श्री चित्रा तिरुनाल आयुर्विज्ञान और प्रौद्योगिकी संस्थान, त्रिवेंद्रम, तिरुवनन्तपुरम - 695 011, केरल, भारत
SREE CHITRA TIRUNAL INSTITUTE FOR MEDICAL SCIENCES AND TECHNOLOGY, TRIVANDRUM
THIRUVANANTHAPURAM - 695 011, KERALA, INDIA
(एक राष्ट्रीय महत्व का संस्थान, विज्ञान और प्रौद्योगिकी विभाग, भारत सरकार)
(An Institution of National Importance, Department of Science and Technology, Government of India)
टेलीफोन नं./Telephone No.: 0471-2443152 फैक्स/Fax: 0471-2446433, 2550728
ई-मेल/E-mail: sct@sctimst.ac.in वेबसाइट/Website: www.sctimst.ac.in

PROJECT COMPLETION REPORT

1. **Project Number** : **8053**

2. **Title of the Project** : Development of smart dental composites consists of calcium containing resins and fillers

3. **Funding Agency Name** : KSCSTE

4. **Project Reference Number provided by the Funding Agency**:

   Council Order No; (T) 036/SRS/2011/CSTE dated 12/05/2011

5. **Principal Investigator (Name & Address) : Dr.Lizymol P.P. ,Scientist, DEP,DBST,BMTW,SCTIMST**

6. **Co-Investigators (Name & Address): Dr.V.Kalliyanakrishnan, retd. Scientist, DEP,DBST,BMTW,SCTIMST**

7. **Implementing Institution** : SCTIMST

8. **Collaborating Institutions** : NIL

9. **Date of Commencement** : 22/06/2011.

10. **Duration** : 3 years

11. **Date of Completion** : 21/06/2014

12. **Objectives as approved :** Our objective is to develop visible light cure smart restorative composites based on calcium containing inorganic-organic hybrid resins with high refractive index and fillers like, calcium hydroxide, zirconium oxide, calcium carbonate, tricalcium silicate/calcium chloride, hydroxy apatite and /or silica along with conventional fillers such as silanated quartz/ radiopaque glass which can enhance dental remineralization by releasing calcium and phosphate ions depending on the pH of the surroundings which controls dental decay. Various formulations will be standardized

13. **Deviation made from original objectives if any, while implementing the project and reasons thereof : NIL**

14. Field/Experimental work giving full details of summary of methods adopted, data collected supported by necessary tables, charts, diagrams and photographs :

1. To synthesis hybrid organic–inorganic materials containing calcium by the sol-gel process.
2. Optimize the synthesis parameters to get resin with high refractive index to match with HAP
3. Optimize the synthesis parameters to get resin with elevated calcium ions and hydroxyl ions which can mimic the natural regenerative potential of the dentine pulp complex and initiate the release of matrix bound bioactive molecules to induce dentinogenesis.
4. Development of new filler based on zirconium oxide rather than the heavy-metal-containing glass particles that are currently added to the plastic-based resins for radiopacity. Current fillers provide sufficient strength, malleability and radiopacity but are too soluble, degrading the polymer material over time.
5. Preparation of Visible Light Cure Composite Paste

Visible light cure composites developed using the newly developed inorganic –organic hybrid resin as the binding resin. Various formulation for visible light cure restorative composites based on calcium containing inorganic-organic hybrid resins with high refractive index and fillers like, calcium hydroxide, calcium carbonate, tricalcium silicate/calcium chloride, hydroxy apatite and /or silica along with conventional fillers such as silanated quartz/ radiopaque glass which can enhance biomineralization were tried to get the optimum composition.

Evaluation of Composites

1. Spectroscopic, microscopic, thermal, physical and mechanical properties were evaluated.
2. Evaluation of curing performance and shelf life of light cure composite using spectroscopic techniques
4. Evaluation of effect of thermal cycling on physical, mechanical properties
5 Evaluation of effect of thermal cycling on shrinkage and internal porosity generation during thermal cycling by micro computerized tomographic (micrCT) techniques .
6. Evaluation of cytotoxicity of cured composite as per international standards

15. Detailed anaylsis of results :

Further details may be referred from the published work given below

1. Vicker's Hardness Number of various resins.

Vicker's Hardness Number of various resins had been tabulated below:

Sl No	Name of the resin	HV	Standard deviation
1	Ca-0.5 resin	89.1	1.53
2	Zn-0.5 resin	82.4	4.79
3	Mg-0.5 resin	92.32	2.2976

4	Ba-0.5 resin	122	7.88
5	Ca+Mg+Zn-0.5 resin	68.7	4.47
6	Ca-0.5 resin + EDMAB	102	3.23
7	Ca-0.1+Mg-0.1+Zn-0.1 resin	146	4.37
8	Ca-0.5 resin 2	27	1.00
9	Ca-0.5 resin+ 0.9% TPO	115	2.42
10	Ca-0.5 resin+ 1% TPO	113	7.48
11	Ca-0.5 resin+ 1.1% TPO	135	6.83
12	Ca-0.5OR10	101	3.14
13	Zn-0.5OR10	102	1.88
14	Mg-0.5OR10+3%TPO	92.1	3.68
15	Mg-0.5OR10+3.1%TPO	93.8	3.53

2. Refractive indices of various resins.

Name of the resin	Refractive index
3-trimethoxy silyl propyl methacrylate	1.4288
Ca-0.5 resin	1.48
Zn-0.5 resin	1.4774
Sr-0.5 resin	1.4802
Mn-0.5 resin	1.474
Mg-0.5 resin	1.479
Ba-0.5 resin	1.481
Ba-1 resin	1.4826
Zr-0.5 resin	1.4752
Ca+Mg+Zn-0.5 resin	1.476
Ca-0.5+Mg-0.1+Zn-0.1 resin	1.475
Phenyl trimethoxy silane	1.4662

Resin 2 wihtout inorganic content	1.5134
3-cloropropyl trimethoxy silane	1.4156
Ormoresin R2	1.4510
Acid hydrolysed Ormoresin R2	1.47
Acid hydrolysed Ca-0.5 Ormoresin R2	1.4656
Acid hydrolysed Mg-0.5 Ormoresin R2	1.4702
Acid hydrolysed Zn-0.5 Ormoresin R2	1.4704
Alkali hydrolysed Ormoresin R2	1.4502

