'A COMPARATIVE EVALUATION OF FLEXURAL STRENGTH OF HEAT POLYMERIZED POLYMETHYL METHACRYLATE DENTURE BASE MATERIAL REINFORCED WITH MONOCLINIC, CUBIC AND TETRAGONAL ZIRCONIUM OXIDE NANOPARTICLES –AN *IN VITRO* STUDY.'

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List of Abbreviations Used

Graph No.	Abbreviation	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.	^{o}C	Degree Celsius
8.	^{o}	Degree
9.	Mm	Millimetre
10.	i.e.	that is
11.	PMMA	Polymethyl methacrylate
12.	µ	Micron
13.	Al_2O_3	Aluminum oxide
14.	TiO_2	Titanium oxide
15.	ZrO_2	Zirconium oxide
16.	SiO_2	Silica
17.	Rpm	Rotations per minute
18.	Mins	Minutes
19.	Gms	Grams

INTRODUCTION

The introduction of many minds into many fields of learning along a broad spectrum keeps alive questions about the accessibility, if not the unity, of knowledge.

Introduction

The loss of teeth by accident or disease has plagued mankind throughout the ages. In order to restore a degree of function and appearance, it has been necessary always to adapt contemporary materials to dental applications as they were available in one period of history. The transition from naturally occurring materials to the application of synthetic resins in denture construction indicates the extent of development taking place. Research carried out by workers has promoted the foundation of future knowledge and it can be hoped that the unending search for denture base materials with desirable qualities will always continue.

Skillfully designed dentures were hand carved in 700 BC.[1] Since ages, dentistry has been dependent on naturally occurring materials, to a large extent, for the fabrication of dentures to rehabilitate partially or completely edentulous patients. During seventeenth century, denture bases were carved from a single piece of wood, bone or ivory with natural teeth held by screws. There was a remarkable advancement in prosthetic and restorative dentistry from 1800 to 1975.[1]

By the 8th century, the Japanese were masters of the art of woodcarving and it was possible that the earliest wooden denture was made at that time. Further progress was slow until the 17th century. Modern dentistry had been said to begin with Pierre Fauchard (1678-1761) who developed many prosthetic techniques. He used human teeth or teeth made from hippopotamus or elephant ivory in the denture. Although the art of firing porcelain was practised in China in the 9th and 10th centuries, it was not until 1774 that Alexis Duchateau, a Parisian apothecary, dissatisfied with his own stained hippopotamus ivory denture, was inspired to attempt to use porcelain for denture fabrication. With the advent of porcelain, ivory, bone and animal substances were replaced. Chemant's denture was popular until the introduction of individually baked porcelain teeth in 1808 by an Italian dentist Giuseppangeio Fonzi. Loomis (1854) fabricated the first porcelain denture with artificial teeth. Charles H Land (1890) made porcelain dentures with platinum bases known as continuous gum dentures.

During the later part of the nineteenth century, polymers entered the field of denture base materials. The transition from use of naturally occurring materials to synthetic resins in denture construction indicates the extent of development taking place.[1]

In 1856 Alfred A Blandy used a low fusing alloy of silver, bismuth and antimony. Dentures made of this low fusing alloy were called cheoplastic dentures and the method of manipulation was called cheoplasty. The first known casting of a complete aluminum base was done in 1867 by Dr. Bean. In 1909, Dr. Leo Bakeland came out with another compound, which was a phenol formaldehyde resin and was termed as Bakelite.

Since the introduction of polymethyl methacrylate (PMMA) by Dr. Walter Wright in 1937, it has been most widely used for the fabrication of complete dentures. Inspite 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 favourable working characteristics, processing ease, accurate fit, biocompatibility, stability in the oral environment, superior esthetics, and use with inexpensive equipment.[2,3] However, it is still far from ideal in fulfilling the mechanical requirements of the denture base material.[4]

There are continuous efforts to improve PMMA and desirable improvements include the enhancement of strength and stiffness, better dimensional stability, better abrasion resistance and the achievement of radiopacity.[4] Different denture base materials such as polystyrene, poly vinyl acrylic, polyamides (nylons) and light activated urethane dimethacrylate resins were also used. Although these materials exhibited desirable properties, none have been proven superior to polymethyl methacrylate (PMMA).[5]

Studies have shown that 68 % of the complete dentures fabricated, fractured within the first three years.[6] The fracture of acrylic resin dentures is an unresolved problem in

removable prosthodontics. The midline fracture of a maxillary denture is most common and is often the result of flexural fatigue and deep incisal notching at the labial frenum.[7]

Smith analyzed the practical situation with respect to the fracture of dentures and showed two types of failure.[2,8]

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.

Any denture base material should have sufficient strength to withstand fracture in service. A variety of physical properties can be used to assess the strength of denture base materials. The most common test is flexural strength i.e. the amount of force needed to deform the material to fracture or yield irreversibly.[3]

Many attempts have been made to enhance the strength of heat polymerized acrylic resin denture base material. Recently incorporation of Ceramic materials to PMMA have been found to be biocompatible and also improve the mechanical properties. Various ceramic powders such as sapphire (Al_2O_3), boron nitride (BN), silicon nitride (Si_3N_4), aluminum nitride (AlN) and zirconium oxide (ZrO_2) have the advantage of being white without compromising the aesthetic appearance of the denture base material than the metal powders.[2,9]

Zirconium oxide (ZrO_2), commonly referred to as zirconia, possesses strong ionic inter-atomic bonding, giving rise to its desirable material characteristics.[10] Zirconium oxide fillers (ZrO2) can be used because of their excellent biocompatibility and also for

being white; so they are less likely to alter esthetics. The Nano-filler particles of Zirconium oxide(ZrO2) yields a better dispersion, eliminate aggregation and improve its compatibility with organic polymer[11]. Zirconium oxide (ZrO_2) exists in three crystalline phases i.e Monoclinic, cubic & tetragonal with the most stable phase being the Monoclinic phase.[12] It has shown to reduce the polymerization shrinkage of polymethyl methacrylate denture base material, decrease its warpage, make the material radio-opaque and inhibit the growth of bacteria over the denture surface.[13]

To modify the physical and mechanical properties of heat cure acrylic denture base resin, it is essential for a good bond to exist between the denture base resin and the filler material. This study is an effort to evaluate and compare the flexural strength of heat polymerized denture base resin with addition of Monoclinic , Cubic and Tetragonal Zirconium oxide nanopowder.

AIM AND OBJECTIVES

Setting Aim is the first thing in turning the invisible into the visible.

Aim and Objectives

AIM:

"To evaluate and compare the flexural strength of heat polymerized polymethyl methacrylate denture base material reinforced with monoclinic, cubic and tetragonal zirconium oxide nanoparticles with that of heat polymerized polymethyl methacrylate denture base material."

OBJECTIVES:

1. To evaluate the flexural strength of heat polymerized polymethyl methacrylate denture base material without reinforcement.

2. To evaluate the flexural strength of heat polymerized polymethyl methacylate denture base material reinforced with monoclinic zirconium oxide nanoparticles.

3. To evaluate the flexural strength of heat polymerized polymethyl methacrylate denture base material reinforced with cubic zirconium oxide nanoparticles.

4. To evaluate the flexural strength of heat polymerized polymethyl methacrylate denture base material reinforced with tetragonal zirconium oxide nanoparticles.

5. To compare the flexural strength of heat polymerized polymethyl methacrylate denture base material reinforced with monoclinic, cubic and tetragonal zirconium oxide nanoparticles respectively with that of heat polymerized polymethyl methacrylate denture base material.

REVIEW OF LITERATURE

2.1 INTRODUCTION

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2.4 REVIEW ON ROLE OF SURFACE TREATMENT OF FIBRES AND METAL OXIDES WITH SILANES FOR REINFORCEMENT OF CONVENTIONAL POLYMETHYL METHARCYLATE .

2.5 REVIEW ON REINFORCEMENT OF CONVENTIONAL POLYMETHYL METHARCYLATE WITH ZIRCONIUM OXIDE PARTICLES.

Review of Literature

Polymethyl Methacrylate (PMMA), introduced by Dr Walter Wright in 1937, is one of the most widely used material in prosthetic dentistry.[1] Despite its popularity which satisfies esthetics, simple processing and easy repair, the common problems associated with PMMA as a denture base material are poor strength, particularly fatigue failure inside the mouth and lack of radiopacity. This material is not ideal in every aspect and it is the combination of virtues rather than one single desirable property that accounts for its popularity and usage.[1]
The clinical problems often experienced are related to flexural strength of heat polymerized acrylic resin denture base material has been stimulating scientific investigations and there are many reports this subject. These reports deal with the cause of the problem or with the methods to improve the same.

Despite the favorable physical characteristics of denture base resins, denture base sometimes fracture. Studies have shown that 68 % of the dentures fabricated, fractured within the first three years.[1]

Many trials have been made to enhance mechanical properties of denture base materials. Ceramic materials have been found to be biocompatible and also improve the mechanical properties.[6] Few have obtained promising results in improving the fracture resistance of heat

polymerized acrylic resin denture base (PMMA). The reinforcement of polymers used in dentistry with these metal-composite systems has been of prime interest.[14]

D.C. Smith (1961)[8] stated that one of the most practical deficiencies of a denture is fracture. Fracture can occur both; inside as well as outside the mouth. The most common are the midline fractures which act as fatigue fractures. It was found that, whether the denture fractures from accidental or masticatory cause, the strength of the denture has been inadequate in each case. It was also observed that the strength of a denture depends on the shape, residual stress, mechanical properties of the material and condition of loading. It is seen that the incisal notch in a maxillary denture acts as a crack initiator.

H.H. Berry and O.J. Funk (1971)[15] said that midline fracture of the denture is common. Breakage is due to:

(1) Difficulty in cleaning,

(2) Coughing which pushes the denture out of the mouth,

(3) Lack of denture base material at the midline,

(4) Greater than average biting force,

(5) Dropping the denture accidentally.

Breakage is prevalent among neuropsychiatric patients, especially those having neuromuscular disorders such as Huntington's chorea, hemiparalysis, muscular dystrophy, and Parkinson's disease. They incorporated vitallium in acrylic resin denture base and concluded that the denture strengtheners used in this study were designed to retain all the qualities of the acrylic resin denture in addition to adding the needed strength to prevent denture breakage.

M.S. Beyli and J.A. Fraunhofer (1981)[16] analyzed the causes of fracture of acrylic resin denture. A survey was conducted where 20 laboratories specialized in denture construction and repair were consulted. The result of the survey showed that the ratio of upper to lower denture fracture was about 2:1 with the most common causes of fracture appearing to be poor fit and lack of balanced occlusion. It was also found that the incisal notch was the most important causative factor in midline fractures and crack initiates at the tip of the notch where there is high local stress concentration. Various methods to prevent denture fracture i.e. good processing technique, high strength polymers, denture with metal plate for patients with heavy occlusions, palatal relief in anterior portion of palate, increasing the bulk of base material palatal to incisors and reinforcement in the anterior part of the palate of the denture, have been suggested.

