polymethyl methacrylate denture base material reinforced with 3% silanized Titanium dioxide nanoparticles. (n=15)	n=15
4.	**D**	Heat polymerized polymethyl methacrylate denture base material reinforced with 5% silanized Titanium dioxide nanoparticles. (n=15)	n=15

Specimens of each group were subjected to flexural strength test on Universal Testing Machine at a crosshead speed of 0.5 mm/min. The maximum load was determined from the chart and recorded as fracture load in N (Newton). The flexural strength was calculated in MPa and the results were statistically analysed.

STATISTICAL ANALYSIS:

The data was analysed using SPSS statistical software. The *p* value was taken as significant when less than $p < 0.05$

The statistical test used for the analysis of the results were:

1. One-way ANOVA (Analysis of Variance)
2. Independent samples t-test
3. Bonferroni multiple comparison test

- The mean, median and standard deviation were calculated by ANOVA (one-way analysis of variance).
- Pair-wise comparison of Mean flexural strength of four groups was carried out by independent samples t-test.
- Statistical significance of all the possible six pairs of means were analysed by Bonferroni multiple comparison test.

Mean is sum of all observations and divided by number of observations.

Median is value of the variable that divides the distribution in two equal parts i.e. 50% of the observations will be below and above it.

Standard Deviation is summarized as the amount of variation (change) in the observation from their average value (mean).

Standard Deviation is the most frequently used measure of deviation. It is defined as root mean square deviation and is denoted by s or SD.

The formula for calculating standard deviation:

$$\boldsymbol{SD = \sqrt{\frac{\Sigma(\bar{x}-x)^2}{n-1}}}$$

Where, $\bar{x}$ = Mean

x = the values of variable

Σ = Sum of the value

n = Number of the observations

Min = Minimum value

Max = Maximum value

FLEXURAL STRENGTH RESULTS AND STATISTICAL ANALYSIS:

The results obtained after flexural strength test revealed that the flexural strength values of all the four groups exceeded the minimal value of 65 MPa for denture base resin according to ADA Specification no. 12.

Table 1 provides the descriptive statistics for flexural strength of test samples in three study groups. As evident from the table, the maximum mean flexural strength (**111.01 MPa**) belonged to the **Group B** and the strength ranged between 87.86667 to 124.4833 MPa. The mean of **Group D** was minimum i.e. **92.37 MPa** and the strength ranged between 78.39167 to 102.9 MPa. For **Group A,** the mean flexural strength was **95.05 MPa** and ranged between 84.59167 to 105.0167 MPa. In **Group C**, the mean flexural strength was **104.19 MPa** and ranged between 91.575 to 112.825 MPa. A graphical visualization of mean strength along with standard deviation bar is given in the **Graph-I.**

Statistically significant difference in mean flexural strength across the four groups was established by the **one-way ANOVA** (Analysis of variance) as reviled in **Table 2** and it shows largest difference in means was observed in the pair-**Group B** versus **Group C** which also exhibited contrasting variability i.e. the highest and lowest coefficient of variation.

Table 3 shows statistical significance of all the possible six pairs of means were analysed by Bonferroni multiple comparison test and it revelled highly significant difference in the means three pairs of groups that is Group A and Group B, Group B and D, Group C and D with p value 0.001 and difference between mean of Group A and C was statistically significant with p value 0.016.

However it was found that, the difference in mean flexural strength of remaining two comparisons that is Group A versus D, Group B versus C was statistically not significant.

Table 4 revels that mean flexural strength was found more in Group B and Group C, but amount of variation was observed more in Group B and Group D.

Both Standard deviation (the measure of absolute variation) and Coefficient of variation (the measure of relative variation) were also found higher in Group B and Group D.

Standard error of the mean which indicates the extent of variability of the observed mean in the samples was found comparable for Group A and Group C, but was the highest in the Group B. **(graph 2)**

Table 5 shows Two-independent samples t-test was used to rule out significance of difference in mean flexural strength in only one-pair i.e. Group A versus D. Remaining five pairs indicated statistically significant mean differences. **(Graph 3)**

FTIR SPECTROMETER ANALYSIS RESULTS:

Before incorporating TiO_2 nanoparticles silanization was done using silane coupling agent trimethoxysilylpropylmethacrylate (TMSPM) and compatibility of TMSPM with TiO_2 particles was confirmed by Fourier-transform infrared (FTIR) spectroscopy

FTIR analysis of TiO_2 nanoparticles before silanization and after silanization of nanoparticles was done and results of infrared (IR) Spectra were obtained by analyzing the characteristic vibrations of functional groups in Nano-TiO2 and modified Nano-TiO2 with silane coupling agent (TMSPM) using FTIR spectrometer (model- SHIMIDZU, IR- AFF INITY-1). **(Fig.12)**

FTIR spectrum was used to measure the different functional groups present in the TiO_2 nanoparticles, **(Fig. 21)** represents FT-IR spectra of bare TiO_2 nanoparticles in the range of 400-4000cm^{-1}. The peaks at 1103, 1242, 1442 cm $^{-1}$ are due to bonding between stretching vibration of –OH group, Ti-O-Ti and Ti-O.

