A STUDY OF ULTRASTRUCTURE, CHEMICAL BOND PROFILING, AND MECHANICAL PROPERTIES OF NANOZIRCONIA AND NANODIAMOND FILLED NOVEL RESIN CEMENT

AAQIL ARSHAD HULIKATTI

UNIVERSITI SAINS MALAYSIA

2026

A STUDY OF ULTRASTRUCTURE, CHEMICAL BOND PROFILING, AND MECHANICAL PROPERTIES OF NANOZIRCONIA AND NANODIAMOND FILLED NOVEL RESIN CEMENT

by

AAQIL ARSHAD HULIKATTI

Thesis submitted in fulfilment of the requirements for the degree of Master of Science

January 2026

ACKNOWLEDGEMENT

All praise and gratitude is for Allah, the most merciful, for His guidance and help without which I would have never been able to accomplish this great achievement of my life. Alhamdulillah.

My sincere and honest thanks to my supervisor Dr. Saleem. D. Makandar for his relentless support, guidance and encouragement throughout the course of my journey. My long standing dream of pursuing masters in research came true because of him. Also, I would like to thank Dr. Huwaina bint Abd Ghani for her support and important feedback which eased my journey. My enormous gratitude to USM for giving me this opportunity and all the professors for their excellent teaching and the non-academic staff for all their efforts and co-operation without which I would not have accomplished this milestone of my life. Finally my wholehearted appreciation for my family members and friends for their prayers and for standing with me through this journey and giving me hope in times of difficulties.

This work was supported by a Universiti Sains Malaysia, Short-Term Grant with project no: R501-LR-RND002-0000001125-0000.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

Page

LIST OF ABBREVIATIONS

SEM	Scanning electron microscopy
EDX	Energy dispersive x-ray
FTIR	Fourier transform infrared ray
NZ	Nanozirconia
ND	Nanodiamond
NP	Nanoparticles
LCRC	Light-cure resin cement
DCRC	Dual-cure resin cement
SCRC	Self-cure resin cement
TMSPMA	3-(Trimethoxysilyl) propyl methacrylate
CS	Compressive strength
FS	Flexural strength
MH	Microhardness
UTM	Universal testing machine
VHT	Vickers hardness test
ANOVA	Analysis of variance
GPa	Giga Pascal
MPa	Mega Pascal
BisGMA	Bisphenol A-glycidyl methacrylate
TEGDMA	Triethylene glycol dimethacrylate
UDMA	Urethane dimethacrylate
HEMA	2-Hydroxyethyl methacrylate
CQ	Campharoquinone
CVD	Chemical vapor deposition
HPHT	High pressure high temperature
SCA	Silane coupling agent
WDS	Wavelength dispersive x-ray spectroscopy
EBSD	Electron backscatter diffraction
TEM	Transmission electron microscope
AFM	Atomic force microscopy
gf	Gram force

N	Newton
BHT	Brinell hardness test
RHT	Rockwell hardness test
KHT	Knoop hardness test
MHT	Meyer hardness test
CTE	Co-efficient of thermal expansion
IR	Infrared
SSB	Stainless steel band
SSC	Stainless steel crown
ZC	Zirconia crown
SARC	Self-adhesive resin cement
RMGIC	Resin modified glass ionomer cement
GIC	Glass ionomer cement
FT	Fracture toughness
DTS	Diametral tensile strength
YSZ	Yttria-stabilized zirconium
TGA	Thermo-gravimetric analysis
μTBS	Micro-tensile bond strength

LIST OF APPENDICES

KAJIAN ULTRASTRUKTUR, PEMPROFILAN IKATAN KIMIA, DAN SIFAT MEKANIKAL SIMEN RESIN TERISI NANOZIRKONIA DAN NANOBERLIAN

ABSTRAK

Kajian ini bertujuan untuk menilai dan membandingkan sifat mekanikal simen resin dwi-pengawet (DCRC) yang diubah suai dengan zarah nanozirkonia (NZ) dan nanodiamond (ND) terhadap simen komersial yang tidak diubah suai dan menjalankan analisis kimia menggunakan mikroskopi elektron imbasan-spektroskopi sinar-x serakan tenaga (SEM-EDX) dan analisis spektroskopi inframerah transformasi Fourier (FTIR). Ideanya adalah untuk memanfaatkan sifat mekanikal nanozirkonia dan nanodiamond yang sangat baik untuk mendapatkan DCRC yang lebih baik kerana nanofiller diketahui dapat meningkatkan sifat simen luting (Anasthasia Beketova et al, 2023). Tiga kumpulan telah dibuat, kumpulan 1: DCRC yang tersedia secara komersial, kumpulan 2: 10 vol% DCRC yang diubah suai NZ, kumpulan 3: 10 vol% DCRC yang diubah suai ND. Sebanyak 90 sampel telah disediakan, 10 sampel untuk setiap kumpulan. Tiub silinder penyukat digunakan untuk mengukur isipadu nanopartikel. 3-(Trimetoksisilil) propil metakrilat adalah agen gandingan yang digunakan. Sampel telah disediakan mengikut piawaian ISO dan digilap sebelum menguji kekerasan mikro (MH), kekuatan mampatan (CS) dan kekuatan lenturan (FS). Bagi analisis SEM-EDX dan FTIR, sampel telah dihancurkan dalam mortar menggunakan alu dan dijadikan serbuk halus. Data dianalisis menggunakan ujian ANOVA sehala dan ujian post hoc Tukey. Keputusan ujian ANOVA Sehala menunjukkan nilai dari tinggi ke rendah untuk mikrokekerasan: kumpulan 2 (62.59 ± 4.09 VHN), kumpulan 3 (57.80 ± 2.55 VHN), kumpulan 1 (39.36 ± 0.97 VHN), kekuatan mampatan: kumpulan 2 (132.18 ± 27.93