3. Water sorption and solubility

Resins	**Water sorption**	**Water solubility**
Ca-0.5	25.72	4.62
	24.05	7
	24.79	7.61
	22.14	6.84
	23.27	3.84
Mean	**23.994**	**5.982**
Zn-0.5	17.6092	1.9036
	15.9874	2.409
	16	2.386
	17.94	3.53
	18.72	3.03
Mean	**17.25132**	**2.65172**
Mg-0.5	26.977	7.23
	32.988	5.791
	27.867	4.644

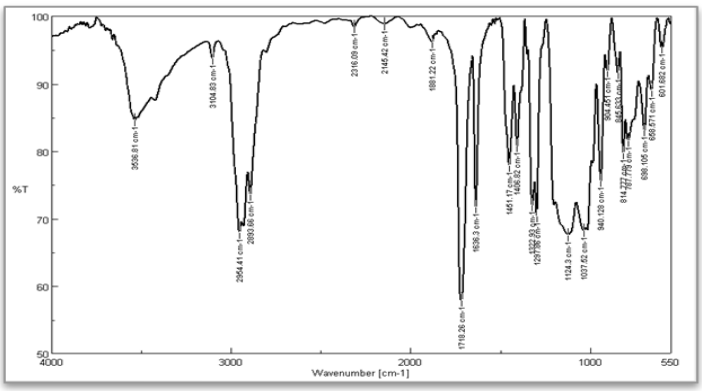
	31.96	5.615
	33.833	4.11
Mean	**30.725**	**5.478**

4. Depth of cure of various resins

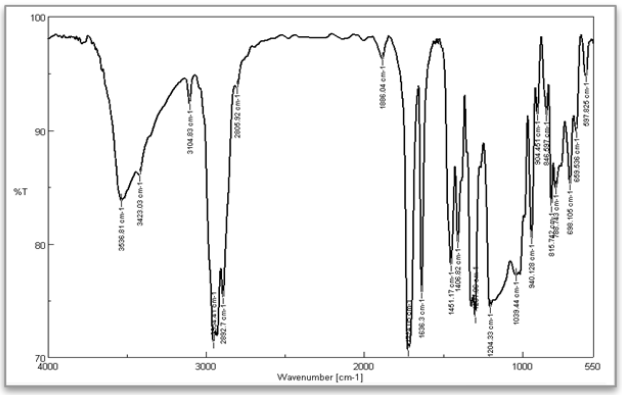
Sl No	Name of the resin	Height (mm)	p value
1	Ca-0.5 resin 1	1.425	0.020594
		1.515	
		1.65	
		1.35	
	Mean	**1.485**	
2	Zn-0.5 resin 1	1.23	0.029703
		1.175	
		1.18	
		1.37	
	Mean	**1.23875**	
3	Mg-0.5 resin 1	1.8	0.501016
		1.395	
		1.73	
		1.38	
	Mean	**1.57625**	

Characterisation of resins

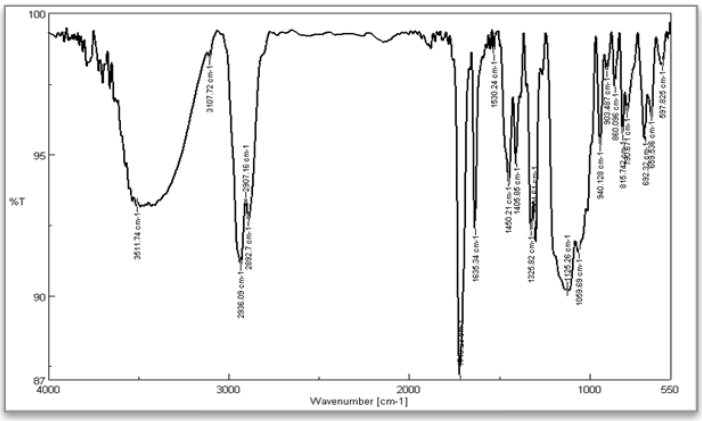
FTIR spectra of Ca-0.5 resin 1, Zn-0.5 resin 1, Mg-0.5 resin 1, Ba-0.5 resin 1, Zr-0.5 resin 1, Ca+Zn+Mg-0.5 resin were taken.