D. C. Jagger, A. Harrison & K. D. Jandt (1999)[17] addressed the need to improve the strength of the denture base in three ways:

i) Introduction of various substitutes for Poly methyl-methacrylate such as nylon, polycarbonates and polyamides.

ii) The chemical modification of Poly methyl-methacrylate through the addition of rubber in the form of butadiene styrene.

iii) Incorporation of metal in the form of wires; sapphire whiskers; polyethylene beads; fibres like carbon fibres, glass fibres, polyethylene fibres, kevlar fibres, PMMA fibres and silica fibres.

2.2 REVIEW ON REINFORCEMENT OF CONVENTIONAL POLYMETHYL METHARCYLATE WITH WHISKERS AND DIFFERENT TYPES OF FIBRES

A.A. Grantt and E.H. Greener (1967)[18] incorporated sapphire (Al_2O_3) whiskers of various diameters in denture base polymethyl methacrylate to evaluate the flexural property of polymethyl methacrylate. Two types of sapphire whiskers were used; one sapphire whisker of 1-10 micron diameter incorporated in a concentration of 8.3% by weight, these were silanized and non-silanized. The other type consisted of sapphire mixed grade fibres incorporated at 10%, 11% and 27% by weight sapphire. Addition of sapphire whiskers to heat cured polymethyl methacrylate produced dramatic changes in the physical properties. With large additions of mixed grade and smaller additions of graded sapphire whiskers the ultimate bending strength is approximately doubled and 25 % changes in the modulus and resilience were noted. The employment of silane increases the surface activity of whiskers permitting better transfer of stress from polymethyl methacrylate to the whisker. They concluded that an enhancement of the flexural strength of denture base polymethyl methacrylate was possible through the technique of whisker reinforcement with sapphire fibres.

C.K. Shreiber (1971)[19] compared the transverse strength of acrylic resin denture base materials, with and without carbon fibre reinforcement. Carbon fibres were in the form of untreated fibres, untreated chopped carbon fibres and surface treated carbon fibres. It was concluded that polymethyl methacrylate reinforced with carbon fibres had a 50% increase in transverse strength as compared to plain polymethyl methacrylate samples.

D.L. Gutteridge (1988)[20] conducted a study to know the effect of including 0.5%, 1%, 2%, 3% and 4% by wt. of 6 mm lengths of ultra high modulus polyethylene fibres on the impact strength of acrylic denture base resin. He concluded that the inclusion of 1% by wt. of 6 mm length of ultra high modulus polyethylene fibres provided an effective means of reinforcing acrylic resin with respect to impact strength.

J.M. Berrong, R.M. Weed and J.M. Young (1990)[21] conducted a study to evaluate the effect of kevlar fibre reinforcement on the fracture resistance of polymethyl methacrylate denture base resin. Kevlar fibres were embedded in the ratio of 0% (control), 0.5%, 1% and 2% by weight to the methyl-methacrylate denture base resin. All specimens were subjected to impact testing. The result showed that all reinforced sample groups were significantly stronger than their unreinforced control group. They concluded that the use of upto 2% kevlar fibres as reinforcement might increase resistance of the resin denture base in traditionally weak areas and reduce the separation of fractured fragments that might be aspirated or lost.

G.S. Solnit (1991)[22] evaluated the effect of methyl methacrylate reinforcement with silane-treated and untreated glass fibres. This study suggests that glass fibres can be pre-treated with a silane coupling agent to obtain a chemical bond between the fibres and the acrylic resin. He concluded that PMMA can be strengthened by the addition of glass fibres in the cloth form and by treating loose-form glass fibres with silane before they are incorporated into the mixture.

P.K. Vallittu and V.P Lasilla (1992)[23] compared metal strengtheners which included semicircle wire (0.l-0x2.0mm), braided wire plate (0.8 x 2.4mm) and clasp wire (1.0 mm). The sandblasting was done with conventional sandblasting device. The sand particles used

were aluminum oxide with grain size, 50 and 250um, and the air pressure applied was 5.5 bar. In some groups the roughening of wires was done by grinding them with a heatless stone and in other groups with a 0,6 mm separating disc. After being handled, all of the wires were cleaned in water with an ultrasonic cleaning device. The semicircular wire had the most marked effect on the fracture resistance of the specimens. They also said that the sandblasting was the most effective method with all the metal wires used in this study. The resistance was not influenced by the grain size of the sand (50μm or 250 μm).

P.K. Vallittu and V.P Lasilla (1992)[24] studied the effect of different types of commonly used metal wire and glass fibre, as well as carbon and aramid fibres on the fracture resistance of polymethyl methacrylate. They found that the unsilanized glass fibres slightly weakened the test specimens. However, the weakening was not statistically significant, in contrast to the silanized glass fibres, which had a significant strengthening effect.

N.H. Ladizesky, Y.Y. Cheng, T. W. Chow and I.M. Ward (1993)[25] evaluated 3 mechanical properties i.e. flexural strength, flexural modulus and impact strength of acrylic resins reinforced with woven highly drawn linear polyethylene fibres (HDLPE) and concluded that the incorporation of three layers of woven HDLPE fibres substantially increases the impact strength of acrylic denture base resins.

N.H. Ladizesky, Y.Y. Cheng, T. W. Chow and I.M. Ward (1993)[26] incorporated over 30% by volume of chopped high performance polyethylene fibres into acrylic denture base resin. The reinforcement produced a substantial improvement in several important properties, namely (1) stiffness and impact strength were higher; (2) mechanical properties were

insensitive to notches that mimic anatomical feature and (3) samples damaged during bending and impact did not break up into separate fragments.

P. K. Vallitu (1993)[27] investigated the effect of metal wire bonding to acrylic resin on the fracture resistance of an acrylic denture base material construction. Two different bonding methods were tested, and after measuring the resistance, the surface of the wires were examined by a scanning electron microscope. The effect that the placement of metal strengtheners in different positions in the acrylic resin had on the fracture resistance of the denture base material construction was also clarified. When three different positions of the metal wires in the acrylic resin were compared, the results showed that bonding of metal wire to acrylic resin somewhat enhanced the fracture resistance of test specimens, while the different positions of the wires had no effect on the fracture resistance.

P. K. Vallittu (1995)[28] studied various methods to reinforce acrylic denture base material that have been used to repair fractures in complete dentures. Metal wires and plates have been tested as reinforcement of polymethyl methacrylate (PMMA) resin. The literature has reported that even thin metal wires incorporated into the PMMA matrix increased the transverse strength of the PMMA construction. Metal mesh inserted into PMMA resin had negligible effects on the transverse strength of the restoration. Macroscopic retention of the metal strengtheners to the PMMA had only a minor effect on the strength in contrast to microscopic retention, which showed a more marked effect. Chemical bonding between the PMMA and metal reinforcement enhanced the strength of the prosthesis with some exceptions.

P. K. Vallittu, H. Vojtkova and V. P. Lassila (1995)[29] compared the impact strength of heat-cured acrylic resin specimens reinforced with metal wire and continuous E-glass fibres. It was found that both types of reinforcement increased the impact strength of the resin. They concluded that concentrations of glass fibre greater than 25 wt% yield better impact strength than steel wire 1.0 mm in diameter.

H. D. Stipho (1998)[30] investigated the transverse strength, maximum deflection, and modulus of elasticity of repaired acrylic resin joints reinforced with different concentrations of glass fibres to the weight of the powder/ liquid mix (0%, 1%, 2%, 5%, 10%, and 15%). It was found that with 1% glass fibre displayed the highest transverse strength before and after repair. Modulus of elasticity of the repaired 1% fibre concentration units was enhanced by approximately 25% over those repaired but untreated with glass fibre.

Gulay Uzun, Nur Hersek and Teoman Tinçer (1999)[31] measured the effect of 5 fibre strengtheners on the fracture resistance of denture base acrylic resin material. Impact strength, transverse strength, deflection and elastic modulus values of a heat-polymerized denture base resin (Trevalon) reinforced with glass, carbon, thin kevlar, thick kevlar, and polyethylene fibres in woven form were studied. Polyethylene and glass-reinforced acrylic resin specimens were significantly more resistant to impact strength. Fibre reinforcement had no significant effect on the transverse strength, polyethylene reinforcement significantly raised deflection value. Carbon, thick Kevlar, and polyethylene-reinforced specimens showed significantly higher elastic modulus values.

Pekka K. Vallittu (1999)[32] evaluated the flexural properties of acrylic resin polymers reinforced with unidirectional and woven glass fibres. Continuous unidirectional and woven pre-impregnated glass fibre reinforcements were used to reinforce heat-curing denture base and autopolymerizing denture base polymers. He concluded that glass fibre reinforcements considerably enhance flexural properties of multiphase dental polymers, which is due to proper impregnation of fibres with polymer matrix.

T. Kanie, K. Fujii, H. Arikawa and K. Inoue (2000)[33] determined the reinforcing effect of woven glass fibres on deflection, flexural strength, flexural modulus and impact strength of acrylic denture base polymer. The flexural strength and deflection in specimens reinforced with silanized glass fibre of 1 mm thickness were significantly higher than those of unreinforced specimens. Further, the impact strength of the specimens reinforced with silanized glass fibre of 2 mm thickness was significantly higher than that of unreinforced specimens.

Foo H et al. (2001)[34] evaluated the effect of unidirectional poly-aramid fibre reinforcement on the transverse strength of intact and repaired heat-polymerized denture base acrylic resins. The denture base resins were Acron MC (microwave polymerized resin), Lucitone 199 (butyl rubber reinforced high impact resin) and Microlon (conventional denture base resin). Polyaramid fibres used in this study were 15 micron in diameter and were organized into a flat mat 1 mm in thickness. They concluded that poly-aramid reinforcement significantly increased the transverse strength of intact heat-polymerized PMMA resins.

San-Yue Chen, Wen-Miin Liang, Pau-Su Yen (2001)[35] evaluated the improvements in mechanical properties of acrylic resin following reinforcement with three types of fibre. Polyester fibre (PE), Kevlar fibre (KF), and glass fibre (GF) were cut into 2, 4, and 6 mm lengths and incorporated at concentrations of 1, 2, and 3% (w/w). Polyester fibre and kevlar fibre both improved the mechanical properties, but the polyester fibre was superior in aesthetics also. So it was concluded that incorporation of 3% (w/w) of 6 mm polyester fibre offers the best formulation for acrylic denture base resin reinforcement.