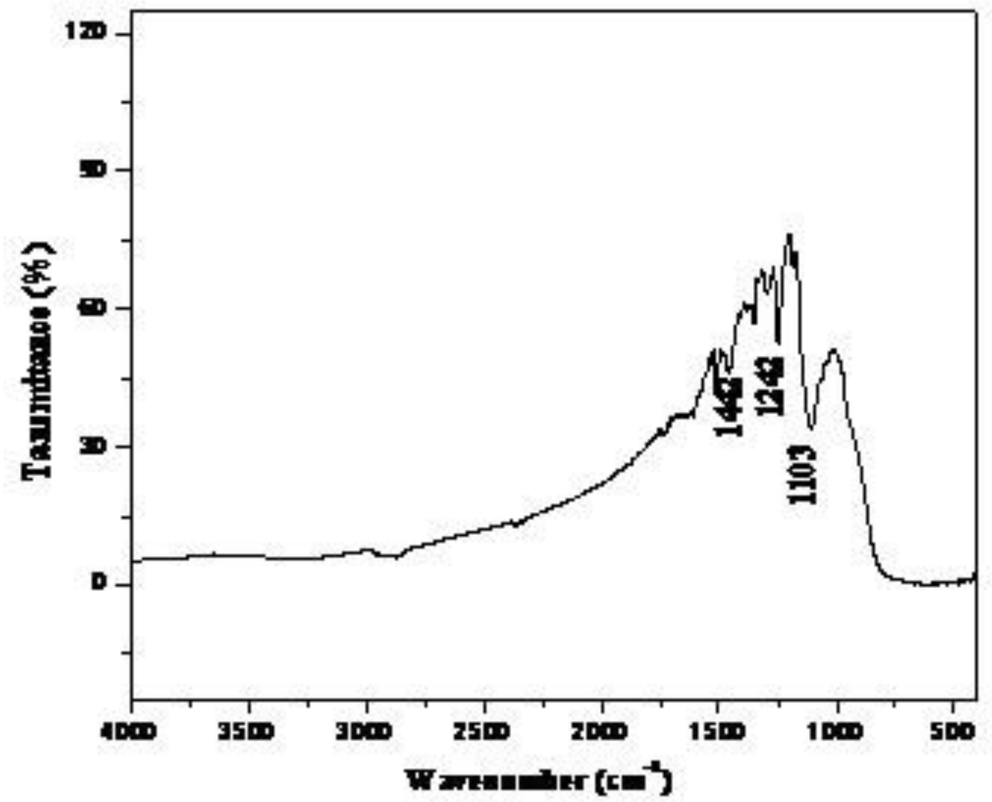

Figure 21: IR Spectra of nano TiO2 before Silanization

FTIR spectrum after silanization **(Fig. 22)** revelled that bond position shifted from 1442 to 1747 and it was due to the silanization and 1747 stretching indicates the presence of 'acrylates' which is a component of silane coupling agent trimethoxysilylpropylmethacrylate (TMSPM) suggestive of successful silanization of silane coupling agent (TMSPM) over TiO_2 nanoparticles.

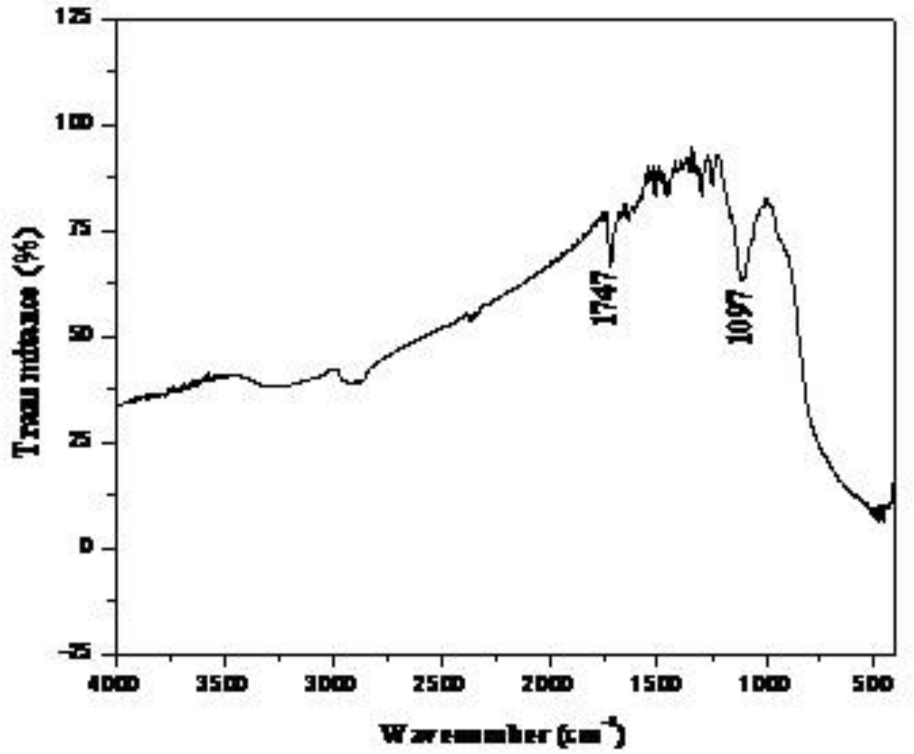

Figure 22: IR Spectra of nano TiO2 after Silanization

Discussion

Since ages, dentistry has been dependant on naturally occurring materials, to a large extent, for the fabrication of dentures to rehabilitate partially or completely edentulous patients. In the past, the materials used for denture bases were vulcanite, celluloid & phenol formaldehyde[60]. Vulcanite was replaced by polymethyl methacrylate in 1937, enhancing both physical and esthetic properties. Since it is easy to manipulate and is inexpensive, polymethyl methacrylate resin is extensively used as the material of choice in removable prosthodontics[61]. But it has certain drawbacks like residual monomer allergy, poor mechanical strength, low fatigue strength and poor conductor of heat. Its disadvantages also include low hardness, high coefficient of thermal expansion, thermal shrinkage, porosity, crazing and warpage. It shows poor adhesion to metal when used with metal base dentures and with porcelain teeth.[36, 60]