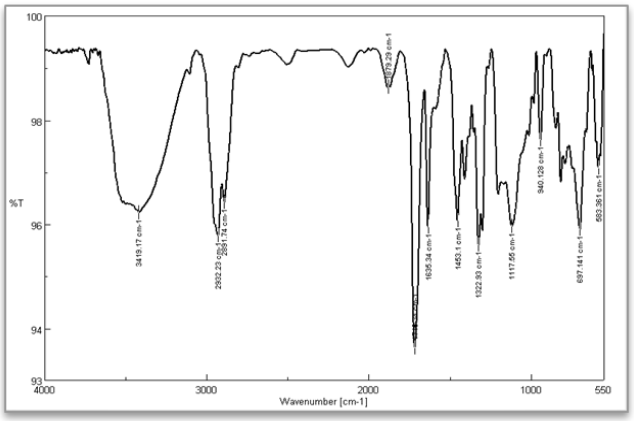
Ca -0.5 resin I



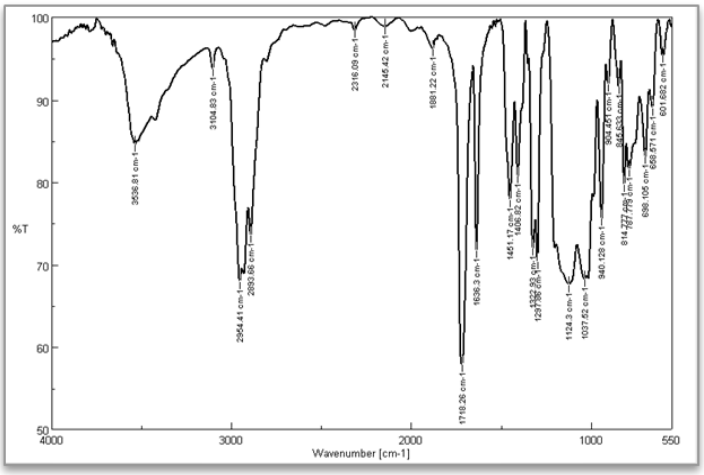
Zn-0.5 resin I



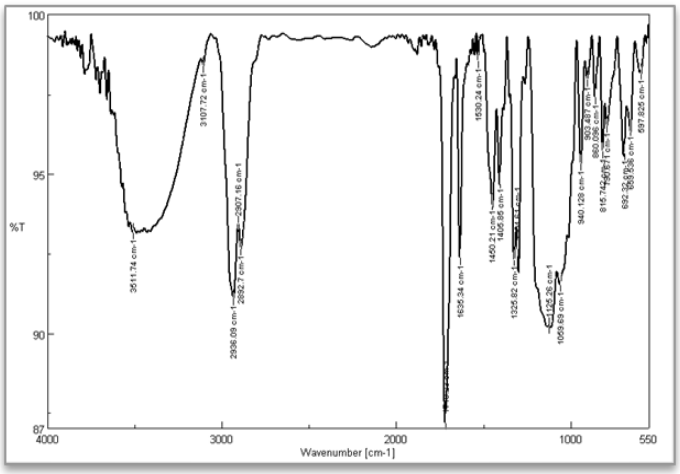
Mg-0.5 resin I



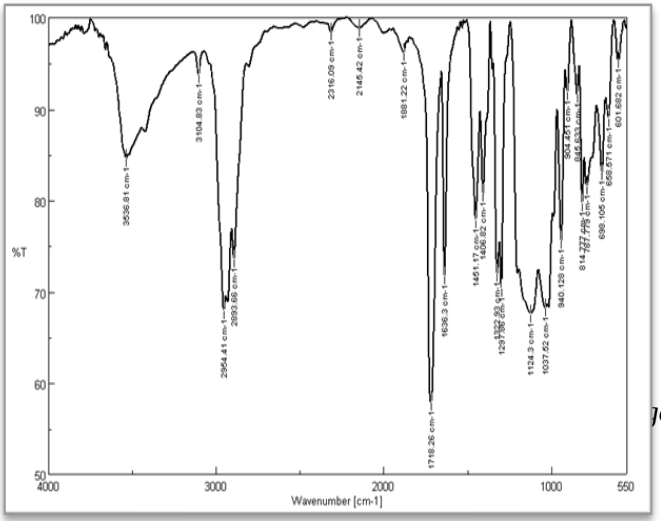
Ca+Mg+Zn-05 resin I

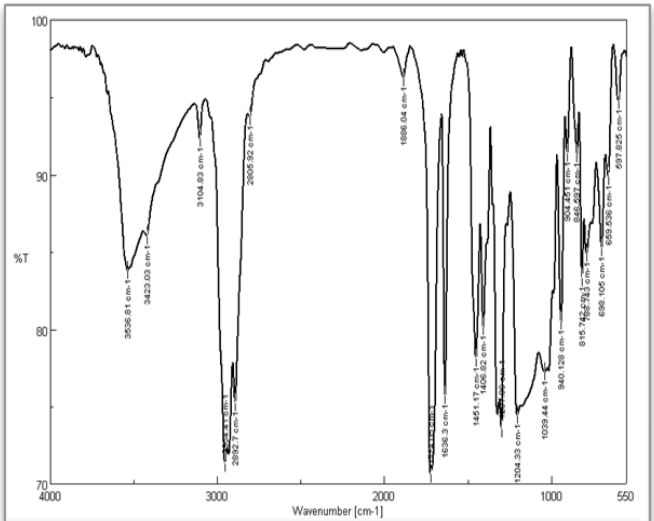