Jacob John, Shivaputrappa A. Gangadhar, Shah (2001)[26] studied and compared the flexural strengths of conventional PMMA resin and the same resin reinforced with glass, aramid, or nylon fibres in loose form. They concluded that glass and aramid fibres appeared to be suitable for long-term use in complete dentures and distal extension partial denture bases, which are considered prone to fracture. Glass fibre reinforcement may also help prevent fracture in provisional fixed partial dentures by strengthening them at the connector sites.

Cemal Aydin, VHandan Yilmaz, VAIper Çaglar (2002)[36] investigated the effect of a glass fibre reinforcement system on the flexural strength of three different denture base resins (heat polymerized, autopolymerized, and photopolymerized). The results showed that the reinforcement of different denture base resins with the glass fibre used in this study may be a useful means of strengthening denture bases beyond their normal limits.

S.H. Kim and D.C. Watts (2004)[37] examined the effect of glass fibre reinforcement on the impact strength of high impact acrylic resin maxillary dentures.

They drew the following conclusion: The crack propagation energy and the impact strength of high impact acrylic maxillary complete denture reinforced with woven E-glass fibres was higher than that of the unreinforced denture both at crack initiation and at complete fracture.

Tacir IH, JD Kama, M Zortuk, S Eskimez (2006)[38] compared the fracture resistance of unreinforced and glass fibre reinforced acrylic resin polymers prepared under both conventional heat curing and microwave curing techniques. They concluded that fracture resistance and impact strength of heat polymerized acrylic resin improved with glass fibre reinforcement. It may be possible to apply these results to distal extension partial and complete denture bases.

M. Vojdani , AAR. Khaledi (2006)[39] conducted a study in which they observed that the transverse strength of heat polymerized denture base resin was considerably enhanced by including either metal wires or glass fibres. Moreover the flexural strength of specimens reinforced with continuous unidirectional glass fibres was significantly higher than that of metal wire or woven fibre reinforcements.

Dogan O, Bolayir G, Keskin S, Dogan A, Bek B, Boztug A (2007)[40] evaluated the changes in impact resistance of a denture base resin reinforced with five types of fibre. E-glass, polyester, rayon, nylon 6, and nylon 6/6 fibres were cut into 2, 4, and 6 mm lengths and added into the resin at a concentration of 3 % by weight. The results indicated that impact energy tended to increase with fibre length, and that the highest value was recorded for rayon fibre-reinforced specimens of 6 mm length. E-glass fibre reinforcement produced relatively stable, high values for each length.

Orhan MD, Giray B, Selda K, Arife D, Bu¨ lent B (2008)[41] conducted a study to determine whether some flexural properties of a denture base resin material could be improved through reinforcement with aesthetic fibres i.e. glass, rayon, polyester, nylon 6 and nylon 6,6 fibres at 3% concentration by weight and in 2, 4, and 6 mm length. It was found that specimens reinforced with nylon 6,6 fibres of 6 mm length showed the highest flexural strength. Young's modulus and maximum load suggested that such reinforcement made resin resistant to fracture.

Sanjiv Dagar, Ashok Pathan, R.U.Thombre, Bhagwandas Motwani (2008)[42] compared the resistance to fracture properties of commercially available heat polymerizing PMMA denture base resin with those of the same material reinforced by glass and nylon fibres. On comparing the flexural and impact strength properties between conventional and fibre reinforced, it was found that fibre reinforced specimens were more resistant to impact and flexural fatigue than conventional PMMA specimens and glass fibre reinforcement improved both impact and flexural strength denture base resin when compared with nylon fibres.

2.3 REVIEW ON REINFORCEMENT OF CONVENTIONAL POLYMETHYL METHARCYLATE WITH VARIOUS METAL OXIDES

S.P. Sejpal and V.K. Sood (1989)[43] conducted a study to determine the effect of adding powdered silver, copper and aluminum on thermal conductivity, tensile strength, compressive strength and radio-opacity of PMMA. Silver, copper and aluminum were added in ratio of 5%, 10%, 15%, 20% and 25% by volume to acrylic resin. The study concluded that with the increase in metal fillers concentration there was a progressive increase in compressive strength of polymethyl methacrylate and decrease in tensile strength. The maximum increase in thermal conductivity was seen with aluminum, silver and copper fillers in 25% by volume concentration.

M.K. Marei , A. El-Sabrooty and A.Y. Ragab (1994)[44] performed a study to evaluate the effect of adding tin and aluminum oxide powder with average particle size of 10µ to heat curing acrylic resin in a concentration of 5% by volume. Four physical and mechanical properties i.e. thermal conductivity, impact strength, compressive strength, and warpage were tested. The addition of 5% by volume of both metal powders to polymethyl methacrylate (PMMA) improved the four tested properties. The addition of aluminum oxide powder improved the thermal conductivity and decreased the warpage of PMMA more effectively than tin.

Phillip B. Messersmith, Ales Obrez, and Sara Lindberg (1998)[45] evaluated the thermal diffusivity of new acrylic resin composite**.** Thermal diffusivity is one material property that has been cited as being important in determining gustatory response. Denture base acrylic

resins have low thermal diffusivity compared with denture base metal alloys. Sapphire (Al_2O_3) whiskers were added to conventional denture base acrylic resin during processing to achieve loadings of 9.35% and 15% by volume. Thermal diffusivities of the sapphire-containing composites were found to be significantly higher than the unmodified acrylic resin. Thermal diffusivity was found to increase in proportion to the volume percentage of sapphire filler, which suggested that the high aspect ratio ceramic particles formed a pathway for heat conduction through the insulating polymer matrix.

Nakamura M, Takahashi H, Hayakawa I (2007)[46] investigated the feasibility of a high short-rod fibre content in denture base resins using commercial PMMA (AC; average particle size, 150 μm) and an industrial PMMA powder (MB; average particle size, 4 μm). Short-rod glass fibres were mixed with two powders at a mass ratio of 0—50 %. The flexural strength of MB composites increased significantly at fibre contents exceeding 40%. The flexural moduli of AC and MB composites at fibre contents exceeding 20% were significantly greater than those of AC and MB resins without short-rod glass fibres, respectively.

Ellakwa AE, Morsy MA, El-Sheikh AM. (2008)[3] conducted a study to evaluate the effect of adding 0%, 5%, 10%, 15%, and 20% by weight aluminum oxide powder (Al_2O_3) on the flexural strength and thermal diffusivity of heat-polymerized acrylic resin. They were divided as group A, B, C, D and E respectively. The study concluded that incorporating Al_2O_3 powder from 5% to 20% by weight into conventional heat-polymerized denture base resin resulted in an increase in both flexural strength and thermal diffusivity. The highest mean flexural strength with addition of 15% by weight of aluminum oxide powder was 130.08 Mpa. Alumina addition (15% by weight) was responsible for a 30% increase in flexural strength of groups D and E in comparison to the unreinforced control. Also, alumina addition

from 15% to 20% (by weight) was responsible for a 25% and 30% increase in thermal diffusivity of groups D and E in comparison to the unreinforced control. Thus increasing the flexural strength and heat transfer characteristics of the acrylic resin base material could lead to more patient satisfaction.

Abdulhamed AN, Mohammed AM (2010)[47] evaluated the thermal conductivity, impact and tensile strength of alumina reinforced heat cure acrylic resin. Alumina powder was added to PMMA powder by weight in three different percentages 5%, 7.5% and 10%. The study concluded that the addition of Al_2O_3 powder to acrylic resin improves the thermal conductivity of acrylic resin, at the same time this addition decreases both impact and tensile strength values. On the other hand there was an increase in surface hardness. Water sorption and solubility were decreased while surface roughness was not affected with small percentages of alumina.

Arora N, Jain V, Chawla A, Mathur VP (2011)[48] investigated the effect of adding sapphire (aluminum oxide) or silver filler particles on the flexural strength, thermal diffusivity and water sorption of polymethyl methacrylate (PMMA) resin. Sapphire (aluminum oxide) or silver filler particles were added in 25% by weight of acrylic resin. The study concluded that as compared to silver fillers, sapphire fillers were better for the reinforcement of polymethyl methacrylate resin. This is because they have potential as added components in denture bases to provide increased flexural strength, thermal diffusivity and decreased water sorption.

Saritha M.K, Shivamurthy Shadakshari, Nandeeshwar D.B, Shivsagar Tewary (2012)[2] conducted an *in vitro* study to investigate the flexural strength of conventional heat polymerized denture base resin with addition of 5%, 10% and 15% by wt. of aluminum oxide

powder. They concluded that highest flexural strength was found with 15% by wt. incorporation of aluminum oxide powder to heat cure denture base resin.

Mahroo Vojdani, Rafat Bagheri, Amir Ali Reza Khaledi (2012)[49] evaluated the effects of 0.5, 1, 2.5 and 5 wt% of aluminum oxide addition on the flexural strength, surface hardness, and roughness of heat-polymerized acrylic resin They concluded that reinforcement of the conventional heat-cured acrylic resin with 2.5 wt% of Al2O3 powder significantly increased its flexural strength and hardness with no adverse effects on the surface roughness.

Yadav P, Mittal R, Sood VK, Garg R (2012)[50] studied the effect of addition of metal filler particles on different strengths of polymethyl methacrylate (PMMA) and to evaluate the thermal perception in vivo. The study was carried out in two parts. Part 1 of the study was an in vitro investigation regarding the effect of addition of metal fillers (aluminum and silver) in concentrations of 10%, 20%, and 30%, by volume on the tensile, compressive, and flexural strength of PMMA. Part 2 of the study comprised the clinical evaluation of the thermal perception by 10 edentulous patients provided with two sets of complete dentures, one fabricated with unfilled PMMA and another with 20% aluminum particle filled PMMA on the palatal portion of the maxillary denture. They concluded that compressive strength increased progressively on increasing the filler concentration for both silver- and aluminum-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.

Neset Volkan Asar, Hamdi Albayrak, Turan Korkmaz (2013)[14] investigated the influence of different types and amounts of the metal oxides on mechanical and physical properties of heat cured PMMA. They concluded that Al_2O_3, TiO_2 and ZrO_2 fillers resulted in significant increase in impact strength and fracture toughness and significant decrease in water sorption and solubility. Modification of heat-cured acrylic resins with certain amounts of metal oxides may be useful in preventing denture fractures and undesirable physical changes resulting from oral fluids clinically.