The fracture of acrylic resin dentures is an unresolved problem in prosthodontics. A study by **Johnston et al** showed that 68% of acrylic resin denture fractures within the first three years after fabrication, [62] and typically the ratio of upper and lower denture fracture is 2:1. These fractures often occur in or close to the midline. Midline fracture of a denture base is because of flexural fatigue failure. The most common causes of denture fracture are poor fit, lack of balanced occlusion and deep notching at the midline i.e. labial frenum.[63]

Smith (1961) analyzed the practical situation with respect to the fracture of dentures and showed two types of failure.[62]

i) Outside the mouth, caused by impact forces, i.e. a high stress rate and

ii) Inside the mouth, usually in function; this is probably a fatigue phenomenon, i.e. a low and repetitive stress rate.

These considerations led to the conclusion that denture fracture occurs through flexural failure under the clinical conditions. For this reason, flexural strength tests were selected as most relevant to evaluate the strength of denture base resins.

Studies have shown that the average values of flexural strength of heat polymerizing acrylic resins are near to 78-92 Mpa[64]. Historically, the search for higher strength polymer denture base material has taken researchers through many avenues. Various substitutes for polymethyl methacrylate have been introduced such as polystyrene, poly vinyl acrylic, polyamides (nylons) and light activated urethane dimethacrylate resins were used. Although these materials exhibited desirable properties, none have been proven superior to polymethyl methacrylate (PMMA).[61]

The chemical modification of polymethyl methacrylate through the addition of rubber in the form of butadiene styrene has been studied. Modifications of the chemical structure, by adding cross-linking agents or copolymerization with rubber resulted in significant increase in impact strength. However, stiffness, fatigue resistance, and transverse strength were reduced.[42]

Other attempts to enhance the properties of strength include incorporation of metal wire, metal mesh and casted framework to resin. The primary problem with using metal wire is poor adhesion between the wire and resin, which leads to insignificant enhancement of mechanical properties[42,24,26]. Failure due to stress concentration around the embedded inserts has been reported. Although metal plates increase the strength, they may be expensive and prone to corrosion.[42]

Certain fillers can be incorporated in heat cure denture base resin to enhance its mechanical properties. These include fibres, metal oxides, and ceramic powders etc[31].The fibre-reinforced plastics are commonly used in many fields of industry because of their good mechanical properties, which can be tailored to specific needs. Various fibres that have been tested and used included kevlar fibres[65,66,33]. glass fibres[49,58,68] and ultra-high molecular weight polyethylene fibres.[68]

Reinforcement of dental resin with short or long fibres has been described in the literature for nearly half a century. Fibres have been used, with varying results but fibre reinforcement has never been adapted to routine clinical practice. Effective fibre reinforcement is dependent on many variables, including the type of the fibres, the percentage of fibres in the matrix, the modulus and distribution of the fibres, fibre length, orientation, forms, and interfacial bond.[5] Although the inclusion of the fibres produced encouraging results, this method has various problems including tissue irritation, increased fabrication time, difficulties in handling, the need for precise orientation of fiber in resin matrix and placement or bonding of the fibres within the resin.[42]

The concept of self-reinforcement (with a material that is chemically identical to the matrix holding the fibre in place) has been studied recently by **Jagger, Harrison and Jandt (2000)**.[20] Unfortunately the effect of the addition of untreated and surface treated chopped PMMA fibres did not produce a significant improvement in either the transverse strength or impact strength of acrylic resin.[5]

Metallic powders have been added to conventional denture base resins by various investigators. Several studies in past by **Sehjpal and Sood(1989)[10] , Abdulhamed and Mohammed Ali (2010)[69], Yadav and Elkawash (2011)[70]** showed that addition of metal oxides (silver, aluminium, or copper powder) to PMMA did not significantly increase the tensile strength of acrylic resin. The thermal conductivity of modified acrylic resin was increased; explanations given for this reduction in strength included a decrease in the cross-section of load-bearing polymer matrix, stress concentration because of filler particles, change in the modulus of elasticity of resin and mode of crack propagation through it because of fillers, void formation from entrapped air and moisture, and incomplete wetting of the fillers by resin.[38]

TiO_2 particles are preferred in dentistry because of their pleasing colour, high biocompatibility, elastic modulus approximately 230 GPa., as well as availability and low cost, have made TiO_2 an appropriate additive for dental resin materials.[71]

Thorat et al. prepared and characterized bis-GMA resin dental restorative composites with glass, silica, and titanium fillers. The researchers concluded that TiO_2 fillers could be useful in future applications because their photocatalytic effects promote local antibacterial or remineralization reactions. Likewise studies have been performed by **Asar NV et al, Alwan SA and Alameer SS** to modify dental composites by incorporating TiO_2 nanoparticles into a standard dental acrylic. Such studies have reported that the most available commercial product for dental restorations could be improved through the addition of nano TiO_2.[14,43]

Gad M, Fouda S et al. investigated the effect of adding titanium dioxide (TiO_2) on the properties of PMMA. It was found that adding TiO_2 particles could improve the flexure strength, fracture toughness, hardness of PMMA, as well as thermal conductivity. In addition, a significant increase in impact strength and a significant decrease in water sorption.[13]

Safi et al found that modifying PMMA with TiO_2 nanoparticles has an effect on its thermal and mechanical stability, while a reduction in flexural strength and toughness was reported. Adhesion between the resin matrix and filler particles is very important in order to enhance the composite’s properties.