MPa), kumpulan 3 (126.21 ± 12.54 MPa) dan kumpulan 1 (121.12 ± 19.35 MPa) dan kekuatan lenturan: kumpulan 2 (72.5±10.4MPa), kumpulan 3 (71.06±6.3MPa) dan kumpulan 1 (66.92±5.27MPa). Terdapat peningkatan kecil dengan CS dan FS kumpulan 2 dan kumpulan 3 berbanding kumpulan 1. Peningkatan ketara dicatatkan dengan MH kumpulan 2, diikuti oleh kumpulan 3 dan kumpulan 1. Kumpulan 2 juga menunjukkan prestasi yang lebih baik daripada kumpulan 3. Penemuan SEM-EDX menunjukkan pelbagai bentuk nanopartikel yang diagihkan secara sama rata dalam simen resin yang diubah suai dan dalam FTIR, molekul dilihat diagihkan secara sama rata dengan kekuatan ikatan yang berbeza-beza antara molekul antara sederhana hingga kuat. Dalam batasan kajian ini, terdapat peningkatan ketara yang dilihat dalam kekerasan mikro simen resin yang diubah suai dengan nanopartikel zirkonia dan berlian. Begitu juga, peningkatan ketara dilihat dalam kekuatan mampatan dan kekuatan lenturan kedua-dua kumpulan yang diubah suai. Secara keseluruhan, simen resin yang diubah suai nanozirkonia menunjukkan hasil yang lebih baik daripada simen resin yang diubah suai nanodiamond. Penemuan ini menggalakkan siasatan lanjut dalam memahami bahan-bahan ini dengan lebih baik untuk membangunkan lebih banyak simen luting buatan sendiri.

A STUDY OF ULTRASTRUCTURE, CHEMICAL BOND PROFILING, AND MECHANICAL PROPERTIES OF NANOZIRCONIA AND NANODIAMOND FILLED NOVEL RESIN CEMENT

ABSTRACT

This study was to evaluate and compare mechanical properties of dual-cure resin cement (DCRC) modified with nanozirconia (NZ) and nanodiamond (ND) particles against commercial unmodified cement and perform chemical analysis using scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDX) and Fourier transform infrared spectroscopy (FTIR) analysis. Idea was to capitalize excellent mechanical properties of nanozirconia and nanodiamond to obtain improved DCRC as nanofiller are known to improve properties of luting cements (Anasthasia Beketova et al, 2023). Three groups were made, group 1: commercially available DCRC, group 2: 10 vol% NZ modified DCRC, group 3: 10 vol% ND modified DCRC. Total 90 samples were prepared, 10 samples for each group. Graduated cylinder tube used to measure volume of nanoparticles. 3-(Trimethoxysilyl) propyl methacrylate was the coupling agent used. The samples were prepared according to ISO standards and polished before testing microhardness (MH), compressive strength (CS) and flexural strength (FS). For SEM-EDX and FTIR analysis, samples were crushed in mortar using pestle and made fine powder. Data was analyzed using one-way ANOVA test and Tukey's post hoc test. Results of One-Way ANOVA test showed values from high to low for microhardness: group 2 (62.59 ± 4.09 VHN), group 3 (57.80 ± 2.55 VHN), group 1 (39.36 ± 0.97 VHN), compressive strength: group 2 (132.18 ± 27.93 MPa), group 3 (126.21 ± 12.54 MPa) and group 1 (121.12 ± 19.35 MPa) and flexural strength: group 2 (72.5±10.4MPa),

group 3 (71.06±6.3MPa) and group 1 (66.92±5.27MPa). There was minor enhancement with CS and FS of group 2 and group 3 compared to group 1. Significant improvement was noted with MH of group 2, followed by group 3 and group 1. Also group 2 performed better than group 3. SEM-EDX finding presents varying shapes of nanoparticles distributed evenly in modified resin cements and in FTIR, molecules were seen distributed evenly with varying bond strength among molecules ranging from medium to strong. Within limitations of this study, there was significant improvement seen in microhardness of resin cement modified with zirconia and diamond nanoparticles. Similarly, noticeable improvement was seen in compressive strength and flexural strength of both modified groups. Overall nanozirconia modified resin cement showed better results than nanodiamond modified resin cement. These findings encourage further investigation in better understanding these materials to develop more improvised luting cement.