Ba-I resin

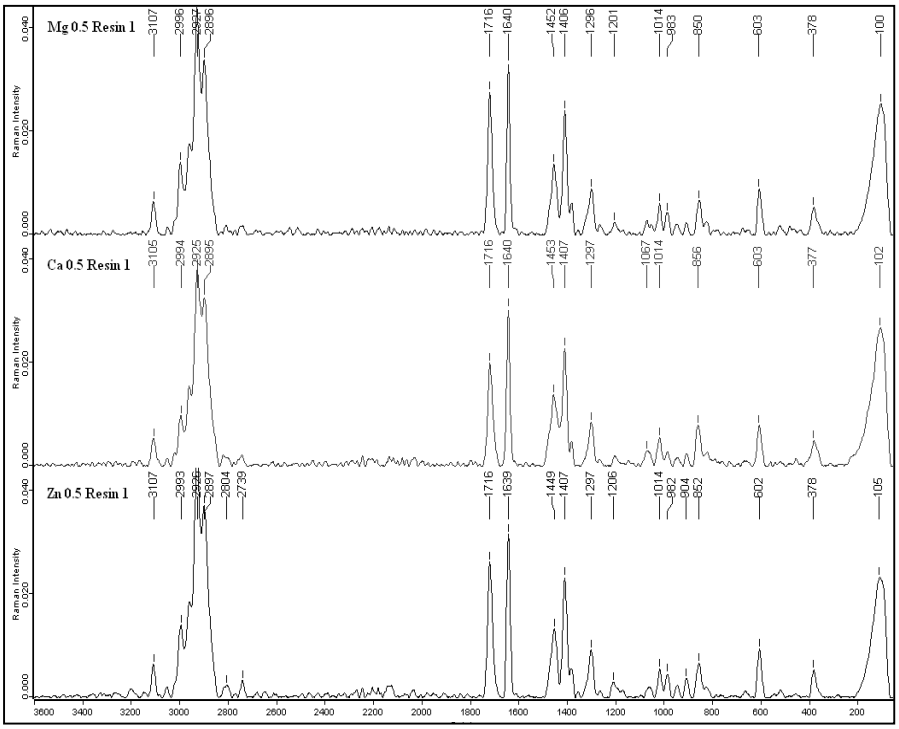


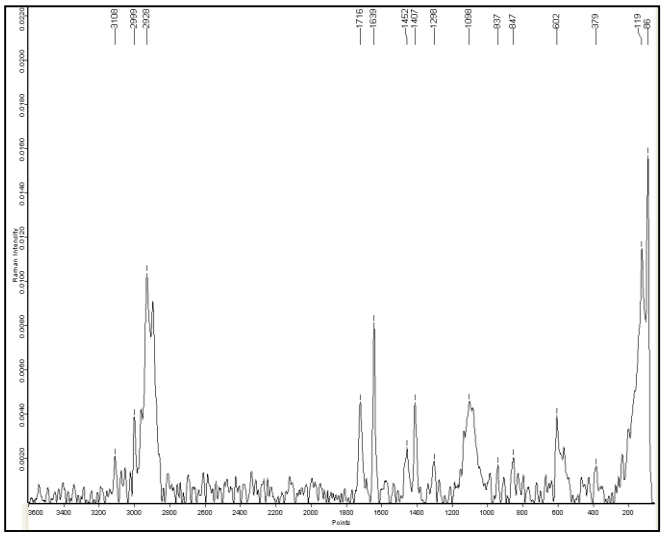
Zr-0.5 resin



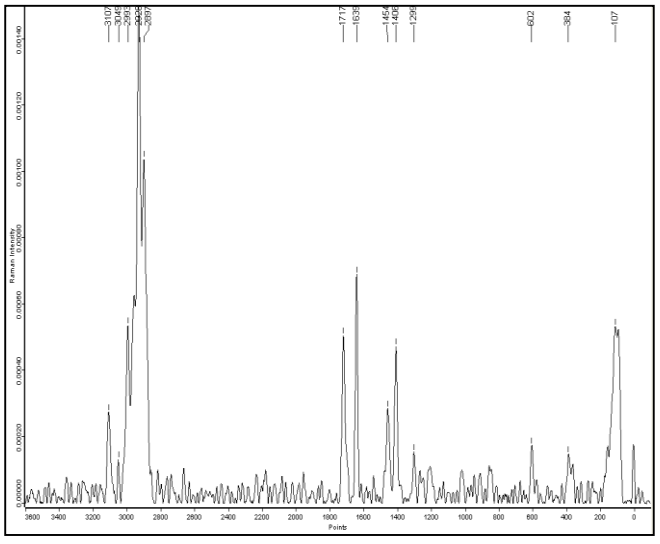


Raman spectra of Ca-0.5 resin 1, Zn-0.5 resin 1, Mg-0.5 resin 1, Ca-0.5 resin 2, Zn-0.5 resin 2 and Mg-0.5 resin 2 were taken.