Accordingly, a titanium coupling agent could be useful for improving the properties of titanium-reinforced PMMA. Incorporation of silanized

TiO_2 nanoparticles in PMMA improved the impact strength, flexural strength, and surface hardness of the resin and decreased its water sorption and solubility. [13]

One of the deficiencies of the available denture base resins is their radiolucency and in some studies it is stated that all, or more portion of a denture may become lodged in the body through accidental ingestion, aspiration, or by automobile accidents and explosions, so to detect those fragments radiographically dentures should be radiopaque. This can be achieved by incorporating metal oxides in to denture base materials.[72] Another major drawback of PMMA is its low thermal conductivity[73] this compromises the patient's appreciation of taste and palpability. It is therefore desirable to make the denture base thermally conductive,[41,45] Polymethylmethacrylate (PMMA) also absorbs water when placed in an aqueous environment like while cleaning, during the use of denture and this affects mechanical and dimensional properties of the polymer.[43] Studies has been done which stated that incorporation of various metal oxides like titanium dioxide, zirconium oxide and aluminium oxide lead to a decrease in water sorption and water solubility values.[43]

Titanium Dioxide nanoparticles (TiO_2) was used in the present study to evaluate the flexural strength of PMMA because it is a biocompatible material (nontoxic) and have pleasing color[74,75],as well as it gives radio opacity to the dentures and also increase its thermal conductivity and reduces the water sorption by the resin.

Nano particles are of size < 100 nm, and the structure of material that has particles of a nanometre size possesses special properties. The reason could be in their high surface area to volume ratio. This results in appearance of new mechanical, chemical, electrical, optical, magnetic, electro-optical, and magneto-optical properties of the nanoparticles that are different from their bulk properties.[46]

Because of this reasons it was decided to incorporate nano sized TiO_2 to improve the physical properties of PMMA denture base resin

Study done by **Nazirkar G. et al.[46]** where non silanized particles was used for reinforcement, results were not found to be promising because of poor bonding between TiO2 nanoparticles and resin matrix, hence silane was used in this study as silane have the ability to bond inorganic materials such as metal and metal oxides to organic resins resulting in improved mixing, better bonding and increased matrix strength.[48]

Vallittu (1993) showed an improved adhesion between any metal and acrylic resin with the use of silanizing agents which produced a subsequent enhancement in fracture resistance.

Silanes are basically chemical substances which bond inorganic fillers or fibers to organic resins, to form or promote a stronger bond at the interface.[65] Silanization of the filler particle phase yields a better dispersion and wetting for filler particles, it also lowers the viscosity between a filler and liquid resin system, thereby improving the physical properties of composites.[24,25,27]

In 2015 Tsuji M, Ueda1 T. conducted a study on biocompatibility of a titanium dioxide-coating method for denture base acrylic resin and stated that silanated nanoparticles is the material of choice for reinforcing denture base polymers.[76]

In 2015 Sama A. Alwan, conducted a study which concluded highly significant increase in impact strength and transverse strength was observed with the addition of (TiO_2) Nano particles after silanization with TMSPM (3-methacryloxypropyltrimethoxy silane) silane coupling agent to PMMA denture base resin.[50]

Hence for this study, Titanium dioxide nanoparticles were silanized before incorporating them into the PMMA denture base resin for better bonding of inorganic compound like TiO_2 nanoparticles with organic resin matrix. FTIR (Fourier Transform Infrared Spectroscopy) was done to verify the compatibility of silane (TMSPM) with TiO_2 nanoparticles

Fourier Transform Infrared Spectroscopy (FTIR) is one of the most widely used and well-established spectroscopic methods to monitor polymerization processes, to characterize polymer structure, to examine polymer surfaces and to investigate polymer degradation processes and for analysing and characterize the structure of polymers. FTIR spectroscopy presents a sensitive analysis tool to detect composition changes in biomaterials.[77] It is based on the interaction between electromagnetic radiation and natural vibrations of the chemical bonds among atoms that compose the matter.[78]

Hence FTIR spectrophotometer was used to determine whether or not functional group of the TMSPM have been attached to TiO_2 Nano filler by analyzing characteristic vibrations of functional groups.[50] FTIR analysis showed successful silanization of TiO_2 nanoparticles with silane (TMSPM) which was confirmed by presence of 'acrylates' on the surface of TiO_2 nanoparticles, which is a component of silane coupling agent.