CHAPTER 1

INTRODUCTION

1.1 Background

Resin cements are composite materials with less viscosity and consist of fillers and initiators that facilitate lower film thickness along with adequate working and setting time (Craig's restorative dental materials, 14^{th} Edition, 2019). They were introduced in dentistry in 1970's. Since their introduction there has been extensive study done to improvise their mechanical properties and today they are the material of choice as luting cement over other dental materials like zinc phosphate, glass ionomer cement (GIC) etc. They have undergone various changes. First resin cement was developed in 1970s and then in 1980s self-curing resin cement (SCRC) was developed followed by light-cured resin cement (LCRC) in 1990s and then dual cure resin in 2000s which were improvised over time and today they are the preferred materials in various applications. N. Hofmann et al found that when dual-cure resin cement was only self-cured (without light exposure), there was a steep decline in its strengths, flexural strength by 68.9%, elasticity by 59.2% and hardness by 86.1% compared to the one cured both by light and self-cure.(N. Hofmann et al, 2001). Resin cements have various applications such as cementation of crowns and bridges, inlays and onlays, endodontic posts, braces for orthodontic treatment, endo crowns, veneers, splints and so on. Though there has been significant improvement in their general properties yet they have their own shortcomings like polymerization shrinkage, poor bond strength, technique sensitivity and insufficient mechanical strength. The ultimate goals in developing these resin cements were to have good mechanical properties, effective bonding strengths, simple handling, biocompatibility, low polymerization shrinkage and favourable aesthetics.

Some of the causes of failed restorations are mentioned here. Most common cause of ceramic restoration failure is the failure of bulk of ceramic material which is because of defects and strains within the joint between resin cement and the restoration and not from the intaglio surface of the restoration (Yaou Wang et al, 2007), failure due to poor bond strength of resin cement with the veneer is the second most important reason for losing veneers, especially if the tooth structure is heavily compromised (Tariq F Alghazzawi, 2024), failure of resin cement bond with the tooth structure (Susan Hattar et al , 2015), insufficient wear resistance along with marginal discrepancy is one of the major shortcoming of veneers in long term (M. Peumans et al, 2000), microleakage due to lack of adhesion of luting cement to the tooth leads to breakdown of luting cement because of seepage of oral fluids and microorganisms (Manjari S Gundewar et al, 2022). The reasons for these causes of failure of resin cement have been investigated and are mentioned in table 2.2.

Studies have found that the use of filler particles, their size and morphology, Silane treatment greatly improvise the strength and reduce the wear and polymerization shrinkage of resin cement (Yasuhiro Tanimoto et al, 2006; Konstantinos Masouras et al, 2008; M Kawaguchi et al 1989; Bum Soon Lim et al, 2002; B R Lang et al, 1992; T. G. Nunes et al, 2007; F Gonçalves et al, 2010). Basically, they provide mechanical reinforcement in the cement. Various filler particles have been used such as hydroxyapatite crystals, quartz, barium silicate, strontium silicate, zinc silicate, lithium aluminium silicate, yttrium, aluminium hydroxide, nanozirconia, etc. In current study we used zirconia and diamond nanoparticles as fillers because of their excellent biomechanical properties. Zirconia has shown promising results in previous study by Guangqing Guo et al. 2012, in improving flexure properties and enhancing the resistance against breaking of composite resin cements. Nanodiamond (ND) is a carbon allotrope having superior physical, mechanical, thermal and optical features (Barbara Gronwald et al, 2022). They also neutralize the resin acidity during setting reaction by providing ions (Ferracane JL et al, 2011). Filler also add radiopacity to the resin cements and this is crucial in digital radiographic monitoring of the restoration, check open gingival margins and also the resulting secondary caries, presence of voids, detect over hanging of margins (Taeko Goshima, Yota Goshima, 1990 and B. O'Rourke et al, 1995).

Hence this research was done to analyse the microhardness, resistance to compression and bending forces and chemical composition analysis using FTIR and SEM EDX.

1.2 Problem Statement

Though a great success has been achieved to overcome various shortcomings, but their mechanical properties still pose a challenge to researchers and clinicians. Ideally resin cement should match the enamel and dentin in their mechanical properties and fracture resistance to withstand the occlusal loads and wear, especially in posterior teeth, but contemporary resin cements are affected by factors such as curing mode (Grace De Souza et al, 2015), exposure to light for polymerization in dual-cured resin cement (Mahmoud Bahari et al, 2014), thickness of restoration (Leila Pisheva et al, 2019), shade of the resin cement (Khalid Dhafer Al Hendi et al , 2024) etc. and thus compromising their mechanical properties and their long-term success. Comparison of mechanical properties of existing dual-cure resin cements with that of the properties of teeth reveals significant shortcoming in overall properties of the cements. Amanpreet Kaur et al. concluded in their study that if compressive strength of the material falls short of the strength of the tooth then the material breaks and if it is superior than the tooth then the tooth fractures therefore compressive strength of material should be similar to that of the tooth (Amanpreet Kaur et al, 2023). Resin cement containing silica fillers showed poor bonding between coupling agent and the filler leading to failure of the cement (Raquel Osorio et al, 2012). As a result, there is a need to develop resin cement with improved mechanical properties and fracture resistance.