Jyothi Atla et al (2013)[13] studied the effect of adding 5% to 20% by weight aluminum oxide powder (Al_2O_3) on thermal diffusivity of heat–polymerized acrylic resin. Incorporating Al_2O_3 powder of 20% by weight into conventional heat polymerized denture base resin, resulted in an increased thermal diffusivity, which ensured a better perception of temperature changes and which ultimately led to enhanced patient satisfaction

Ahmad Sodagar et al (2013)[51] evaluated the effect of TiO_2 and SiO_2 nano-particles on flexural strength of polymethyl methacrylate acrylic resins containing nanoTiO_2, SiO_2 and TiO_2 with SiO_2 in two concentrations of 1 wt % and 0.5wt % were made. It was concluded that incorporation of TiO_2 and SiO_2 nano-particles into acrylic resins adversely affected the flexural strength of the final products, and this effect was directly correlated with the concentration of nano-particles. The reason for this decrease was attributed to incorporation of nano-particles into polymethyl methacrylate acrylic resin which caused these particles to agglomerate and aggregate. The agglomerated compounds can act as stress concentrating centres in the matrix and adversely affect mechanical properties of the polymerized material. Hence it was suggested to use appropriate substances as silane coupling agent between nano-TiO_2 and SiO_2, thus alleviating its deleterious effect on mechanical properties.

2.4 REVIEW ON ROLE OF SURFACE TREATMENT OF FIBRES AND METAL OXIDES WITH SILANES FOR REINFORCEMENT OF CONVENTIONAL POLYMETHYL METHARCYLATE

P. K. Vallitu (1993)[52] studied the effects of two different silane compounds on the adhesion between the different fibres and acrylic resin. The silane compounds tested were A174 and AP133 and the different fibres used were glass, carbon and aramid fibres. The amount of fibres in a weight percentage of the mass of the acrylic resin was as follows: 7.39% for glass fibres, 2.08% for carbon fibres and 2.30% for aramid fibres. The results showed that the glass fibres and the aramid fibres when treated with A174 silane compound increased the fracture resistance of the specimens.

Jukka P. Matinlinna, Lippo V. J. Lassila,, Mutlu Özcan, Antti Yli-Urpo, Pekka K. Vallittu (2004)[53] overviewed organo functional trialkoxysilane coupling agents (silanes), their chemistry, properties, use, and main clinical applications in dentistry. In prosthetic and restorative dentistry, high bond strength between material phases is essential. The silane most commonly applied in dental laboratories and chair side is a monofunctional 3-trimethoxysilylpropyl methacrylate (MPS). MPS is used to optimize and promote the adhesion, through chemical and physical coupling, between metal-composite, ceramic-composite, and composite-composite. They concluded that any composite material that contains methacrylate groups in the molecules can be used, since the methacrylate end copolymerizes better to the composite than acrylate.

2.5 REVIEW ON REINFORMENT OF CONVENTIONAL POLYMETHYL METHARCYLATE WITH ZIRCONIUM OXIDE PARTICLES

Ayad NM, Badawi MF, Fatah AA (2008)[54] evaluated the effect of reinforcing high-impact acrylic resin (Metrocryl HI) with zirconia powder in two different concentrations (5% and 15%) on the transverse strength, impact strength, surface hardness, water sorption and solubility. They concluded that the addition of zirconia resulted in a highly significant increase in transverse strength of high-impact acrylic resin. This increase was proportional to the concentration of zirconia. No significant difference was detected in each of impact strength, surface hardness and water solubility.

Ihab NS, Moudhaffar M (2011)[55] evaluated the effect of addition of modified nano-zirconium oxide (ZrO_2) on strength and radio-opacity of heat cured acrylic denture base material. The nanoparticales were coated with a layer of trimethoxysilypropylmethacrylate (TMSPM) before they were dispersed and sonicated in monomer (MMA) in different percentages 2%, 3%, 5% and 7% by weight. It was found that maximum increase in impact strength, transverse strength and radio-opacity was observed in denture base containing 3wt% of nano-ZrO_2.

Ahmed Omran Alhareb and Zainal Arifin Ahmad (2011)[56] evaluated the effect of 5wt% of Al_2O_3/ZrO_2 reinforcement on the fracture toughness, flexural, and tensile properties of PMMA denture base. They concluded that the incorporation of Al_2O_3/ZrO_2 into PMMA improved the fracture toughness, tensile modulus, and flexural properties of this denture base composite material.

Ihab NS, Hassanen KA, Ali N.A (2012)[10] assessed the impact strength, tensile strength and color stability of heat polymerized denture base after addition of silanated and non-silanated zirconium oxide (ZrO_2) nanofillers. The maximum increase in impact strength was observed with nano composite containing 5% wt of silanated ZrO_2 nano-fillers. On the other hand, significant color differences were detected between control group and specimens incorporated with zirconium oxide nano-fillers in different immersion solutions.

Mohamed Ashour Ahmed, Mohamed I. Ebrahim (2014)[11] studied the effect of Zirconium oxide (ZrO_2) nano-fillers powder with different concentration (1.5%, 3%, 5% and 7%) on the flexural strength, fracture toughness, and hardness of heat-polymerized acrylic resin. Addition of 3 wt% and 5wt% of ZrO_2 nano-fillers to PMMA significantly increased the flexural strength, fracture toughness, and hardness of heat polymerized acrylic resin.

Xiu-Yin ZHANG, Xin-Jing ZHANG, Zhuo-Li HUANG, Bang-Shang ZHU and Rong-Rong CHEN (2014)[57] investigated the hybrid effects of ZrO_2 nanoparticles (nano-ZrO_2) and aluminum borate whiskers (ABWs) on flexural strength and surface hardness of denture base resin, polymethyl methacrylate (PMMA). ZrO_2 nanoparticles had an average granularity of 90 nm and an average surface area of 7±2 m2/g. Aluminum borate whiskers were of 5–30 μm length and a diameter of less than 1.5 nm, with a surface area of 2.0–2.5 m2/g. Both nano-ZrO_2 and ABWs were modified by silane coupling agent (Z6030 i.e. 3 Methacryloxy propyl trimethoxysilane) before being mixed with PMMA. The nanocomposites were divided into four groups according to different amounts of nano-ZrO2 at 1, 2, 3, and 4 wt%. Each group was subdivided according to ZrO_2/ABW mass ratios of 2:1, 1:1, 1:2, and 1:3. Unsilanized ZrO_2-ABW/PMMA nanocomposites were prepared in the same way by admixing unsilanized

nano-ZrO_2 and ABWs, and were regarded as the control groups. Pure PMMA was used as the blank group. They concluded that maximum flexural strength was achieved with 2% of nano-ZrO_2 at ZrO_2/ABW ratio of 1:2, causing flexural strength to increase by 52% when compared with pure PMMA.

Asopa V et al (2015)[58] evaluated 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.

MATERIALS AND METHOD

Methodology should not be a fixed track to a fixed destination but a conversation about everything that could be made to happen.

Materials and Method

Since the introduction of polymethyl methacrylate (PMMA) by Dr. Walter Wright in 1937, it has been most widely used for the fabrication of complete dentures. Inspite 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 favourable working characteristics, processing ease, accurate fit, biocompatibility, stability in the oral environment, superior esthetics, and use with inexpensive equipment.[3,4] Flexural failure of denture base resins is considered the primary mode of clinical failure.[59] 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 Monoclinic, Cubic and Tetragonal zirconium oxide nanopowder.

Material and methods are divided under the following heads:

I. Materials
II. Armamentarium and equipments
III. Method

The basic methodology consisted of -

a) Die preparation
b) Preparation of gypsum mold for fabrication of specimens.
c) Preparation of heat polymerized acrylic resin denture base specimens **(Group N)**
d) Preparation of heat polymerized acrylic resin denture base specimens reinforced with Monoclinic zirconium oxide nanopowder. **(Group M)**
e) Preparation of heat polymerized acrylic resin denture base specimens reinforced with Cubic zirconium oxide nanopowder **(Group C)**
f) Preparation of heat polymerized acrylic resin denture base specimens reinforced with Tetragonal zirconium oxide nanopowder **(Group T)**
g) Testing of specimens for flexural strength

I. Materials: (PLATE I)

SR. NO.	MATERIALS	MANUFACTURER	BATCH NO.
1	Heat polymerized acrylic resin (Fig.1)	DPI Heat Cure™, (Dental products of India Ltd)	81415
2	Die stone (Fig.2)	Ultrarock; Kalabhai Karson Pvt Ltd, India	22120013
3	Zirconium oxide nanopowder(monoclinic) (zr2o3) (Fig. 3)	Plasmachem	D-12489
4	Zirconium oxide nanopowder(cubic) (zr2o3) (Fig. 4)	Plasmachem	D-12488
5	Zirconium oxide nanopowder(tetragonal) (zr2o3) (Fig. 5)	Plasmachem	D-12487
6	Cold mould seal (separating medium) (Fig. 6)	Pyrax	8117

II. Armamentarium and equipments (PLATE II & III)

1. High accuracy balance (Fig.7)
2. Ultrasonicator (Fig.8)
3. Acrylizer with thermostat (Fig. 9)
4. Universal testing machine (Fig10.)
5. Rubber bowls and plaster spatula (Fig.11)
6. Sand paper (No. 120) (Fig.11)
7. Varsity flasks and clamps (Fig11.)
8. Camel hair brush (Fig. 11)
9. Vernier caliper (Fig.12)
10. Glass Beaker (Fig.13)

11. Sterile Syringe (Fig.13)
12. Glass bowl with metal plate (Fig.13)
13. Mixing spatula (Fig.13)
14. Petroleum jelly (Fig.13)
15. Para-film (Fig.14)
16. Brass metal dies (Fig.15)
17. Hydraulic bench press (Sirio dental hydraulic press 400) (Fig.16)
18. Distilled water (Fig.17)

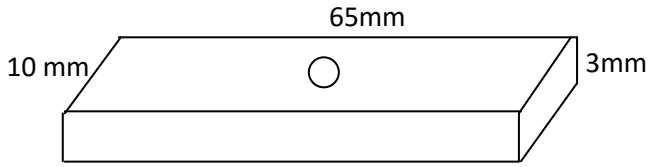
III. Methodology

A total of 100 specimens were prepared with each group having 25 specimens. The specimens were divided under the following groups:-

Group N	The control group; heat polymerized polymethyl methacrylate denture base material without reinforcement. (n=25)
Group M	Heat polymerized polymethyl methacrylate denture base material reinforced with Monoclinic zirconium oxide nanoparticles. (n=25)
Group C	Heat polymerized polymethyl methacrylate denture base material reinforced with Cubic zirconium oxide nanoparticles. (n=25)
Group T	Heat polymerized polymethyl methacrylate denture base material reinforced with Tetragonal zirconium oxide nanoparticles. (n=25)

a) Die preparation:

Metal dies were fabricated to prepare molds 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) [3,9]



These fabricated metal dies had a threaded hole at the centre. 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) Preparation of gypsum mold for fabrication of specimens

Gypsum molds 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.[60] 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)[61] 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 molds formed were then immersed in hot water to remove any traces of petroleum jelly, wax and also to facilitate application of separating medium. These mold cavities thus obtained were used for the fabrication of heat polymerized acrylic resin denture base material specimens (PMMA). (PLATE IV, Fig.19)

c) Preparation of heat polymerized acrylic resin denture base specimens (Control Group N)

25 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.[62] An electronic balance of high accuracy was used to weigh the materials. 7.5 gms 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.[63] It was then immersed in water in an acrylizer at room temperature. The temperature was raised slowly upto 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.[63]

The polymerized specimens were carefully removed. 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. [1,9] (PLATE V, Fig.21)

d) Preparation of heat polymerized acrylic resin denture base specimens reinforced with Monoclinic Zirconium oxide nanopowder (Group M)

25 samples were prepared using conventional heat polymerized denture base material (PMMA) reinforced with Monoclinic Zirconium oxide nanopowder.