The concentration of NP added is an important factor in determining its effect on the mechanical properties of the substrate. For instance, in a study conducted by Elsaka et al. on the influence on physical properties of TiO_2 NP added to conventional glass ionomer cement (GIC), TiO2 were incorporated in 3, 5 and 7 % concentration. GIC-containing 3 and 5 % TiO2 NP improved the mechanical properties. However, a decrease in mechanical properties was found as the concentration increased to 7 %. In another study conducted by Sodagar et al. on the effect of TiO_2 and SiO_2 NP on cold cure resin, the strength decreased as the concentration of NP increased. Also, addition of nanosized oxides up to 2.5 % increased the tear strength of silicone elastomer, above which the strength decreased.[46]

Alwan SA and Alameer SS in 2015[50] conducted a study to evaluate the effect of addition of 3% weight of treated (silanized) Titanium oxide Nano filler on some physical and mechanical properties of heat cured acrylic denture base material. They concluded that addition of Titanium dioxide Nano particle to heat cure acrylic resin improve the impact strength, transverse strength and surface hardness of heat cure acrylic resin.

There was not much studies performed on the effect of silanized TiO_2 nanoparticle on flexural strength of PMMA denture base material in last decade. Only one study was reported which shows increase in flexural strength after incorporating only 3wt% silanized TiO2 nanoparticle. Therefore it was decided to check flexural strength of PMMA denture base material by incorporating different percentages i.e. 1wt%, 3wt% and 5wt% of Silanized TiO2 nanoparticles so as to find optimum wt% of TiO_2 nanoparticles for reinforcement.

In this study there was an increase in the value of flexural strength when 1wt%, 3wt% of silanized TiO_2 nanoparticles were added to PMMA with mean value of **111.01 Mpa** and **104.19 Mpa respectively** when compared to control group with mean value of **95.06 Mpa**. However it was found that the value of flexural strength was lesser than control group when reinforced with 5wt% TiO_2 with mean value of **92.37 Mpa**, but that decrease in the flexural strength was not statically significant.

Maximum value of flexural strength belongs to 1wt% TiO_2 nanoparticles with mean value of **111.01Mpa** which was statically significant.

This increase in flexural strength with addition of nano fillers (TiO_2) might be due to high interfacial shear strength between nano fillers and matrix, also the crack propagation could have decreased because of bonding between nano filler and resin matrix. Dispersion of the <100 nm size of Nano particles in the resin matrix because as particle size decrease, the total particle-resin matrix interfacial surface area available for energy dissipation increase and the critical stress for particles- resin matrix debonding also increase. The result of this study is in the favour with result obtained by Alwan SA and Alameer SS in 2015[50] who also reported improved flexural strength after incorporation of silanized TiO_2

The decrease in flexural strength values is seen above 1 wt% concentration of TiO_2 nanoparticle which might be because after certain concentration of filler particle in resin matrix can act as an impurity and interfere with the polymerization reaction. The nanoparticles additive acts as a plasticizer leading to increase in amount of residual unreacted monomer, decreasing the strength of the material which is in acceptance with study done by Girish Nazikar in 2014.

CLINICAL IMPLICATION

When the entire spectrum of this study was analyzed, it become evident that the heat polymerized denture base material reinforced with 1wt% silanized Titanium dioxide nanoparticles increases the flexural strength of the denture base material and thus, reduces the probability of occurrence of fracture. As it contains metal oxides It also increases the thermal diffusivity of the denture base material, which enhances the patient’s perception to hot and cold, hence improving the adaptability of the patient to the denture. This in turn, aids in better comfort and satisfaction with the prosthesis during use. In addition to this, it imparts radio-opacity to the material so that any fractured remnants can be detected radiographically.[40]

SCOPE FOR FURTHER STUDIES

1. Further studies are required to find out the precise optimum concentration of silanized TiO_2 nanoparticles by incorporating concentration around 1 wt%, as in this study concentration above 1wt% showed decrease in flexural strength.
2. Fatigue testing of these materials under dynamic loading using the denture base configurations in simulated oral conditions, using saliva or its substitutes is an area for further research.
3. Further research is needed to evaluate the effect of aging on the new reinforced denture base material in simulated oral conditions before clinical application.
4. Other physical and mechanical properties like thermal diffusivity, hardness, abrasion resistance, color stability and disinfectant property can be studied.
5. Further research is also needed to quantify the filler distribution in the polymer matrix by Scanning electron microscopy (SEM)

LIMITATIONS OF THE STUDY

In this study samples were prepared in accordance with ADA specification number 12 and the study was designed and carried out with utmost accuracy. The present study has certain limitations which are enlisted below.

1. In the oral cavity, reinforced denture base is exposed to forces of varying magnitudes acting in different directions. The same situation could not be simulated in this in vitro study.

2. Scanning electron microscopy (SEM) examination of the samples to evaluate the adhesion of zirconium oxide nanofillers on the surface of PMMA was not performed.

Summary

Success is lousy teacher.

It seduces smart people into thinking they can't lose.

– Bill Gates

The heat cure denture base resins are extensively used in dentistry because of their excellent properties such as ease of handling, polishing and esthetics. However, the flexural strength is not sufficient to maintain the longevity of the denture. The fracture of acrylic resin denture is a common occurrence and it is an unresolved problem in prosthodontics.

This study was conducted to evaluate and compare the flexural strength of heat polymerized acrylic resin denture base material reinforced with 1 wt%, 3wt% and 5wt% silanized Titanium dioxide nanoparticles and one control group. Standard heat cured acrylic resin specimens were fabricated according to ADA specification no. 12 and were reinforced with silanized titanium dioxide nanoparticles, with 15 specimens in each group.