1.3 Justification

Long-term cements are either water based or resin based (Grzegorz Sokolowski et al, 2018). Resin cements have superior properties than water-based cements. They are the most recent luting cements introduced in dentistry.

Julia Fehrenbach et al, 2021, found conventional resin cements performed better than resin cements that are self-adhering (SARC) to the teeth. In another study by Lívia Duarte Santos Lopes et al, 2021, mixed and adhesive failures were noted for conventional resin cement whereas SARC showed mostly adhesive failures. Self-adhesive cements when compared with conventional cement showed poor mechanical properties and the type of monomer used was found to interfere directly with mechanical properties of resin cements (Maria Helena Rossy Borges et al, 2020). Rahaf kurdi et al in their in-vitro study compared conventional resin cement against self-adhesive resin cement for water solubility and found conventional cement performed better and this was attributed to hydrophilic nature of self-adhesive cement as well as their filler characteristics (Rahaf kurdi et al, 2013).

This study aims to do chemical analysis and compare the properties of modified resinous cement with incorporation of nanozirconia and nanodiamond particles in a measured proportion in commercially available dual-cure resin cement. From studies it is evident that the strengths of existing resin cement are unsatisfactory and lower than standard properties of teeth. It is necessary to enhance their properties to improve their performance and last longer. Since nanozirconia and nanodiamond have superior mechanical properties and are biocompatible, non-toxic and economical so with their addition the expectations are to strengthen the resin cements

1.4 General Objectives

The purpose of this study was to modify commercially available dual cure resin cement with nanozirconia and nanodiamond particles and analyze its chemistry and compare microhardness, resistance to compression and flexure of modified cement with commercially available dual-cure resin cement.

1.5 Specific Objectives

1.5.1 Objective 1: SEM-EDX Analysis

To perform chemical analysis of experimental resin cement modified with 10% nanozirconia and 10% nanodiamond particles and compare it with chemistry of commercially available dual-cure resin cement using electron microscopy and dispersive X-ray analysis (SEM-EDX).

1.5.2 Objective 2- FTIR Analysis

Determining the chemical composition of experimental resin cement modified with 10% nanozirconia and 10% nanodiamond particles and compare it with chemistry of commercially available dual-cure resin cement using FTIR analysis.

1.5.3 Objective 3: Microhardness testing

To compare microhardness of 10% nanozirconia filled and 10% nanodiamond filled experimental resin cement with that of commercially available dual-cure resin cement.

1.5.4 Objective 4: Compressive strength testing

To compare compressive strength of 10% nanozirconia filled and 10% nanodiamond filled experimental resin cement with that of commercially available dual-cure resin cement.

1.5.5 Objective 5: Flexural strength testing

Comparison of 10% nanozirconia filled and 10% nanodiamond filled experimental resin cement with that of commercially available dual-cure resin cement for the resistance to bending forces.

1.6 Research Questions

1) Will there be a significant variation in the chemistry and surface morphology of experimental resin cement modified with nanozirconia and nanodiamond fillers compared to commercially available dual-cure resin cement when investigated under electron microscopy and with x-ray analysis (SEM-EDX)

2) Will there be significant difference in the constituents and adhesion strength of experimental cement modified by nanozirconia and nanodiamond fillers compared to commercially available dual-cure resin cement when analyzed with FTIR analysis?

3) Will the microhardness of experimental resin cement modified with nanozirconia and nanodiamond fillers be superior to its unmodified commercially available variant?

4) Is compressive strength of experimental resin cement modified with nanozirconia and nanodiamond fillers improved than that of its commercially available cement type?

5) Is the flexure property of experimental resinous cement modified with nanozirconia and nanodiamond fillers better than that of commercially available dual-cure resin cement?

1.7 Null Hypothesis

1) There could be no changes in the chemistry and surface morphology of experimental resin cement modified with nanozirconia and nanodiamond fillers as compared to commercially available dual-cure resin cement.

2) The ingredients and adhering strength of the cement under study modified using nanozirconia and nanodiamond is not expected to be different from commercial duel-cure resin cement.

3) There is no significant improvement expected in the microhardness of experimental resin cement modified with nanozirconia and nanodiamond fillers than that of commercially available dual-cure resin cement.

4) The compressive strength of experimental resin cement modified with nanozirconia and nanodiamond fillers is expected to show insignificant enhancement than that of commercially available dual-cure resin cement.

5) The expectation of flexural strength of experimental resin cement, modified with nanozirconia and nanodiamond fillers, to perform better than commercially available dual-cure resin cement is insignificant.