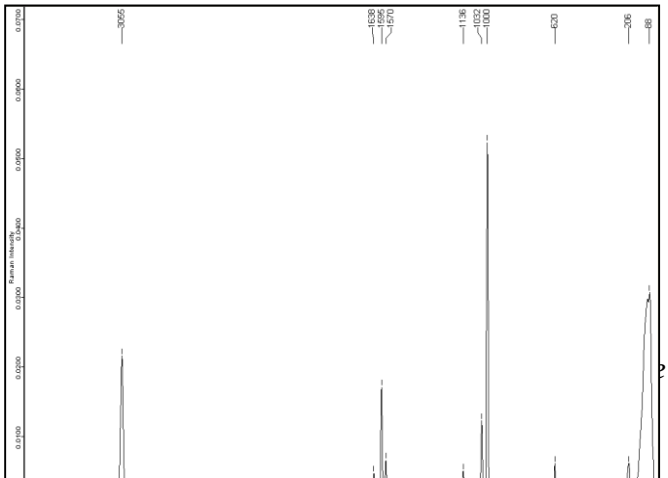


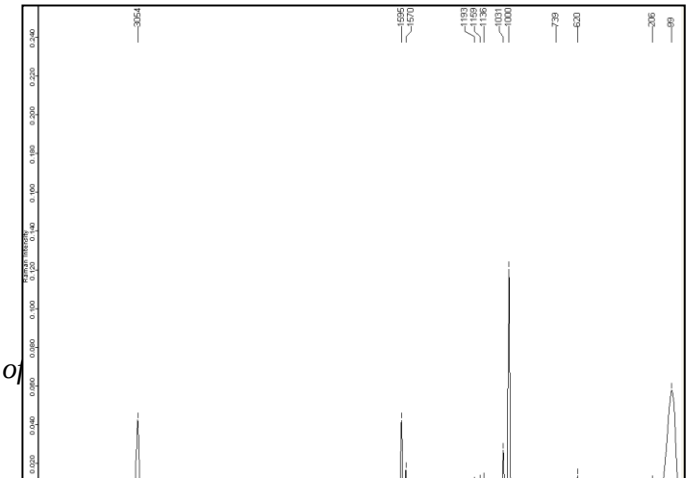


Ba-1 resin 1



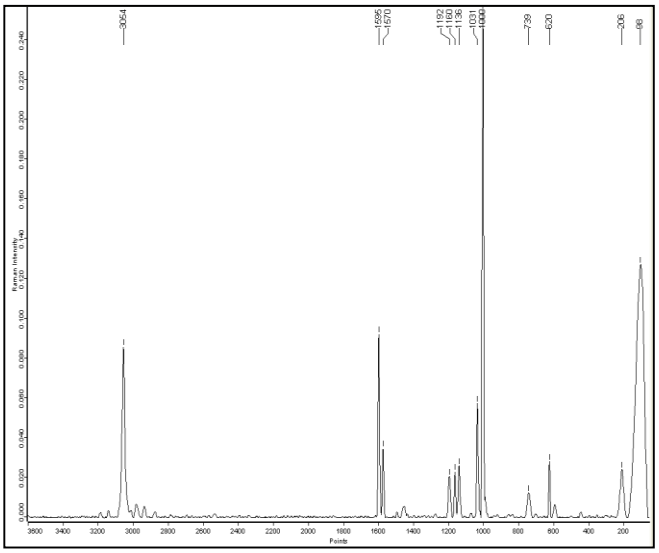
Zr-0.5 resin

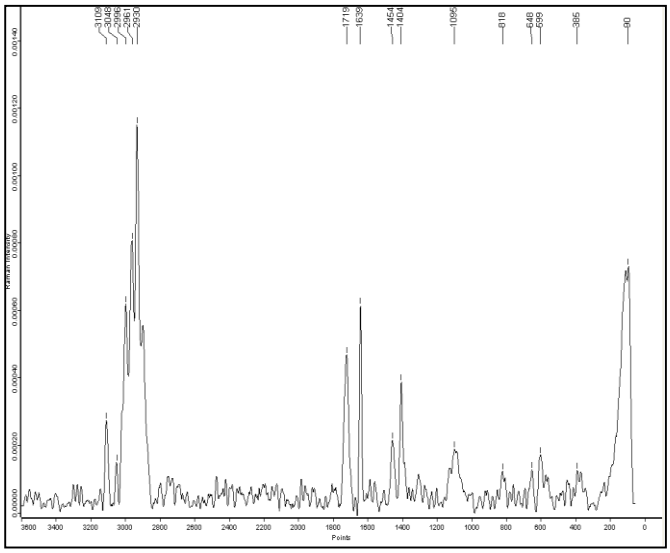




Ca-0.5 resin 2

Mg-0.5 resin 2

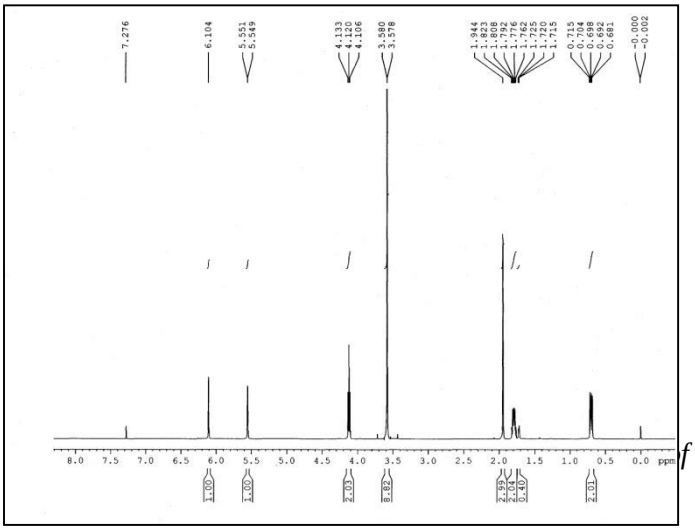


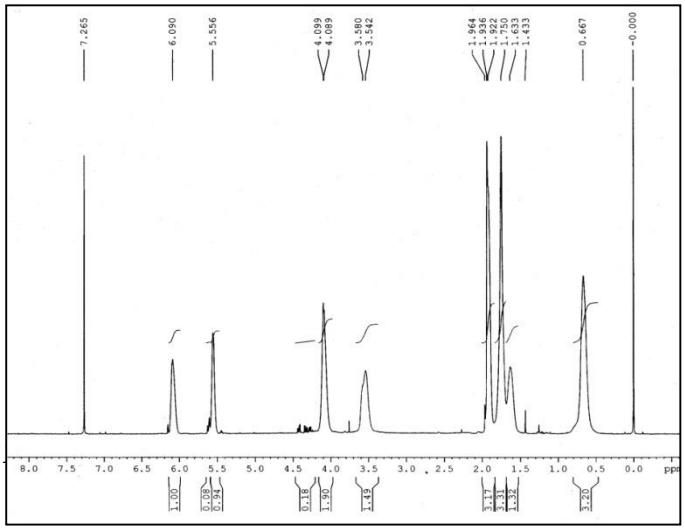


Zn-0.5 resin 2

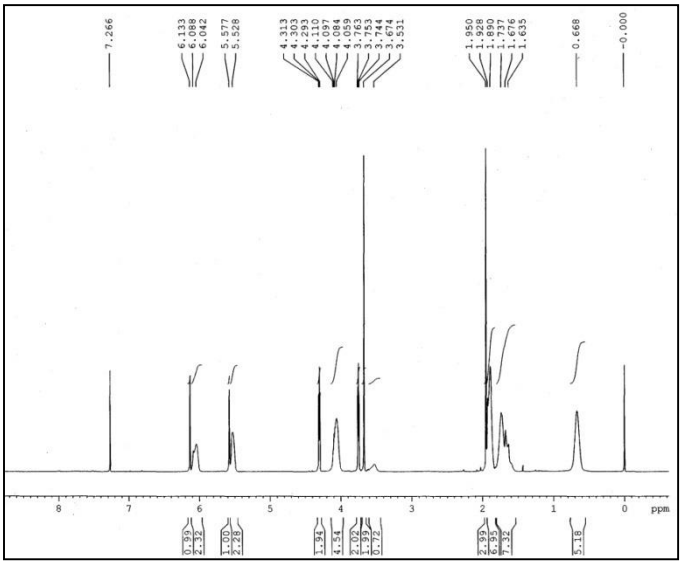
ORMORESIN R1O Acid

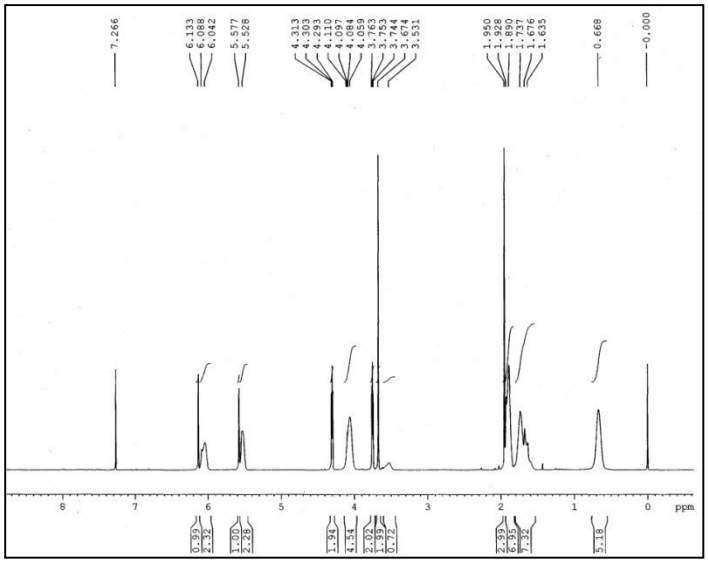
9. NMR spectra of Ca-0.5 resin 1, Zn-0.5 resin 1, Mg-0.5 resin 1 and silane 1 were taken.