For complete homogenous dispersion, Monoclinic Zirconium oxide nanopowder was added to the monomer.[10,58] As per group N, same proportion was followed for fabrication of specimens. 7.277 gm of polymer powder, 3 ml of monomer and 0.223 gm of Monoclinic Zirconium oxide nanopowder was taken for fabrication of 3 specimens. An electronic balance of high accuracy was used to weigh the materials.

Monoclinic Zirconium oxide nanopowder was well dispersed in monomer by using an ultrasonicator. The ultra sonication was done at 120 W, 60 KHz for 3 minutes. This allowed the homogenous dispersion of Monoclinic Zirconium oxide nanopowder in the monomer. [10,58] (PLATE IV, Fig.18)

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 N). Specimens with defects were discarded. The finished specimens were stored in distilled water for 1 week at room temperature.[1,9] (PLATE V, Fig.22)

e) Preparation of heat polymerized acrylic resin denture base specimens reinforced with Cubic Zirconium oxide nanopowder (Group C)

25 samples were prepared using conventional heat polymerized denture base material (PMMA) reinforced with Cubic Zirconium oxide nanopowder .

For complete homogenous dispersion, Cubic Zirconium oxide nanopowder was added to the monomer. [10,58] As per group M, same proportion and procedure was followed for fabrication of specimens reinforced with Cubic Zirconium oxide nanopowder.

The finished specimens were stored in distilled water for 1 week at room temperature. (PLATE V, Fig.23)

f) Preparation of heat polymerized acrylic resin denture base specimens reinforced with Tetragonal Zirconium oxide nanopowder (Group T)

25 samples were prepared using conventional heat polymerized denture base material (PMMA) reinforced with Tetragonal Zirconium oxide nanopowder .

For complete homogenous dispersion, Tetragonal Zirconium oxide nanopowder was added to the monomer. [10,58] As per group M, same proportion and procedure was followed for fabrication of specimens reinforced with Tetragonal Zirconium oxide nanopowder.

The finished specimens were stored in distilled water for 1 week at room temperature. (PLATE V, Fig.24)

g) **Testing of specimens** (PLATE IV, Fig.20)

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 5.0mm/minute crosshead speed.[1] The specimens were supported on the jig separated at a distance of 50 mm. Load was applied at the centre 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.

Flexural strength (FS) was calculated using the formula.[9]

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

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

MATERIALS

Fig1: Heat polymerized acrylic resin

Fig2: Die stone

Fig3: Monoclinic zirconium oxide nanopowder

Fig 4:cubic zirconium oxide nanopowder

Fig5: Tetragonal zirconium oxide nanopowder

Fig6: Separating medium

Plate II

Armamentarium and equipments

Fig.7 High accuracy balance

Fig.8 Ultrasonicator

Fig:9 Acrylizer with thermostat

Fig.10 Universal testing machine

Plate III

Armamentarium and equipments

Fig.11 Sandpaper (No.120), rubber bowl, plaster spatula, camel hair brush, varsity flask and clamp

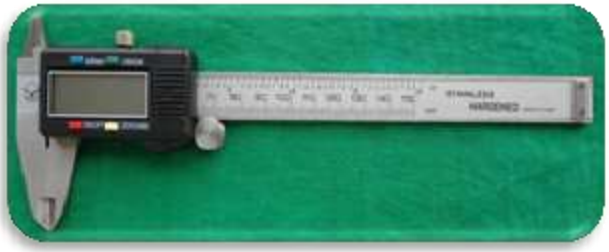


Fig.12 Vernier caliper

Fig.13 Glass beaker, glass bowl with metal plate, mixing spatula, sterile syringe, petroleum jelly

Fig.14 Parafilm

Fig.15 Brass metal dies

Fig.16 Hydraulic bench press

Fig.17 Distilled water

Plate IV

Methodology

Fig.18 Homogenous dispersion of zirconium oxide nanopowder in monomer

Fig.19 Preparation of gypsum mold to obtain specimens

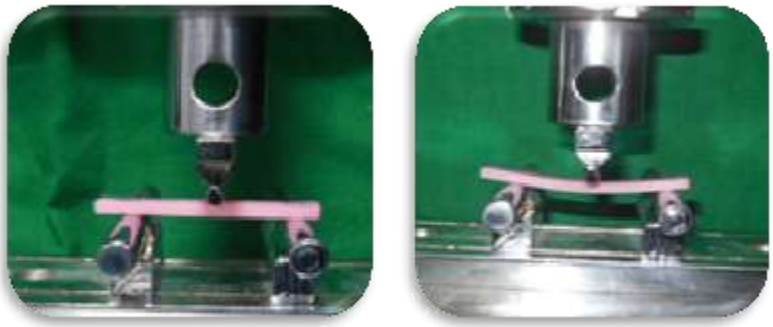


Fig.20 Testing of specimens

Plate V

Methodology

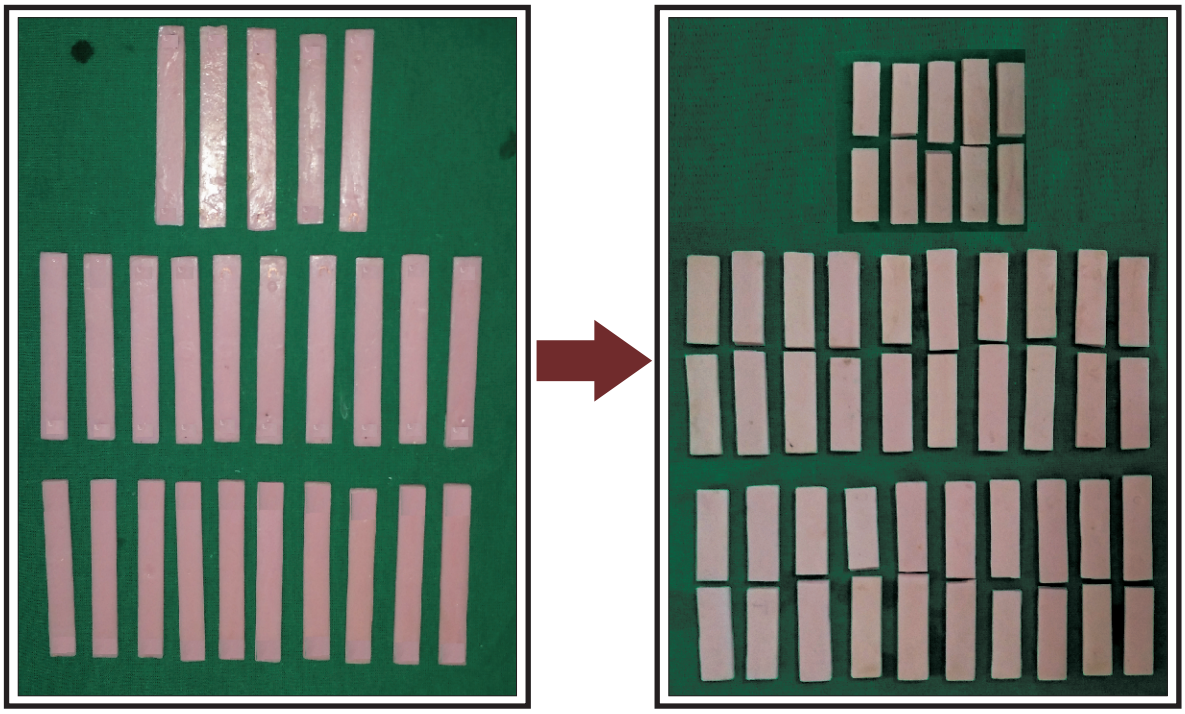


Fig.21 Group N: The control group; heat polymerized acrylic resin without reinforcement before and after testing of flexural strength

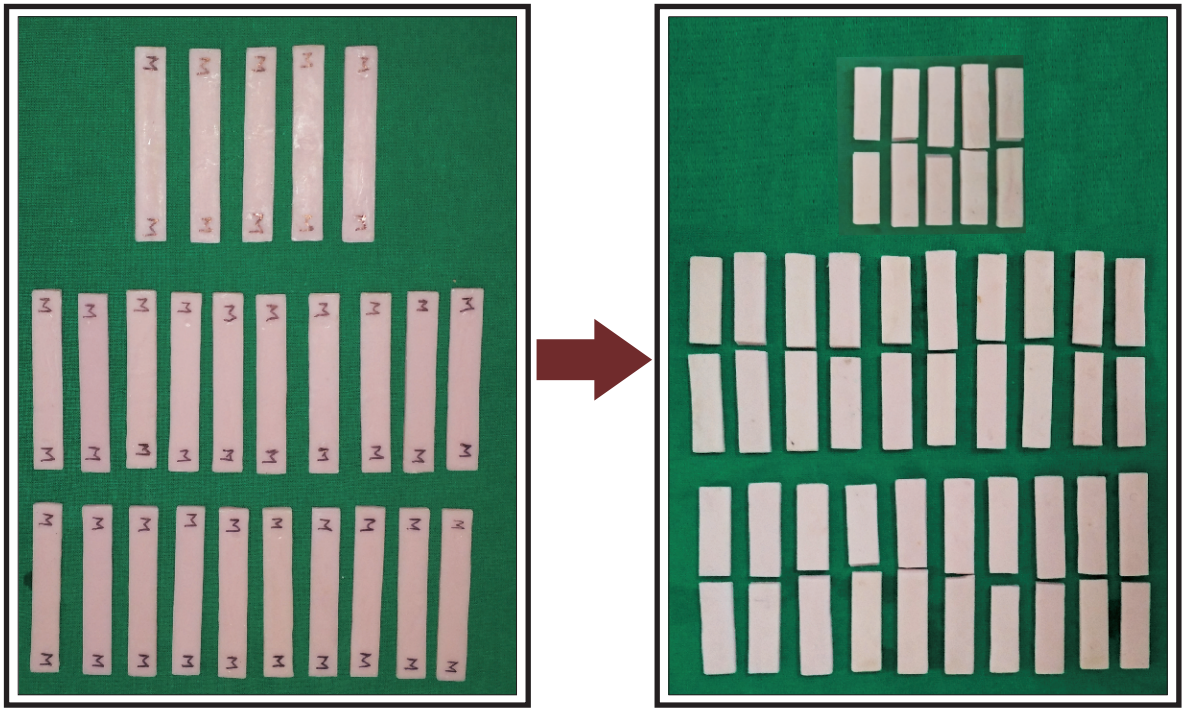


Fig.22 Group M: Heat polymerized acrylic resin reinforced with Monoclinic zirconium Oxide Nanopowder before and after testing of flexural strength