CHAPTER 2

LITERATURE REVIEW

2.1 Resin cements in dentistry

Resinous dental cements are the materials containing filler and initiator and possess less density to aid a low film thickness and working and setting time (Craig's Restorative Dental Materials, 14th Edition, 2019). Resin luting cements are unique compared to other luting agents in that the resin cement forms a polymerized layer between the tooth and the restoration while other cements prepared from mixing powder and liquid form hydrogel matrix (Hill EE, Lott J, 2011). In early 1950s, resin based luting compounds consisted of methyl methacrylate. They had poor adhesion with tooth structure, had high volumetric constriction, high expansion to thermal exposure, absorbed water resulting in micro leakage at the junction of tooth and the cement and removing of excess material was tough. (Kenneth J. Anusavice et al, 2013). Contemporary resin cements have better properties compared to earlier resin cements. These latest cements come in various delivery forms such as powder-liquid, paste-paste materials dispensed with a “clicker” device, capsules which are mixed in a trituration device, and some as auto-mix materials. A recent study evaluating retention of different resin cements and manipulating systems discovered that the powder-liquid hand-mixed cements were significantly more retentive than the paste-paste versions of the same cements (Glen H. Johnson et al 2009).

Various luting cements are mentioned below in fig 2.1, (Aleksandra Maletin et al, 2023).

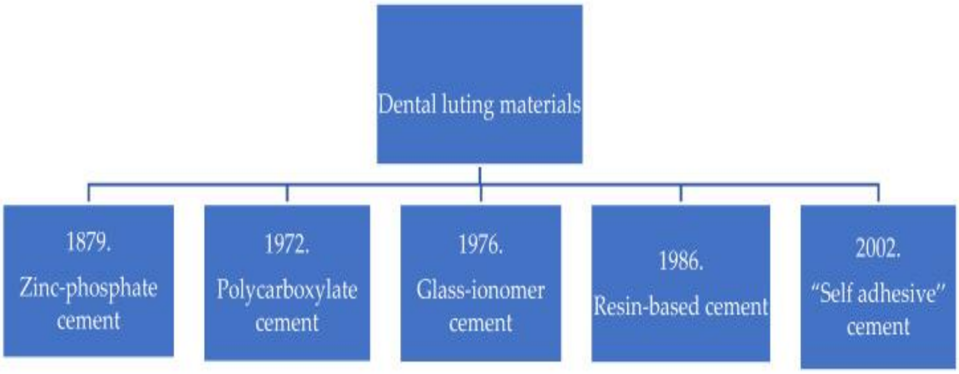

Figure 2.1 Various Luting cements

Though contemporary resin cements have superior mechanical properties compared to other luting cements, they are poor when compared to enamel and dentin. Properties of enamel and dentin of human teeth are mentioned in Table 2.1.

Table 2.1 Mechanical properties of human teeth, enamel and dentin

	Property	**Value**	**Reference**
Enamel	Hardness	2.0-3.5 GPa	(Cuy, J.L et al, 2002)
	Young's modulus	8.-120 GPa	Biswas Nilormi et al 2013, Li Hong He et al 2006
	Fracture toughness	0.67-3.93 MPa $m^{1/2}$	Yeau-Ren Jeng et al 2011; Devendra Bajaj, Dwayne Arola, 2009
	Compressive strength	384 MPa	G Willems et al 1993; Grzegorz Milewski 2005
Dentin	Hardness	0.3-0.7 GPa	(Kinney, J.H et al , 2003)

Table 2.1 Continued

	Property	Value	Reference
	Young's modulus	10-40 GPa	Biswas Nilormi et al, 2013, Mahoney E et al 2000, Angker Linny et al 2005
	Fracture toughness	1.1-2.3 MPa $m^{1/2}$	Yan, J et al 2009, Iwamoto Nanako et al 2003)
	Compressive strength	297 MPa	G Willems et al 1993, Grzegorz Milewski 2005

There are various reasons that cause failure of resin cement and restorations. Understanding the reasons will guide in developing a better resin cement. Some of the reasons are mentioned in Table 2.2.

Table 2.2 Correlation between failure of cements and their mechanical properties

Cause	Reason	Description	Reference
Microleakage	Micro fracture of resin cement	Due to high stress in localized areas, e.g.- marginal area. These are initial mode of restoration failure	W J Libman et al, 1995; P Fan et al, 1995
	Plastic deformation of resin cement	It is associated with high dislodgement rate of bridges	O Hansson, 1994; N H Creugers et al, 1991
	Poor metal-cement bond	It leads to dissolution of resin cement at the finish margin leading to microleakage, secondary caries and dislodgement of restoration	Marina Di Francescantonio et al, 2010

Table 2.2 Continued

Cause	Reason	Description	Reference
Cohesive failure (Failure within cement)	High C-Factor	High C-factor (>25) is another potential cause of high shrinkage and stress leading to instant cohesive failure	A.J. Feilzer et al, 1987
	Polymerization shrinkage	Volumetric shrinkage leads to stress within restoration and ultimately bond failure. Curing mode is crucial factor.	Saad A. Osman et al, 2008, Thomas Spinell et al, 2009
	Film thickness of resin cement	Film thickness of resin cement- Thin film layer showed low plastic deformation and stress and lower failure rate than high thickness layer of resin cement	Niek De Jager et al, 2005
Adhesive failure (Frequently seen at resin cement-tooth interface	Some of the reasons are choice of adhesive and primers, surface pre-treatment, adhesion protocol etc.	May be related to poor mechanical properties of resin cement which results in debonding	Venkata Suresh Venkataiah et al, 2025