Flexural strength was tested using universal testing machine at a crosshead speed of 0.5mm/min. The findings were statistically analysed and the flexural strength was calculated in MPa.

Results show that the mean flexural strength for **Group B** was maximum i.e. **111.01** Mpa. For **Group A**, the mean strength was **95.05** Mpa, for **Group C** was **104.19** Mpa and the mean strength in **Group D** was minimum among all i.e **92.37** Mpa. The statistical analysis shows **highly significant** difference in the means of Group A and Group B ($p < 0.0001$). Also, the difference between Group A and Group C, Group B and Group D, Group C and Group D is statistically significant ($p < 0.0001$.

However, the difference between Group A and Group D was **statistically insignificant** as revealed by p-value of 0.3281 ($p > 0.05$).

Thus reinforcement with 1 % by wt silanized Titanium Dioxide nanoparticles **(Group B)** showed a highly significant increase in flexural strength compared to 3 wt% Titanium Dioxide nanoparticles **(Group C)** and to 5 wt% Titanium Dioxide nanoparticles **(Group D)** and unreinforced specimens i.e. heat polymerized acrylic resin denture base specimens **(Group A)**

Conclusion

Within the limitations of this study following conclusions were drawn:

1. PMMA denture base material reinforced with silanized TiO_2 nanoparticles reveled increase in flexural strength in order 1wt% > 3wt% > 5wt% concentration.

2. Increasing concentration beyond 1wt% led to reduced flexural strength and hence reinforcement with more than 1wt% is not recommended.

3. Optimum concentration for reinforcement was found to be 1wt%.

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Tables and Graphs

Table 1: Descriptive statistics for Flexural Strength

GROUPS	N	Mean	Median	SD	Range
Group A (Control)	15	95.06	95.39	6.43	[84.59167 to 105.0167]
Group B (1 wt% TiO_2)	15	111.01	111.87	10.13	[87.86667 to 124.4833]
Group C (3 wt% TiO_2)	15	104.19	103.00	6.33	[91.575 to 112.825]
Group D (5 wt% TiO_2)	15	92.37	94.24	8.26	[78.39167 to 102.9]

Table 2: Comparison of Mean flexural strength across the groups by one-way ANOVA (Analysis of Variance)

Source	Sum of Squares	Degrees of Freedom	Mean Sum of Squares	F-value	P-value
Between groups	3295.47	3	1098.49	17.42	0.0001**
Within groups	3531.56	56	63.06		
Total	6857.03	59	115.71		

** Highly Significant

Table 3: Pair-wise comparison of Mean flexural strength of four groups by Bonferroni Multiple Comparison test

Group-wise Pairs	Means of two comparison groups	Mean difference (95% CI)	P-value
Group A versus B	111.01 versus 95.06	15.95 (9.60 – 22.30)	**0.001****
Group A versus C	104.19 versus 95.06	9.13 (4.36 – 13.90)	**0.016***
Group A versus D	92.37 versus 95.06	-2.69 (-2.85 – 8.23)	**1.0**
Group B versus C	111.01 versus 104.19	6.82 (0.51 – 13.14)	**0.133**
Group B versus D	111.01 versus 92.37	18.64 (11.73 -25,55)	**0.001****
Group C versus D	104.19 versus 92.37	11.82 (6.32 -17.33)	**0.001****