Methodology

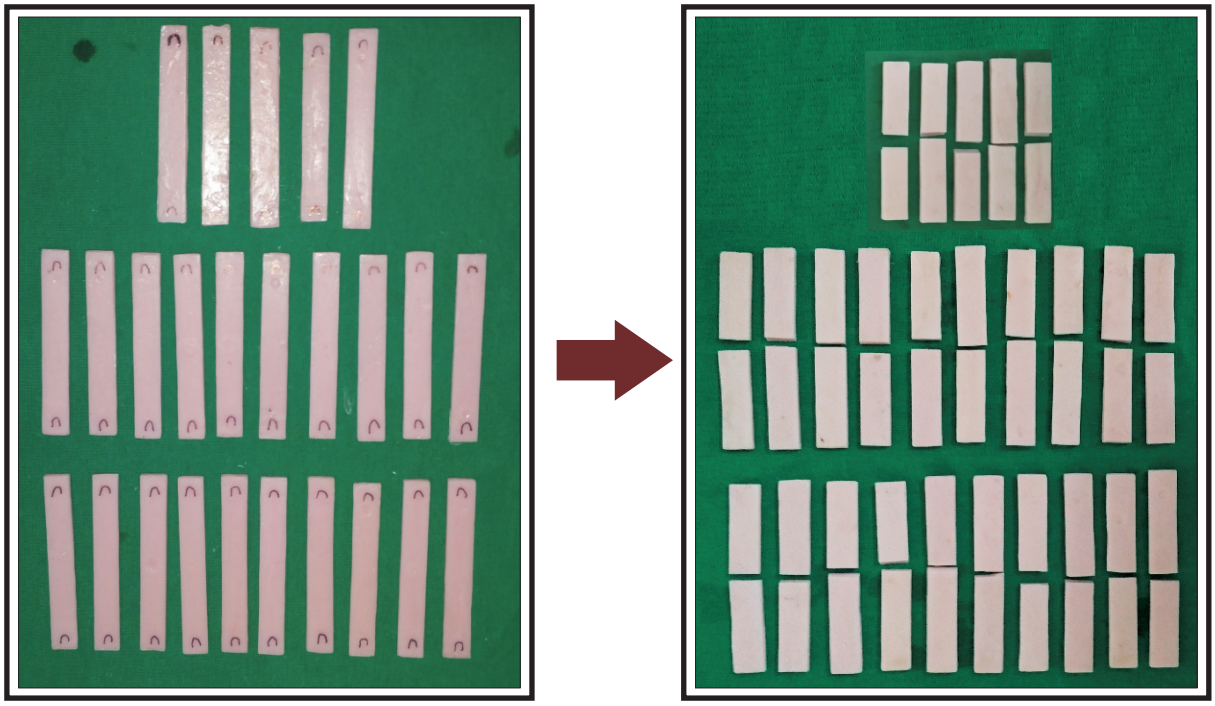


Fig.23 Group C: Heat polymerized acrylic resin reinforced with Cubic zirconium Oxide Nanopowder before and after testing of flexural strength

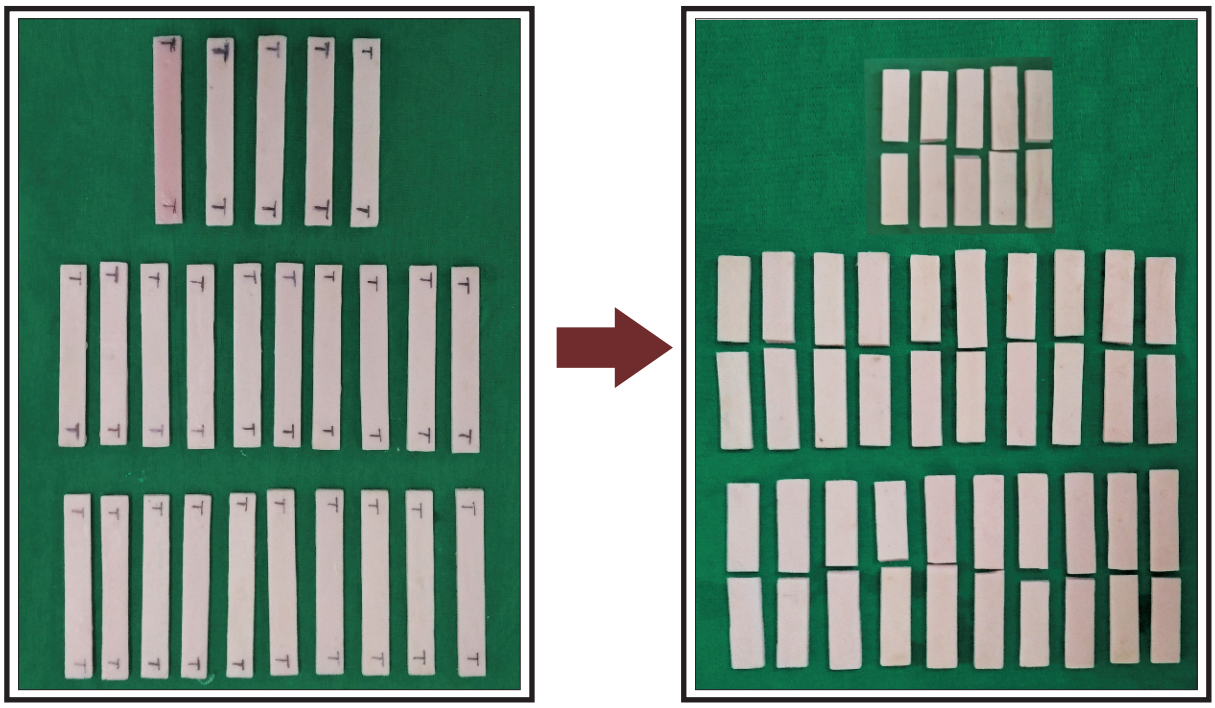


Fig.24 Group T: Heat polymerized acrylic resin reinforced with Tetragonal zirconium Oxide Nanopowder before and after testing of flexural strength

RESULTS

The results will be in direct proportion to the efforts you apply.

Results

In this study flexural strength of heat polymerized acrylic resin specimens reinforced with Monoclinic, Cubic and Tetragonal zirconium oxide nanopowder was evaluated and compared with conventional heat polymerized denture base resin.

A total of prepared 100 specimens were divided into four groups. Each group included 25 specimens.

Distribution of samples into groups

Sr. No.	Group	Code	n = no. of samples
1	The control group; heat polymerized acrylic resin without reinforcement	N	25
2	Heat polymerized acrylic resin reinforced with Monoclinic zirconium oxide nanofiller in 3% weight to that of polymer powder	M	25
3	Heat polymerized acrylic resin reinforced with Cubic zirconium oxide nanofiller in 3% weight to that of polymer powder.	C	25
4	Heat polymerized acrylic resin reinforced with Tetragonal zirconium oxide nanofiller in 3% weight to that of polymer powder.	T	25
	TOTAL NO. OF SAMPLES		**100**

25 specimens of each group were tested for flexural strength. Flexural strength was tested with INSTRON universal testing machine at a 5.0 mm/minute crosshead speed. The maximum load was determined from the chart and recorded as a fracture load in

N (Newton) and the flexural strength was calculated in MPa and the results were then statistically analyzed.

STATISTICAL ANALYSIS

The statistical calculations were performed using the software SPSS for Windows (Statistical Presentation System Software, SPSS Inc. 1999, New York) version 19.0.The following statistical methods were employed in the present study.

- Descriptive statistics including mean ,standard deviation.
    - **Mean** is sum of all observations divided by the no. of observations.
    - **Median** is value of the variable that divides the distribution into two equal parts i.e. 50 % observations will lie below and above it.
    - **Standard Deviation** is summarized as the amount of variation (change) in the observation from their average value (mean).

The formula used for calculating standard deviation:

$$SD = \sqrt{\frac{\sum(\overline{X} - X)^2}{n-1}}$$ Where:

$\overline{X}$ = Mean
X = Values of the variables
Σ = Sum of the value
n = Number of observations
Min = Minimum Value
Max = Maximum Value

- Analysis of Variance - one way.

- Tukey's multiple post hoc.
  - **Null Hypothesis:** There is no significant difference in the score between the groups i.e. N=M=C=T
  - **Alternate Hypothesis:** There is a significant difference in the score recorded between the groups i.e. $N \neq M \neq C_{\neq} T$
  - **Level of Significance:** $\alpha=0.05$
  - **One-way ANOVA**
  - The One-Way ANOVA test produces a one-way analysis of variance for a quantitative dependent variable by a single factor (independent) variable. Analysis of variance is used to test the hypothesis when several means are equal. This technique is an extension of the two-sample t test.
- In addition to determining that differences exist among the means, we may require to know which means differ. and post hoc tests was used. In the present study one- way ANOVA was applied to find out the mean difference.
  - **Tukey's multiple post hoc Test**
  - Once it is determined that differences exist among the means, post hoc range tests and a pair-wise multiple comparisons aid in determining which means differ. Range tests identify homogeneous subsets of means that are not different from each other. Pairwise multiple comparisons test the difference between each pair of means, and yield a matrix where asterisks indicate significantly different group means at an alpha level of 0.05.

- Tukey's HSD (Honestly significant Difference) is one of the widely used post hoc tests. In the present study Tukey's HSD post hoc Test was applied to make pairwise multiple comparisons to find out the difference between each pair of mean values of the four groups included in the study.

Table 1 provides the descriptive statistics for flexural strength for four study groups. The mean for **Group T** was maximum i.e. 106.69 MPa and the strength ranged between 91.22 MPa to 124.86 MPa. **For group N**, the mean strength was 79.11 MPa, and ranged between 62.14 MPa to 96.28MPa. The mean strength in **Group M** was 101.91 MPa, and it ranged between 85.26 MPa to 120.94 MPa.