Table 2.2 Continued

Cause	**Reason**	**Description**	**Reference**
Wear resistance	Filler size	Wear of resin is affected by filler size and mode of wear test. In toothbrush test, an increase in the filler size lead to decreased wear value whereas in three-body wear test, a decrease in filler size resulted in lower wear value. Large filler size also leads to poor wear resistance due to crack propagation at filler/resin interface and small filler sizes leads to reduced particle projections at the surface thus improving the resistance to wear	Koichi Shinkai et al, 2001 Farah Elfakhri et al, 2022
	Filler amount	Higher the filler content, greater is the wear resistance	Y Torii et al, 1999
	Incompletely polymerized resin matrix	Improper curing leaves more uncured monomer which wears of easily, higher the degree of conversion lesser is the wear.	J.L. Ferracane, et al, 1997; C.P. Turssi et al, 2005

Table 2.2 Continued

Cause	Reason	Description	Reference
	Abrasive resistance of the resin matrix	Crack propagation in resin cement occurs mainly in resin matrix as the matrix is softer than the fillers hence increasing the abrasive resistance of the resin matrix is very helpful in increasing the wear resistance	K. Kawai et al, 2004; Erik Asmussen, 1998
	Bond between the filler and the resin matrix	Hydrolysis of the Silane coupling agent results in degradation of cement hence a hydrophilic coupling agent enhances bond strength and wear resistance	Tomotaro Nihei et al, 2008
	Modulus of elasticity	High elastic modulus cements have better wear resistance but they exhibit high stresses leading to debonding	A.O Spazzin et al, 2009

Composition of resin cements-

The main constituents of resin cements are resin matrix and filler particles. Table 2.3 describes the general composition and their function in resin cements.

Table 2.3 Composition and their role in resin cement

Organic matrix	Inorganic contents
BisGMA (it is highly viscous hence reduces degree of conversion of monomer (Bhanu Pratap et al , 2019), reduces polymerization shrinkage of resin matrix) UDMA [used as a replacement of BisGMA, have greater polymerization rate and degree of conversion than BisGMA based resin cements (J.W. Stansbury, S.H. Dickens, 2001)] TEGDMA (used as diluent, reduces viscosity of matrix and makes it flexible) HEMA (reduces viscosity, prevents collagen collapse and restores collapsed collagen network), reduces the surface tension of acid-etched dentin by increasing its wetting ability and increases bond strength (Nakabayashi N, Takarada K 1992, Carvalho RM et al 1996, Hitmi. L et al 2002). Silane coupling agent (bonds resin matrix with filler particles) Camphoroquinone (photo-initiator)	Various filler particles have been used such as amorphous silica, strontium glass, zirconium silicate, barium borosilicate glass, fluoro-aluminosilicate glass, sodium persulfate cupric acetate, and ytterbium fluoride (Marcionilia Santos et al, 2024).

Classification of resin cements-

There are various ways of classifying resin cements.

1) Classification based on mode of curing: ISO (4049) 2009, (

   (Fourteenth edition of Craig's restorative dental materials, 2019)

   a) Class 1 – self cured resin cements (SCRC)
   b) Class 2- light cured resin cements (LCRC)
   c) Class 3- Dual cured resin cements (DCRC)

2) Based on polymerization mechanism: (Burgess John. O et al, 2010)

   a) Light cured- photo initiation, curing activated by exposure to light
   b) Chemical cured- curing happens by chemical reaction of two materials (base and catalyst)
   c) Dual cured- curing activated by chemical reaction and exposure to light

3) Based on adhesive scheme: (Burgess John. O et al, 2010)

   a) Total etch- 30%-40% of phosphoric acid is used to clear the debris coating before adhesive is applied. They can be chemical-cured, photo-cured or both.
   b) Self-etch- self etching primer is first applied and then mixed cement is placed. These are usually dual-cured cements.
   c) Self-adhesive (all in one cement or universal cement) - Here phosphoric acid is replaced by phosphoric acid esters hence do not require bonding agent application (S Christy, MS Nivedhitha, 2022). These too are primarily dual-cured cements.

Properties of resin cement (Dr. Rashmi R. Shah 2021):

- Strength resisting compression:- 180 MPa
- Resistance to tensile load:- 30 MPa
- Cementing layer thickness:-10-25um
- Biocompatibility: - affects pulp, safety layer with GIC, $Ca(OH)_2$ as lining material is essential.
- Dissolving ability:- Doesn’t dissolve in fluids in mouth
- Volumetric constriction:– High
- Bond strength to enamel :– 7.4Mpa

2.2 RelyX Unicem 200

It is self-adhesive, DCRC introduced in 2011 by 3M ESPE. It is available in 2 forms based on their dispensing system.