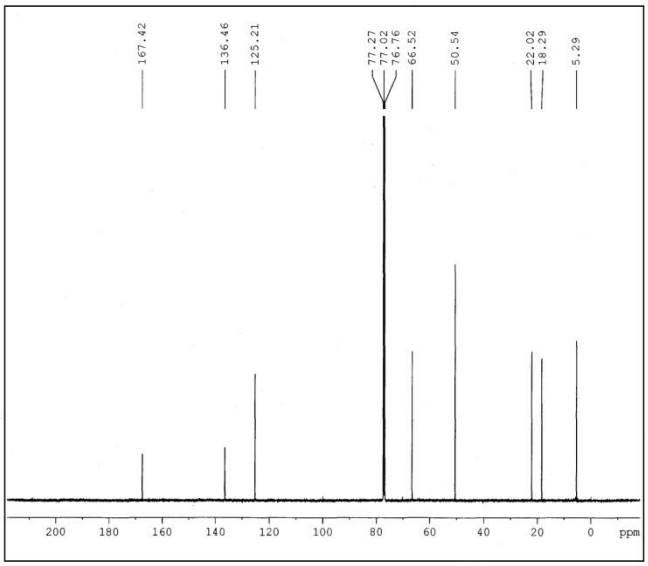
Silane1 **Mg-0.5 resin 1**

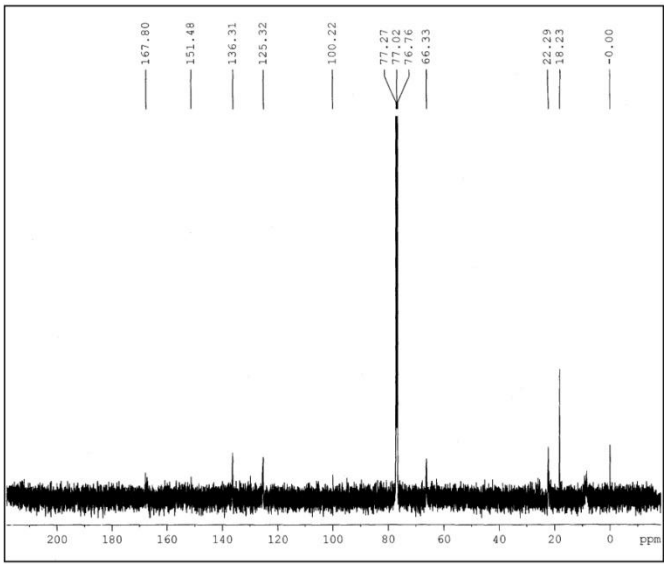




Zn-0.5 resin 1 **Ca-0.5 resin 1**

10. C-13 NMR spectra of silane 1 and Ca-0.5 resin 1 were taken.





silane 1 **Ca-0.5 resin 1**

Further details may be referred from the published work given below

16. Summary sheet of not more than 2 pages under following heads : (Title, Introduction, Rationale, Objectives, Methodology, Results, Translational Potential)

Title, Development of smart dental composites consists of calcium containing resins and fillers

Introduction

Preparation of the composite paste

Inorganic-organic hybrid resin (50 parts) diluted with Triethylene glycol dimethacrylate (TEGDMA) (50 parts) was used as the resin matrix and purified, silanated quartz was used as the filler for the preparation of restorative paste [19-20]. (-) Diphenyl(2,4,6-trimethyl benzoyl) phosphine oxide (TPO) was used as the photoinitiator. Other chemicals used for the preparation of paste are 4-methoxy phenol, phenyl salicylate, 2-hydroxy-4-methoxy benzophenone, and 2,6 di-tert-butyl-4-methyl phenol (which act as inhibitors and UV stabilizers). The diluent monomer, TEGDMA, can also acts as the crosslinking agent. To 50 parts organically modified ceramics resin mixed with 50 parts of TEGDMA mixture, photoinitiator (TPO), catalyst, inhibitor, and UV stabilizer were mixed to prepare the resin mixture. The prepared resin mixture was mixed with 300% of silanated quartz and 12% pyrogenic silica in an agate mortar to get a uniform paste.

Evaluation of dental composites

Physico-mechanical properties of photo cured composites were evaluated in terms of Diametral tensile strength, Vickers Hardness, Flexural strength and Polymerization shrinkage.

Remineralization studies

The cured composites were stored in Stimulated Body Fluid (SBF) for a period of 21, 45, 60 and 180 days 37°C. After the time period, the samples were washed with deionised water, dried and SEM and EDS analysis were carried out.

Scanning Electron Microscope-Energy Dispersive Spectroscopy **(SEM-EDS Analysis)**

Surface morphology of the composite samples before and after storage in SBF was studied using JOEL –JSM-6390 Scanning Electron Microscope equipped with Oxford Swift EDS. The sample surfaces were coated with platinum by makes use of JEOL-JFC-1600 platinum coating. Composite resin surfaces without SBF and specimens in SBF for a time period of 21, 45, 60 and 180 days were analyzed to study the extent of remineralization.

Rationale, Dental products account for 30-35% of the total medical devices sold in the country and the dental market is valued at around 446 million US $ annually (around Rs. 2230 crores). Growth rates of 15 to 20% are forecast for this market in the coming years. Unfortunately 80-85% of the devices are imported and the

indigenous production is limited to a few items such as amalgams, dental cements and some equipments. As a result of this and also due the generally high cost of the imported products, there has been a consistent demand for developing indigenous products, which can help bring down the prices and reduce the cost of dental care

Translational Potential : There is good scope for product development. MTA signed with Anabond Stedman Pharma Research Private Limited (ASPR). Material evaluation by industry as part of TT activities is going on.

17. Contributions made towards increasing the state of knowledge in the subject :

Innovations/ Technologies generated: A process for the preparation of various inorganic organic hybrid resins with polymerizable methacrylate groups was developed
Further details may be referred from the published work given below

18. Conclusions summarising the achievements and indication of scope for future work :

Optimized the various synthesis parameters of the new inorganic organic resins. SEM studies showed that the newly developed resins have excellent remineralization capability along with superior mechanical properties and lower shrinkage.
b. New observations: Inorganic elements such as calcium, magnersium ,zinc, strontium, barium and manganese can be effectively bonded to the organic molecules with polymerizable dimethacrylate groups by sol gel process.