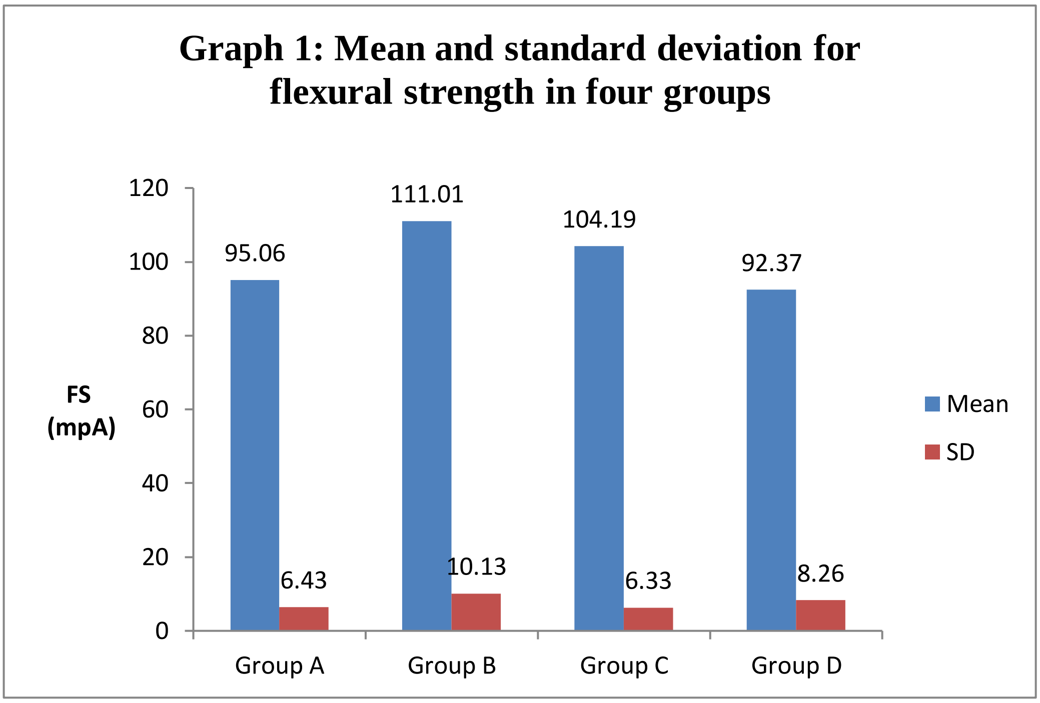
** Highly Significant *Significant

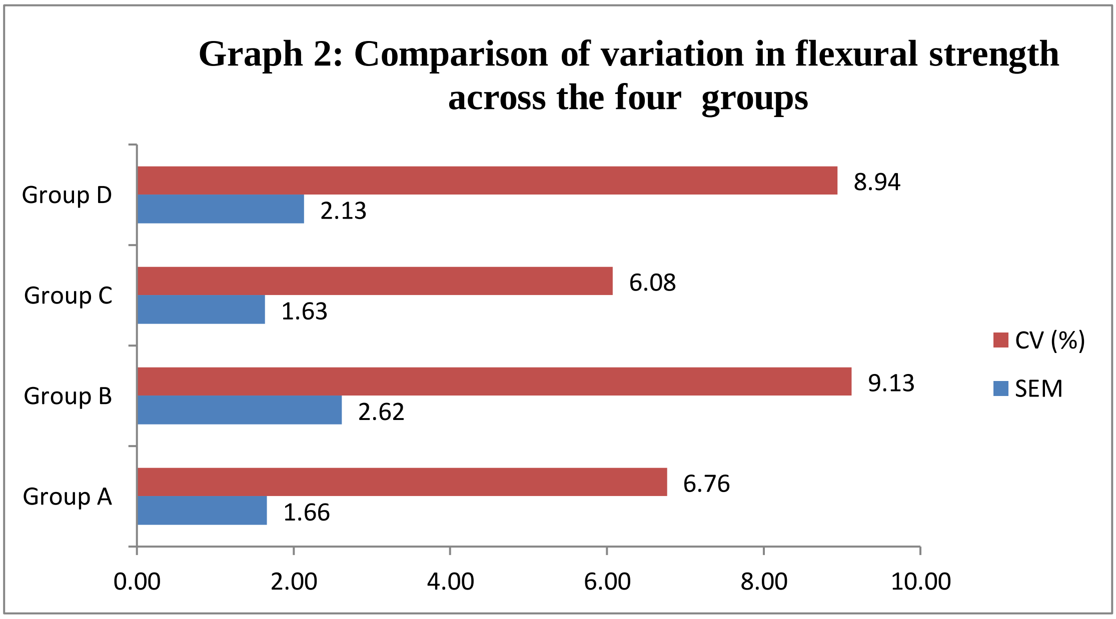
Table 4: Mean flexural strength (FS) in control and three study groups along with different measures of variation

Groups	n	Mean	Standard Deviation	Standard error of Mean	Coefficient of Variation (%)
A	15	95.06	6.43	1.66	6.76
B	15	111.01	10.13	2.62	9.13
C	15	104.19	6.33	1.63	6.08
D	15	92.37	8.26	2.13	8.94

Table 5: Pair-wise comparison of Mean flexural strength of four groups by two-independent samples t-test.

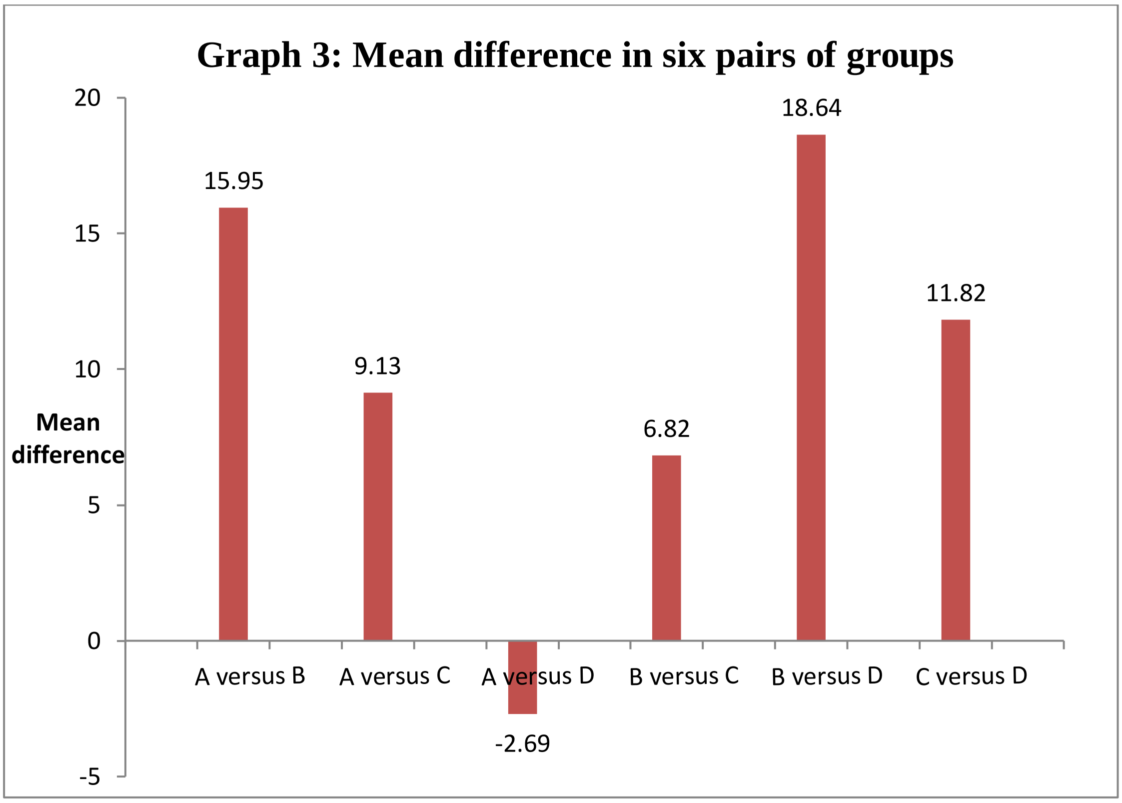
Pairs for comparison	t-value (with 28 degrees of freedom)	P-value	Significance
Group A versus B	5.1485	0.0001	**Highly Significant**
Group A versus C	3.9189	0.0005	**Highly Significant**
Group A versus D	-0.9953	0.3281	**Not Significant**
Group B versus C	2.2113	0.0354	**Significant**
Group B versus D	5.5232	0.0001	**Highly Significant**
Group C versus D	4.399	0.0001	**Highly Significant**