1) RelyX U200 Auto mix
2) RelyX U200 Clicker

Table 2.4 Chemical composition of RelyX U200

Base paste	**Catalyst paste**
Monomers of methacrylate with phosphoric acid	Monomeric methacrylate
	Non-acidic inorganic fillers
Monomers of methacrylate	Fillers coated with coupling agent
Fillers coated with Silane agent	Compounds for initiating the reaction
Compounds for initiation of reaction	Components to stabilize
Stabilizing agents	Colouring agents
Ingredients controlling the flow	Substances to control the flow

Source: 3M ESPE internal data

Mechanical properties of RelyX U200

Table 2.5 Mechanical properties of RelyX U200

Properties	**Values**
Resistance to bending load	99 MPa
Compression strain resistance	291 MPa
Elasticity	6.6 GPa
Hardness	190 MPa
Cementation layer thickness	13 µm
Absorption of water	28 $\mu g/mm_3$
Solubility	0 $\mu g/mm_3$
Expansion after one month	0.63 %

Source: 3M ESPE internal data

Hardness of photo-cured and dual method cured cement were investigated. The cements were polymerized through single piece zirconia specimens with varying transparency, such as translucent (T); high translucent (HT); super translucent (ST); and extra translucent (XT) and the samples were cured at 0, 24hrs and 48hrs. Two LCRCs (Variolink N LC; VL and RelyX Veneer; RL) and two DCRC (Variolink N DC; VD and RelyX U200; RD) were utilized. In result, all materials exhibited increased microhardness from 0 h to 24 h ($P < .001$). After 2 days, the hardness of LCRCs reduced greatly in T group than XT group. After every curing cycle, VD had higher strength than VL ($P < .05$), and RD had higher VHN than RL ($P < .05$). The transparency of zirconia affected hardness of LCRC but not on DCRC. DCRC exhibited higher VHN than the LCRC from the same brand. Hardness of all cements was greatly improvised from 0 h to 24 h (Sawanya Pechteewang, Prarom Salimee, 2021).

To understand the CS of RelyX U200 along with other physical properties it was studied and compared with different SARCs and conventional resin cement. RelyX ARC was used as conventional cement and 3 self-adhering cements (RelyX U200, Maxcem Elite, Bifix SE) were used. Apart from CS, all these resin cements were investigated for their DTS, MH and the rheological properties. The result of this study was that the resistance to compressive strain of RelyX ARC and Maxcem Elite cements was more than RelyX U200 and Bifix cements ($p<0.05$). According to microhardness analysis done with Knoop hardness test, all the cements were same ($p>0.05$) but Maxcem presented lower strength than other cements ($p<0.05$). For diametric tensile strength test, RelyX U200 and RelyX ARC cements were statistically similar ($p>0.05$), presented higher value when compared to the Maxcem and Bifix cements ($p<0.05$). Regarding the rheology test, Maxcem Elite and RelyX ARC cements showed greater elasticity. This study concludes that the self-adhering cements had poor properties than conventional cement. The chemistry, its structure and the monomers used directly impacted on their properties (Maria Helena Rossy Borges et al, 2020).

FS of RelyX U200 was compared with two different resin cements (RelyX™ Universal and Duo-Link Universal). The results showed that Duo-Link Universal cement having the best average of resistance to bending forces (104.7±7.8 MPa). Huge differences were noted between these groups ($p< 0.001$) but not between both RelyX variants. It can be concluded that Duo-Link cement presented higher resistance to flexure than other two thus indicating that Duo-Link Universal is suitable in cases where high load is expected and it would last longer especially in load bearing areas and in huge restorations (Socorro Noa-Yarasca, Ana López-Flores , 2025).

2.3 Nanodiamond particles (ND)

NDs are allotrope of carbon that possesses superior physical, mechanical, thermal and optical characteristics due to their shape (Barbara Gronwald et al, 2023). Along with excellent mechanical properties, NDs also have low toxicity (X. Zhang et al, 2010), biocompatibility (Y. Zhu et al, 2012), stable fluorescence (M.H. Alkahtani, 2018) and other properties of bulk diamond but superior to them (Muhammad Khan et al 2018, Muhammad Khan et al 2017).

Impact strength is the material's strength to absorb and bear sudden, forceful impacts without breaking. Different percentages of ND particles (0.25%, 0.5%, 0.75%, and 1% ND by weight) were added to auto-polymerized repair resin and its influence on impact strength of repaired denture PMMA resin was evaluated and compared against unmodified group. When compared, the modified groups (0.25% and 0.5%) whereas it declined marginally with 0.75% and 1% ND and 1% presented the lowest value (3.48±0.43 KJ/m2) and 0.25% the highest (6.24±0.55 KJ/m_2) and then 0.5%ND (5.93±0.21 KJ/m_2) (Abdel-Nasser M. Emam, 2024).