For group C, the mean strength was 102.96 MPa, and ranged between 85.17MPa to 129.11 MPa. A graphical visualization of mean strength along with error bars is given in Graph 1.

Table 2 reveals that the mean flexural strength across groups differed highly significantly across four groups, as indicated by ***p*-value < 0.0001**. In order to determine, which groups contributed to overall significance, a pair-wise comparison of mean strength was performed using *Tukey's HSD test*.

Table 3 shows highly significant difference in the means of **Group T** and **Group N** ($p < 0.0001$). The difference between **Group M** and **Group N** was statistically significant ($p < 0.0001$). Also, the difference between **Group C** and **Group N** was statistically significant ($p < 0.0001$).However, the difference between **Group M, Group C** and **Group T** was statistically insignificant as revealed by p-value of ($p > 0.05$). This has been graphically shown in Graph 2.

DISCUSSION

A Good rule for Discussion is to use hard facts and soft voice

Discussion

Since ages, dentistry has been dependent 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.[64] 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.[5] 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 as metal base dentures and with porcelain teeth.[3,64] Thus this material is not ideal in every respect and it is the combination of virtues rather than one single desirable property.

The fracture of acrylic resin dentures is an unresolved problem in prosthodontics. A study by **Johnston et al** showed that 68% of acrylic resin dentures fracture within the first three years after fabrication.[8] 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. Any factor that exacerbates deformation of the base or alters its stress distribution predisposes the denture to fracture. The most common causes of denture fracture are poor fit, lack of balanced occlusion and deep notching at the midline i.e. labial frenum.[65]

Smith (1961) analyzed the practical situation with respect to the fracture of dentures and showed two types of failure.[8]

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 general conclusion that denture fracture occurs through flexural fatigue under the respective 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[7]. 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).[5]

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.[9]

Other attempts to enhance the properties of strength include addition of metal wire to resin and fabrication of cast metal. The primary problem with using metal wire is poor adhesion between the wire and resin, which leads to insignificant enhancement of mechanical properties.[9,23,28] 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.[9]

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.[17]

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. Reinforcement of dental resin with short or long fibres has been described in the literature for nearly half a century. Several different types of 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.[2] 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, and placement or bonding of the fibres within the resin.[9]

Carbon fibres have been added to the resin matrix and have proved to be successful in increasing the strength of the denture base. Despite producing successful reinforcement, the black colour of the fibres impart to the resin can be unacceptable to some denture wearers. This together with the problems associated with different handling characteristics and the possibility of toxicity, has restricted their use.[19]

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)**.[17] 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. They found that the fibre arrangement and inter fibre spacing, may be important factors in the success of the reinforcement.[2]

Various other fibres that have been tested and used included kevlar fibres[21,31,35], glass fibres[37,45,57] and ultra-high molecular weight polyethylene fibres.[20] Commercially, reinforcement of polymers with long, continuous fibres has been established as an effective means of developing engineering materials. However, dental applications of fibre-reinforced resin require a unique balance of properties like biocompatibility, esthetics and stability in the oral environment.[2]

Metallic powders have been added to conventional denture base resins by various investigators. Several studies in past by **Sehjpal and Sood(1989)[43], Abdulhamed and Mohammed Ali (2010)[47], Yadav and Elkawash (2011)[59]** showed that addition of metal oxides (silver, aluminum, 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.[3]

One of the most remarkable events in the field of dental material science has been the recent development of composite materials of great strength and low mass. These materials are a combination of very high modulus fibres and a resin matrix which binds them, so that the reinforced material work together to resist the load.[2]

The reason for the use of ceramic filler as opposed to metal filler is the lower filler density. Furthermore, these ceramic powders have the advantage of being white, and therefore are less likely to alter the finished appearance of the denture base material than are metal powders.[2, 3] Hence for this study zirconium oxide nanofiller was used as it had least density.

Incorporation of filler to resin matrix greatly increases its mechanical properties as zirconium oxide is well bonded to resin matrix. The primary purpose of

fillers is to strengthen the resin composite. Several important properties of dental composites are improved by increasing filler loading like increased hardness, strength and decreased wear; reduction in polymerization shrinkage.[2]

Zirconium oxide, commonly referred to as zirconia (ZrO_2), possesses strong ionic inter atomic bonding, giving rise to its desirable material characteristics. Zirconium oxide (ZrO_2) exists in three crystalline phases i.e Monoclinic, cubic & tetragonal and the most stable phase is Monoclinic phase.

We principally aimed to assess possible improvements in the flexural strength of PMMA, through incorporating of three different phases of ZrO2 Nano particles. 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.[11, 37]

The mechanism and kinetics of phase transitions in ZrO2 and its solid solutions were studied in details in[17, 66] ; as well as physical , chemical , and mechanical properties of the materials on its base.[67] It is known that monoclinic zirconia is the most thermodynamically stable phase; however , less stable modification of ZrO2(cubic or tetragonal) could form during amorphous gel crystallization.[29]

$$\text{Monoclinic} \overset{1173^\circ C}{\Leftrightarrow} \text{Tetragonal} \overset{2370^\circ C}{\Leftrightarrow} \text{Cubic}$$

The effect of crystallite size on phase formation both in pure zirconia and its solid solutions was studied carefully and it was demonstrated that the diminishing of the

crystallite size in the material leads to the stabilization of high symmetric zirconia based solid solutions.[69]

ZrO2 possesses strong ionic interatomic bonding, giving rise to its desirable material characteristics, that is, hardness and strength.

Addition of Zirconia Nano fillers to acrylic resin was found to improve mechanical properties. In addition to that ZrO2 was used because it has excellent biocompatibility and white color which less likely to alter esthetics. The Nano-filler particles were used in this study as it yields a better dispersion, eliminate aggregation and improve its compatibility with organic polymer.[70,71] Proper percentage range of zirconium oxide Nano-fillers (Percentages of 3% by weight) was selected because percentages above 7% leads to massive changes occurred in the color of acrylic.[10] It is noted that the concentration of ZrO2 (3%wt) lead to the maximum value of fracture toughness. There is no significant improvement in fracture toughness values of the modified acrylic resin at the concentrations of ZrO2 above that limit (5%wt and 7%wt). It is probably due to complete saturation of the polymer matrix with the ZrO2 particles.[72]

The particle size is another important factor as larger particle size decreases the tensile strength because they settle down when mixed with monomer.[9] The small metal oxide particles fill the interstitial polymer particles to give a heterogeneous mixture. Thus, it was more advantageous to use a smaller particle sized filler .

Ihab (2011)[36] gave a method for homogenous dispersion of filler particles in polymer matrix. It plays a major role in the mechanical properties of particulate-filled polymer composites. The reason for increase in flexural strength with addition of

aluminium oxide powder was attributed to proper distribution of alumina spheres within denture base powder which acts as potential fillers in the resin matrix.

Many attempts, however, to strengthen acrylic resin in this way failed because stress concentrations occurred around embedded materials, and the net effect of embedding fibres or metals is actually to weaken the polymer. This is often due to poor adhesion between the fibre, metal inserts and acrylic resin matrix.[3]

Although, acrylic resin is popular for denture construction, there is a frequent problem of lack of perception of temperature of food and beverages.[37] Interestingly, many of the ceramic materials have thermal conductivities approaching or even exceeding that of some metals.[3]

H. H. Chandler et al (1971)[38,39] suggested that one of the deficiencies of the available denture base resins is their radiolucency. Thus there are chances of ingestion or aspiration of either broken or portions of ill-fitting complete dentures by the patient. **Sehjpal and Sood(1989)[43]**stated that reinforced PMMA with metal oxide fillers like silver, copper, aluminium and zirconium not only increases strength but also provides radio-opacity to the heat polymerized denture base material.

The ceramic powders have the advantage of being white, and therefore are less likely to alter the finished appearance of the denture base material than are metal powders.[28] When higher concentrations of ZrO2 are used, slight discoloration of PMMA may be seen as it is white in colour so this may result in an esthetically unpleasant denture base material.[35] In present study lower concentration of 3% by wt of ZrO2 was used and slight visible change in colour of the specimens was seen.

The average values of flexural strength of heat polymerizing acrylic resins are near to 78-92 Mpa[7]. As discussed earlier ultimate goal of this study was to compare and evaluate the flexural strength of heat polymerized acrylic resin denture base material reinforced with 3wt% Monoclinic, Cubic and Tetragonal Zirconium oxide nanopowder. The mean flexural strength of Group T (106.69 MPa), Group C (102.96 Mpa) and Group M(101.91Mpa) which is greater than Group N (79.11 Mpa). This study shows that flexural strength can be increased by reinforcement with 3 wt% of Zirconium oxide nanopowder.

CLINICAL IMPLICATION

When the entire spectrum of this study is analyzed, it becomes evident that the heat polymerized acrylic dentures reinforced with Zirconium oxide nanopowder increases the flexural strength of the denture base material and thus, reduces the probability of occurrence of fracture. 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 in place. In addition to this, it imparts radio-opacity to the material so that any fractured remnants can be detected radiographically.[55]

SCOPE FOR FURTHER STUDIES

1. 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.

2. Further research is needed to evaluate the effect of aging on the new reinforced denture base material before clinical application.

3. Other physical and mechanical properties like thermal diffusivity, hardness, abrasion resistance, color stability and disinfectant property can be studied.

4. The heat polymerized acrylic dentures can be reinforced with even further different sized nanoparticles and various physical and mechanical properties can be evaluated.

5. Further research is also needed to quantify the filler distribution in the polymer matrix.

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

Summary

The heat cure denture base resins are extensively used for their excellent properties such as ease of handling, polishing and esthetics. However, the mechanical strength is not sufficient to maintain the longevity of the denture. The fracture of acrylic resin denture is a common occurrence.

This study was conducted to evaluate and compare the flexural strength of heat polymerized acrylic resin denture base material reinforced with 3 wt% of Monoclinic ,Cubic and Tetragonal zirconium oxide nanopowder. Standard heat cured acrylic resin specimens were fabricated according to ADA specification no. 12 and were reinforced with Monoclinic, Cubic and Tetragonal zirconium oxide nanopowder, with 25 specimens in each group.

Flexural strength was tested using Star system universal testing machine at a crosshead speed of 5mm/min. The findings were statistically analyzed and the flexural strength was calculated in MPa

Results show that the mean flexural strength for **Group T** was maximum i.e. **106.69 Mpa**. For **Group M**, the mean strength was **101.91 Mpa,** for **Group C** the mean strength was **102.96 Mpa** and the mean strength in **Group N** was **79.11 Mpa**. The

statistical analysis shows that there was highly significant difference in the mean flexural strength of **Group M,C,T** and **Group N ($p < 0.0001$).** However, there was no statistical difference between **Group M** , **Group C ($p > 0.05$) & Group T.**

Thus reinforcement with 3 wt% of Monoclinic, Cubic and Tetragonal Zirconium oxide nanopowder (Group M,C&T) showed a highly significant increase in flexural strength as compared to unreinforced specimens i.e. heat polymerized acrylic resin denture base specimens (Group N).