Further details may be referred from the published work given below

19. Science and Technology benefits accrued :
a. List of research publications with complete details : NIL

1. Vibha C.Lizymol P.P*., Effect of inorganic content on thermal stability and antimicrobial properties of inorganic organic hybrid dimethacrylate resins International Journal of Scientific Research, 04,2015(8)58-59.
2. Vibha C., Lizymol P.P*., Multifunctional inorganic-organic hybrid resins with polymerizable methacrylate Groups for biomedical applications; Effects of synthesis parameters on polymerisation shrinkage and molecular weight Advanced Materials Letters, Volume 7, Issue 4, Page 289-295, 2016.
3. Vibha C, Lizymol P P*.Effect of pH during synthesis on molecular weight and polymerization shrinkage of photo polymerized hybrid resins for biomedical applications, Journal of Bionanoscience, Volume 10, Number 5, 2016, 414-417(4).
4. Vibha C., Lizymol P.P*., A bioinspired bioactive multi-component polymerizable material for dental restorative applications; Effects of calcium content on physico mechanical properties, Advanced Materials Letters , 2017, 8(1), 58-64
5. Vibha C, Lizymol P.P*. Development of hydroxyapatite-reinforced biocomposites based

on polymerizable multifunctional strontium containing inorganic-organic hybrid resins for biomedical applications. Materials Letters , Volume 197, 2017, 63–66

Patents

1. Lizymol Philipose Pampadykandathil, Vibha Chandrababu. A process for the synthesis of inorganic-organic hybrid resins comprising of alkoxides or mixture of alkoxides of calcium,magnesium, zinc, strontium, barium and manganese with polymerizable (di/tetra) methacrylate groups, Patent Application Number 4027/CHE/2014.
2. Lizymol Philipose Pampadykandathil, Vibha Chandrababu. A visible light cure dental restorative composite with excellent remineralization ability with good physico- mechanical properties and low shrinkage based on a novel calcium containing inorganic organic hybrid resin with polymerizable methacrylate groups Patent Application Number 4996/CHE/2014.
3. Lizymol Philipose Pampadykandathil, Vibha Chandrababu. Dental Composites for Dental restoration, Patent Application Number 390/CHE/2015 dated 28/01/2015.

Book Chapters

1. Lizymol P.P., Vibha C, Effect of processing parameters on physico- mechanical properties of visible light cure composites, Functionalized Engineering Materials and Their Applications, Apple Academic Press, Hard ISBN: 9781771885232, E- Book ISBN: 9781771885249, 15, September 11, 2018.
2. Vibha C, Lizymol P.P., Novel bioactive Strontium containing (tetra methacrylate resin) composites for medical applications, Advanced Polymeric Materials for Sustainability and Innovations, Apple Academic Press, CRC Press, Taylor and Francis Group, Hard ISBN: 9781771886338, E-Book ISBN: 9781315102436, 6, October 2, 2018.
3. Vibha C., Lizymol P P. Development of bioactive multifunctional inorganic-organic hybrid resin with polymerizable methacrylate groups for biomedical applications‖ in Nanoparticles in Polymer Systems for Biomedical Applications, Apple Publications, ICNT 2016 Hard ISBN: 9781771887038,9, November 2018 .

Conference Papers

1. Lizymol P P, Vibha C, Studies on visible light cure composites based on novel inorganic-organic hybrid resins for dental applications, Proceedings of 3rd International Conference on Nanotechnology, United Arab University Al Ain, November 28-30, 2011; 118.
2. Vibha C., Lizymol P P , Effect of inorganic content on surface hardness and shrinkage of dental restoratives based on novel inorganic- organic hybrid resin, Proceedings of 24 th Kerala Science Congress, Rubber Research Institute of India, Rubber Board, Kottayam, 29–31 January 2012., 538-540.

3. Vibha C., Lizymol P P, Studies on surface hardness, mechanical properties and surface remineralization of visible light cure composite based on novel inorganic organic hybrid materials, Proceedings of National Seminar on Advanced Polymers, Department of Polymer Engineering Mahatma Gandhi University College of Engineering, Thodupuzha, September 28 & 29, 2012, 16.
4. Vibha C., Lizymol P P, Effect of inorganic content on shrinkage of visible light cure composites prepared from inorganic-organic hybrid resins, Proceedings of PolyTech – 2012: International Conference on Advances in Polymer Materials & Nanotechnology, BharatiVidyapeeth Deemed University, Pune and National Chemical Laboratory, Pune during December 15 – 17, 2012.
5. Vibha C., Lizymol P P , Effect of calcium content in inorganic-organic hybrid resins on properties of dental restoratives, Proceedings of 3rd FAPS Polymer Congress and MACRO-2013, May 15-18, 2013, Indian Institute of Science, Banglore; 419.
6. Vibha C., Lizymol P P Effect of strontium and manganese on physic-mechanical properties of visible light cure composites prepared from inorganic-organic hybrid resins. Proceedings of International Conference on Advanced Polymeric Materials, School of Chemical Science Auditorium, Mahatma Gandhi University, Kottayam, October 11-13, 2013; 59-60.
7. Vibha C., Lizymol P P. Effect of strontium and manganese on bioactivity and physico-mechanical properties of novel inorganic-organic hybrid resin based visible light cure dental restorative materials. Proceedings of 26th Kerala Science Congress, Kerala Veterinary and Animal Sciences University (KVASU), Wayanad, 28-31 January, 2014.3052-3059
8. Vibha C., P P.Lizymol. Effect of strontium on bioactivity and physico-mechanical properties of novel inorganic-organic hybrid resin based visible light cure composites for medical applications. 2nd International Conference on Advanced Functional Materials, Mascot Hotel, Thiruvananthapuram. February 19-21, 407-408, 2014.
9. Lizymol PP., Vibha C. Recent Developments in Dental Restoration, NANOBIO-2014, International Conference on Nano Biomaterials, Mahatma Gandhi University, Kottayam, July 4-6, 20-21.
10. Vibha C., P P.Lizymol .Novel Bioactive Strontium containing composites for medical applications, NANOBIO-2014, International Conference on Nano Biomaterials, Mahatma Gandhi University, Kottayam, July 4-6, 71-72.
11. Lizymol P P, Vibha C., Effect of processing parameters on physico-mechanical properties of visible light cured composites, 3rd International Conferenc on Polymer Processing and