NDs enhance MH of composite resins. Polymer–matrix composites were reinforced with NDs (0.8, 1.6, and 3.2 wt%) with particle size below 10nm and compared with SiO_2-reinforced composites. Both these modified composites were then compared with commercially available composites (Tetric Evoflow, 3 M ESPE Filtek, and Tetric Restorative). The incorporation of 0.8 wt% of ND causes an increase in microhardness of ~95%, while the quantity needed to reach similar microhardness for micrometric SiO_2 reinforcement is above 3.2 wt%. Moreover, microhardness increases by ~420% in the case of using ND with a content of 3.2 wt%; this value has not been reached with SiO_2 even with concentrations up to 25 wt%. A maximum hardness exceeding 65 HV is achieved with a ND reinforcement of 3.2 wt%. Additionally, it is important to point out that the microhardness of composites reinforced with 10 wt% of micrometric SiO_2, which is 23.7 ± 0.4, is still lower than the one of Nano composites filled with 1.6 wt% of ND, being 27.7 ± 3.4. If these values are compared with the microhardness of commercial dental composites, Nano composites reinforced with contents as low as 0.8 wt% present values above some of the mentioned commercially available composites (Rocío Moriche et al, 2024).

NDs enhance FS of PMMA resin. The influence of, less quantity of nanodiamond (ND) addition and curing in autoclave, on the resistance to bending forces by PMMA denture base resin was investigated. Thermally cured PMMA was reinforced with lesser amount of ND of varying strengths of 0.1%, 0.25%, and 0.5% and compared with conventional PMMA denture base resin. This resulted in a marked improvement in the resistance to flexure in first two groups with the values of 128.8 MPa at 0.25% ND for group I and then 124.7 ± 9 MPa at 0.1% for group II whereas at 0.5% there was a decline in the FS (113.5 ± 8.7 MPa). From these results it can be concluded that at low concentration (0.1%, 0.25%) of NDs FS of PMMA denture base resin increased but with further increase (0.5%) there was a decline in FS (Shaimaa M Fouda et al, 2022).

Similarly, Utkarsh mangal et al. investigated the role of ND on the properties and fungal resistance of PMMA denture base resin. They used different percentage of ND (0.1, 0.3 and 0.5 wt%) and compared with control group and 5% ZrO_2

nanoparticles and tested for FS, elasticity, Vickers hardness, rough texture and fungal adhesion. All the groups of ND-PMMA had greater FS, elasticity compared to control group and ZrO_2 group (P<0.001). FS of control group was 66.12 ± 4.27, 5% ZrO_2 group had 67.21 ± 3.32, 0.1% ND group had 85.96 ± 4.15, 0.3% ND group was 83.19 ± 8.43 and 0.5% ND group was 81.75 ± 8.76. Among the ND groups higher FS was noted in 0.1% group than that of 0.3% and 0.5%. Vickers hardness values were also better than the unmodified group (P<0.001). VHT of control group was 12.89 ± 1.81 kg/mm2, ZrO_2 was 14.327 ± 1.38 kg/mm2, 0.1% ND had 13.860 ± 1.27 kg/mm2 (comparable to control group), 0.3% ND was 14.487 ± 1.51 kg/mm2, and 0.5 wt% ND had15.653 ± 1.223 kg/mm2. Fungal adhesion too reduced significantly (Utkarsh Mangal et al, 2019).

Types of ND:

According to primary particle size, existing commercial ND are categorized into 3 groups (Shenderova Olga. A, Garry McGuire, 2006),

a) Nano crystalline particles- 1 to ≥150 nm is the filler size. Of all the nanodiamond materials, the purest form is monocrystalline natural nanodiamond powder.
b) Ultra crystalline diamond particles- particles is in range of 2 to 10 nm. There are several types but detonation ND has been commercially useful.
c) Diamondiods- There size is ~1-2nm. They are building block of nanotechnology as they are strong and well structured. They are extracted from petroleum and are not easy to manufacture.

Mechanical properties of ND:

1) ND possesses excellent properties like high strength, resistance to wearing, superior modulus of elasticity, chemically stable, low expansion and high heat conduction (Meng-jie Zhai et al, 2021).
2) Hardness ranges from 56 GPA-257 GPA. The variation depends on the load applied by the indenter (V. Blank et al, 1999). On Mohs scale it measures 10 (I. Neitzel et al, 2012).
3) Compressive strength of ND is ~54 GPa (Zihe Li et al, 2022).
4) Young's modulus- 1050 GPa (Claude A. Klein et al, 1993).
5) Co-efficient of thermal expansion (CTE)- $\approx 1.1 \times 10^{-5}\ K^{-1}$ (S. Bogatyrenko, A. Kryshtal, 2021)

Applications of ND:

1) The use of NDs in resin cements hasn't been studied well though some data, which is inconclusive, is available on their use in dentistry such as in guided tissue regeneration, reinforcement of polymers, dental implants coating with antibacterial, drug delivery to treat infections (Najeeb Shariq et al, 2016).
2) To boost the qualities of luting and restorative cements.

2.4 Nanozirconia particles (NZ)

Zirconium is a durable transition metal that, in its oxide state, also known as zirconia or zirconium oxide, has an immense number of uses. Due to its inherent hardness, abrasiveness, high melting point, and low frictional resistance, zirconia is also referred to as ceramic steel. It is available in amorphous and crystalline