CONCLUSION

Conclusion

Within the limitations of this study following conclusions were drawn:

- Specimens with reinforcement increase the flexural strength.

- Reinforcement with 3 wt% of Monoclinic, Cubic & Tetragonal Zirconium oxide nanopowder (ZrO_2) showed highly significant increase in flexural strength.

- There was no clinically significant differences between the heat polymerized acrylic resin denture base specimens reinforced with 3 wt% of Monoclinic Zirconium oxide nanopowder (Group M), Cubic Zirconium oxide nanopowder (Group C) and Tetragonal Zirconium oxide nanopowder (Group T).

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TABLES AND GRAPHS

TABLE I

Descriptive statistics for flexural strength according to study groups

Groups	Number	Mean	SD	Min	Max
Control-N	25	79.1120	8.64779	62.14	96.28
Group-M	25	101.9132	8.10500	85.26	120.94
Group-C	25	102.9668	9.52661	85.17	129.11
Group-T	25	106.6952	9.70171	91.22	124.86

Table II

Comparison of mean flexural strength across four groups

Groups	Number	Mean	SD	f-value	p-value
Control	25	79.1120	8.64779	48.34	0.001*
Group-M	25	101.9132	8.10500		
Group-C	25	102.9668	9.52661		
Group-T	25	106.6952	9.70171		
Degrees of freedom			3		
Sum of squares			11797.861		
Mean square			3932.620		

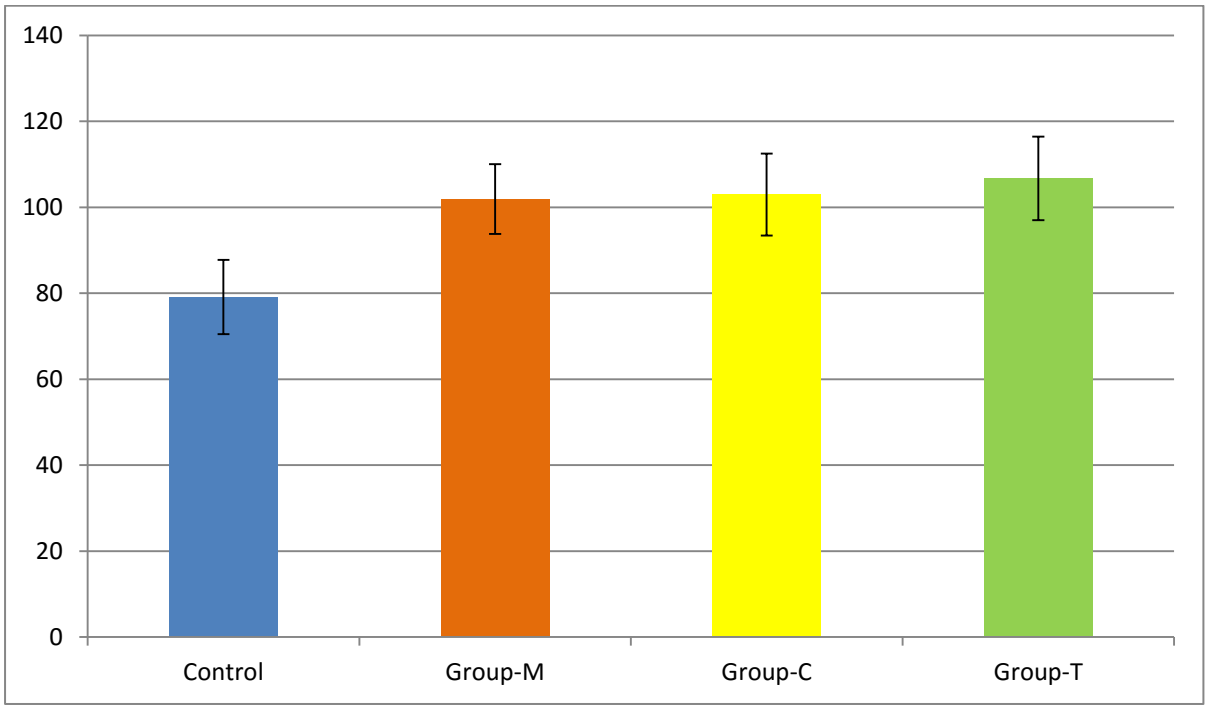
*****P-value obtained using *one-way analysis of variance and* significant at the 0.05 level.

Table III

Pair wise comparison of groups for flexural strength using *Tukey HSD test*

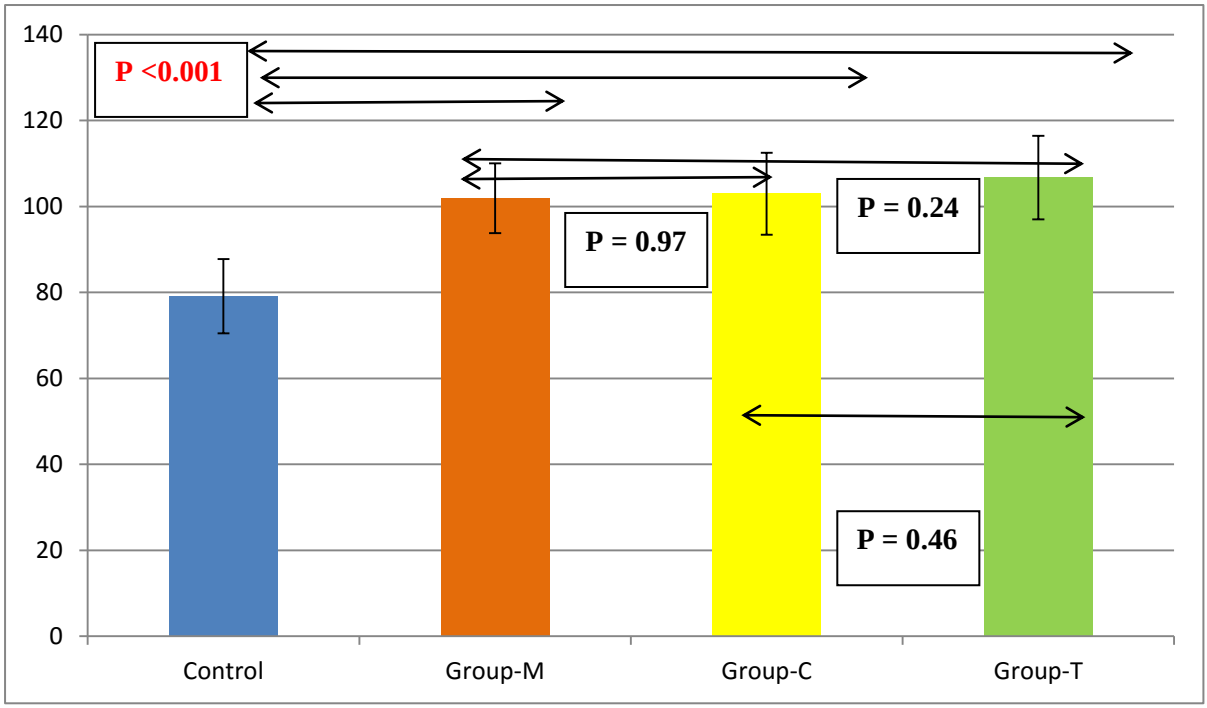
(I) value	(J) value	Mean Difference (I-J)	Sig
Control	Group-M	-22.80120*	0.001*Highly Significant
	Group-C	-23.85480*	0.001* Highly Significant
	Group-T	-27.58320*	0.001* Highly Significant
Group-M	Group-C	-1.05360	.976 Not Significant
	Group-T	-4.78200	.246 Not Significant
Group-C	Group-T	-3.72840	.465 Not Significant

*****P-value is significant at the 0.05 level



Graph I

Mean and error bar for flexural strength according to study groups



Graph II

Mean and error bars for Pair wise comparison of groups for flexural strength

ANNEXURE

Group : N			Group : M	
Sr. No	Flexural Load (N)	Flexural Strength (MPa)	Flexural Load (N)	Flexural Strength (MPa)
1	112.5	93.75	136.22	113.51
2	84.67	70.56	132.79	110.65
3	102.41	85.34	109.76	91.46
4	115.54	96.28	118.97	99.14
5	95.35	79.46	126.42	105.36
6	107.6	89.67	145.13	120.94
7	81.73	68.11	126.12	105.1
8	88.39	73.66	122.59	102.16
9	85.55	71.29	109.56	91.3
10	99.47	82.89	122.7	102.24
11	85.35	71.13	117.2	97.67
12	88.88	74.07	129.65	108.04
13	99.37	82.81	102.31	85.26
14	85.75	71.45	127.1	105.92
15	81.24	67.7	120.54	100.45
16	74.57	62.14	118.87	99.06
17	91.43	76.19	130.73	108.94
18	92.21	76.84	124.75	103.96
19	108.38	90.32	115.34	96.12
20	99.27	82.72	118.97	99.14
21	104.95	87.46	138.18	115.15
22	101.72	84.77	113.29	94.4
23	94.76	78.97	115.34	96.12
24	95.74	79.78	117.5	97.91
25	96.53	80.44	117.4	97.83
Mean		79.11		101.91

Group : C			Group : T	
Sr. No	Flexural Load (N)	Flexural Strength (MPa)	Flexural Load (N)	Flexural Strength (MPa)
1	121.61	101.34	124.46	103.71
2	128.67	107.22	112.7	93.91
3	122.59	102.16	149.84	124.86
4	122.3	101.92	128.47	107.06
5	112.3	93.59	124.75	103.96
6	117.89	98.24	133.67	111.39
7	141.9	118.25	114.57	95.63
8	102.21	85.17	109.46	91.22
9	108.58	90.48	113.68	94.73
10	124.85	104.04	134.65	111.4
11	122.99	102.49	141.8	118.17
12	131.41	109.51	114.85	95.71
13	119.75	99.79	124.85	104.04
14	112.01	93.34	119.16	99.3
15	130.92	109.1	120.93	100.77
16	131.9	109.92	148.53	124.82
17	120.34	100.28	126.32	105.26
18	138.08	115.06	121.22	101.02
19	132.49	110.41	121.03	100.85
20	115.54	96.28	140.92	117.43
21	109.07	90.89	141.02	118.17
22	117.89	98.24	124.67	103.89
23	124.26	103.55	138.9	116.8
24	154.93	129.11	128.1	106.75
25	124.55	103.79	139.84	116.53
Mean		102.96		106.69