Characterisation (ICPPC-2014), Mahatma Gandhi University, Kottayam October 11-13, 2014

12. Vibha C., Lizymol P P ., Kalliyana Krishnan V., Development of a novel antibacterial visible light cure dental composite based on inorganic-organic hybrid resin containing zinc, Polymer Conference for Young Researchers (PCYR-2014), CSIR-NIIST, Pappanamcode, Thiruvananthapuram, October 18, 2014, 27.
13. Vibha C, Lizymol P.P., Effect of photoinitiators on the physico-mechanical properties of photo polymerized composites based on hybrid resins, Frontiers of National Seminar on Frontiers of Polymers and Advanced Materials (FPAM-2014), University of Kerala, Kariyavattom, November 05-07, 2014, 29-30.
14. Vibha C, Lizymol P.P., Effect of pH during synthesis on molecular weight and polymerization shrinkage of photo polymerized hybrid resins for biomedical applications, Fourth International Conference on Natural Polymers and Biomaterials (ICNP 2015)Mahatma Gandhi University, Kottayam, April 10-12, 2015, 80 .
15. Vibha C., Lizymol P.P, Effect of inorganic content on thermal stability of inorganic-organic hybrid dimethacrylate resins, National Conference on Materials Science and Technology - 2015 (NCMST-15), IISST, Valiyamala, July 6-8, 2015, 129-130 (**Best poster award**).
16. Vibha C., Lizymol P.P, Novel bioactive thermally stable strontium containing inorganic-organic hybrid resin for customised applications, NCMST-2016, IIST, Thiruvananthapuram (July 12-14, 2016) (accepted).
17. Vibha C., Lizymol P.P, Development of bioactive multifunctional inorganic-organic hybrid resin with polymerizable methacrylate groups containing manganese for biomedical applications, Fourth International Conference on Nanomedicine and Tissue Engineering (ICNT 2016), Mahatma Gandhi University, Priyadarshini Hills P.O., Kottayam, Kerala, 12-14 August 2016.
18. Vibha C., Lizymol P.P, Novel Bioactive Strontium containing (Tetra Methacrylate Resin) Composites for Medical Applications International Conference on Macromolecules: Synthesis, Morphology, Processing, Structure, Properties and Applications (ICM-2016), Mahatma Gandhi University, Kottayam, Kerala, India May 13- 15, 44, 2016.
19. Vibha C, Lizymol P.P. "Multifunctional inorganic-organic hybrid resins with polymerizable tetramethacrylate groups containing strontium for biomedical applications"International Conference on Advances in polymer Technology, APT 16. CUSAT, 25, 26 February 2016 (**Received the Best Poster Award**).

b. **Manpower trained on the project :**
   i. **Research Scientists or Research Fellows : NIL**
   ii. **No. of PhD's produced : 1**
   iii. **Other Technical Personnel trained : 3**

c. **Patents taken, if any :**

d. **Products developed, if any :**

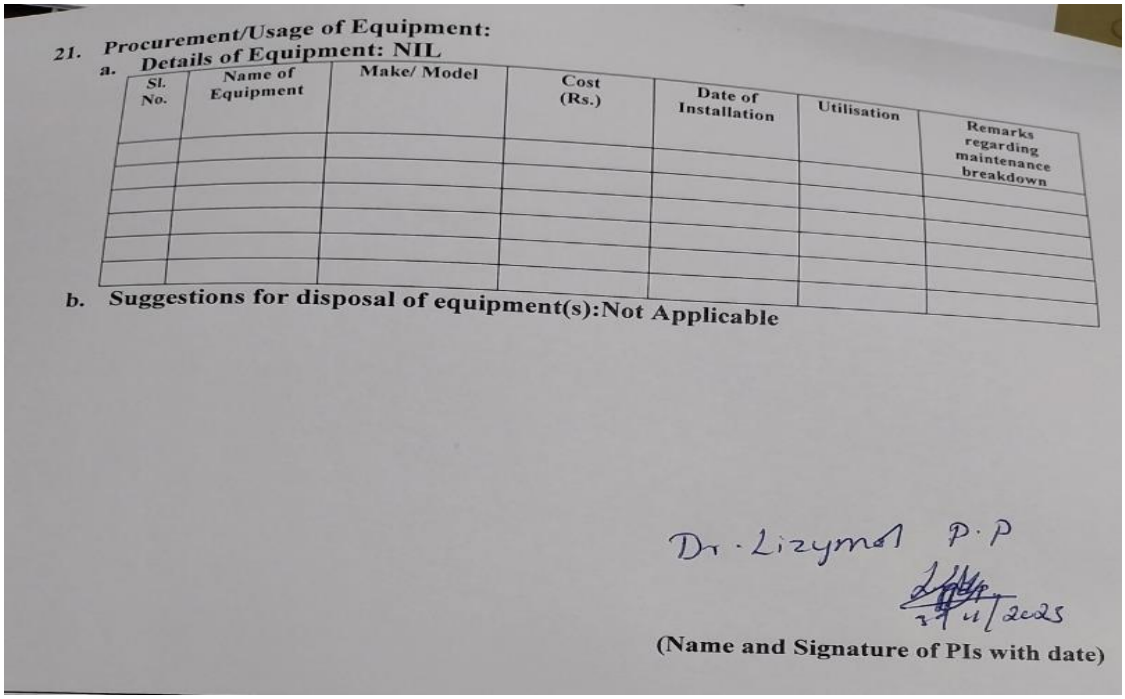
20. **Abstract: (In 300 words for possible publication in ..... Bulletin) NA**

a. **Background:**

b. **Materials:**

c. **Results:**

d. **Conclusion:**



21. *Procurement/Usage of Equipment:*

a. *Details of Equipment: NIL*

Sl. No.	Name of Equipment	Make/ Model	Cost (Rs.)	Date of Installation	Utilisation	Remarks regarding maintenance breakdown

b. **Suggestions for disposal of equipment(s):Not Applicable**

Dr. Lizymol P.P

27/11/2025

(Name and Signature of PIs with date)

Routing: *Signed copy of "Project completion Report" by PI → root@sctimst.ac.in, rpc@sctimst.ac.in*