Standard error of the mean (**SEM**)

Coefficient of variation (**CV**)


Graph 3: Mean difference in six pairs of groups
20
15
10
5
0
-5
Mean difference
15.95
9.13
-2.69
6.82
18.64
11.82
A versus B
A versus C
A versus D
B versus C
B versus D
C versus D

ANNEXURE

Master Chart

GROUP – A (control group) (Heat polymerized polymethyl methacrylate without any reinforcement)			
Sr. No.	**Sample No.**	**Flexural Load (N)**	**Flexural Strength (MPa)**
1.	No. 1	122.79	102.325
2.	No. 2	112.89	94.075
3.	No. 3	123.77	103.1417
4.	No. 4	114.96	95.8
5.	No. 5	118.81	99.00833
6.	No. 6	126.02	105.0167
7.	No. 7	116.71	97.25833
8.	No. 8	111.52	92.93333
9.	No. 9	121.12	100.9333
10.	No. 10	112.52	93.76667
11.	No. 11	114.46	95.38333
12.	No. 12	101.51	84.59167
13.	No. 13	102.5	85.41667
14.	No. 14	106.38	88.65
15.	No. 15	105.1	87.58333
			Average- 95.05

GROUP – B (Heat polymerized polymethyl methacrylate reinforced with 1wt% silanized TiO_2 nanoparticles))			
Sr. No.	**Sample No.**	**Flexural Load (N)**	**Flexural Strength (MPa)**
1.	No. 1	134.55	112.125
2.	No. 2	128.5	107.0833
3.	No. 3	125.36	104.4667
4.	No. 4	141.71	118.0917
5.	No. 5	134.17	111.8083
6.	No. 6	138.25	115.2083
7.	No. 7	143.23	119.3583
8.	No. 8	123.38	102.8167
9.	No. 9	134.25	111.875
10.	No. 10	105.44	87.86667
11.	No. 11	149.38	124.4833
12.	No. 12	133.35	111.125
13.	No. 13	149.35	124.4583
14.	No. 14	115.39	96.15833
15.	No. 15	141.91	118.2583
			Average- 111.01

GROUP – C

(Heat polymerized polymethyl methacrylate reinforced with 3wt% silanized TiO_2 nanoparticles)

Sr. No.	Sample No.	Flexural Load (N)	Flexural Strength (MPa)
1.	No. 1	122.79	102.325
2.	No. 2	133.22	111.0167
3.	No. 3	135.31	112.7583
4.	No. 4	120.8	100.6667
5.	No. 5	109.89	91.575
6.	No. 6	127.51	106.2583
7.	No. 7	121.6	101.3333
8.	No. 8	125.46	104.55
9.	No. 9	123.6	103
10.	No. 10	128.05	106.7083
11.	No. 11	135.39	112.825
12.	No. 12	121.37	101.1417
13.	No. 13	113.38	94.48333
14.	No. 14	134.55	112.125
15.	No. 15	122.5	102.0833
			Average- 104.19

GROUP – D (Heat polymerized polymethyl methacrylate reinforced with 5wt% silanized TiO_2 nanoparticles)			
Sr. No.	**Sample No.**	**Flexural Load (N)**	**Flexural Strength (MPa)**
1.	No. 1	111.91	93.25833
2.	No. 2	98.29	81.90833
3.	No. 3	119.65	99.70833
4.	No. 4	108.24	90.2
5.	No. 5	115.23	96.025
6.	No. 6	121.37	101.1417
7.	No. 7	113.09	94.24167
8.	No. 8	123.48	102.9
9.	No. 9	98.14	81.78333
10.	No. 10	121.71	101.425
11.	No. 11	95.65	79.70833
12.	No. 12	116.54	97.11667
13.	No. 13	110.92	92.43333
14.	No. 14	114.4	95.33333
15.	No. 15	94.07	78.39167
			Average - 92.37