

STUDIES ON FILLED ACRYLATE BASED DENTAL RESTORATIVE COMPOSITES

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INDIAN INSTITUTE OF TECHNOLOGY DELHI

AUGUST 2018

STUDIES ON FILLED ACRYLATE BASED DENTAL RESTORATIVE COMPOSITES

by
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Submitted
in fulfilment of the requirements of the degree of Doctor of Philosophy
to the



INDIAN INSTITUTE OF TECHNOLOGY DELHI
AUGUST 2018

Dedicated

to

My Mother

CERTIFICATE

This is to certify that the thesis entitled “**Studies on filled acrylate based restorative composites**” being submitted by **Ms. Harshita**, to the Department of Material Science and Engineering, Indian Institute of Technology Delhi, India, is worthy of consideration for the award of the degree of **Doctor of Philosophy** in Material Science and Engineering and is an authentic record of original bonafide research work carried out by her under my supervision and has fulfilled the requirements for the submission of this thesis.

The ideas, experimental work, results, analyses and conclusions reported in this thesis are original and have not been previously, to the best of my knowledge, submitted, in part or full, to any other University or Institute for the award of any degree or diploma.

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ACKNOWLEDGEMENTS

I express my profound sense of gratitude and sincere regards to my esteemed supervisors, **Prof. Bhabani K. Satapathy** and **Prof. Alok R. Ray** for guiding me all the way during my research work. Their constant inspiration and encouragement has been a great motivation for me behind all the work which I have conducted. I appreciate their patience, cool composure, enthusiasm, critical comments and generous co-operation throughout this investigation which helped me to tide over the difficult situations.

I express my deep sense of gratitude to the SRC members, Prof. Harpal Singh, Prof. S. Aravindan, and Prof. J. Jacob, who have monitored my work and provided me the valuable suggestions. I am also thankful to Prof. A. K. Ghosh, Prof. Veena Chaudhary, Prof. S. N. Maiti, Dr. Leena Nebhani, Dr. Sampa Saha and Dr. Bijay P Tripathi for valuable discussions and support.

I owe thanks to laboratory staffs Mr. Ashok Kapoor, Mr. Surender Sharma and Mr. Shiv Kant for their timely help and suggestions.

Last but not the least I would like to express my heartiest gratitude to my parents, family members and friends especially, Sucharita Sethy and Deepika Sharma who patiently stood beside me during entire research work.

Finally, I would like to thank ‘Almighty God’ for everything.

Harshita

Abstract

The thesis comprehensively deals with fabrication and evaluation of dental restorative composites, composed of a visible light-curing monomer mixture (bis-Glycidyl methacrylate in combination with Triethylene glycidyl dimethacrylate as resin-matrix system) and silica and hydroxyapatite (Hap) particles as reinforcing fillers. The composites have been systematically evaluated for the effects of varying volume fraction of fillers on mechanical, thermal, structural, cytotoxic, tribological and fracture toughness properties. The study revealed that the addition of filler into the matrix led to an increase in compressive strength (CS) and diametral tensile strength (DTS), whereas flexural strength (FS) surpassed the clinical requirements of 50 MPa. Addition of filler did not significantly change the glass transition temperature and thermal degradation temperature of the matrix. It has been noted that the thermal decomposition of the composites has started at $\sim 350^{\circ}\text{C}$. Final degradation temperature was at $\sim 450^{\circ}\text{C}$. Fourier-transformed infrared (FTIR) spectroscopy showed the interactions and functionality whereas Scanning Electron Microscopy (SEM) and Energy Dispersive Analysis of X-ray (EDX) revealed the uniform dispersion and distribution of Hap and silica fillers in the composites. Dynamic mechanical properties revealed reinforcement effectiveness correlated to immobilized polymer network estimated by using Kerner equation. The silica/Hap combination filled composites showed greater diametral tensile strength (DTS) as compared to the Hap filled composites. Cytotoxicity studies revealed that the fabricated composites were found to be non-toxic and therefore exhibited a favorable biological behavior, making it a promising formulation in dental tissue engineering applications.

Conditional fracture toughness (K_{Ic}) values were determined using pre-cracked single-edge-notch-beam (SENB) specimen in three-point-bending test (mode-I fracture). Silica/Hap filled restorative composites showed fracture toughness values that were comparable to Hap filled

dental composites. Irrespective of the nature of the filler or their combinations, the composites with 20 wt. % fillers showed maximum value of K_Q while those with 50 wt. % filler showed minimum value of K_Q . The fracture toughness (K_Q) values determined experimentally were compared to theoretical predictions from micromechanical modeling, which revealed that K_Q of these composites primarily attributed to crack-tip shielding mechanism. The sliding wear assessment of the composites on a pin-on-disk set-up was carried out as a function of applied-load, sliding-duration and sliding-velocity. From Taguchi analysis it was concluded that combination of factors A5 (25 N), B2 (20 %), C2 (0.05 m/s), D5 (25 min) (under dry sliding conditions) and A5 (25 N), B4 (40 %), C4 (0.07 m/s), D3 (23 min) (under water lubricated condition) offer minimum wear. It was observed that the load factor has greater influence on wear rate ($p=0.001$, Hap filled composites and silica/ Hap filled composites, dry as well as lubricated condition). Dental composites with 30-40 wt.% of filler-loading showed highest wear resistance during steady state wear. Worn surface morphology revealed intensive traction marks in case of composites with 50 wt.% of filler. A suggestive correlation between Brittleness parameter (B) and fracture toughness and wear behaviors indicated that highly-filled composites are more prone to exhibit poor dimensional stability.

सार

थीसिस व्यापक रूप से दंत पुनर्स्थापनात्मक कंपोजिट्स के निर्माण और मूल्यांकन से संबंधित है, जो दृश्यमान प्रकाश-curing मोनोमेर मिश्रण (बीस-ग्लाइसीडिल मेथाक्राइलेट के साथ ट्राइथिलीन ग्लाइसीडिल डिमेथैक्राइलेट के साथ राल-मैट्रिक्स सिस्टम के रूप में संयोजन में) और सिलिका और हाइड्रोक्साइपेटाइट (हैप) कणों को मजबूत करने वाले fillers के रूप में बना है। कंपोजिट्स को मैकेनिकल, थर्मल, स्ट्रक्चरल, साइटोटोक्सिक, ट्राइबोलॉजिकल और फ्रैक्चर toughness गुणों पर fillers के अलग-अलग वॉल्यूम अंश के प्रभावों के लिए व्यवस्थित रूप से मूल्यांकन किया गया है। अध्ययन से पता चला कि मैट्रिक्स में फिलर के अतिरिक्त ने संपीड़न शक्ति और हीराल तन्यता ताकत में वृद्धि की है, जबकि flexural strength ने 50 एमपीए की नैदानिक आवश्यकताओं को पार कर लिया है। फिलर के जोड़ ने ग्लास संक्रमण तापमान और मैट्रिक्स के थर्मल गिरावट तापमान में काफी बदलाव नहीं किया। यह ध्यान दिया गया है कि कंपोजिट्स का थर्मल अपघटन $\sim 350^\circ\text{C}$ पर शुरू हुआ है। अंतिम गिरावट तापमान $\sim 450^\circ\text{C}$ पर था। फूरियर-ट्रांसफॉर्मेटेड इन्फ्रारेड (एफटीआईआर) स्पेक्ट्रोस्कोपी ने इंटरैक्शन और कार्यक्षमता दिखायी, जबकि एक्स-रे (ईडीएक्स) के स्कैनिंग इलेक्ट्रॉन माइक्रोस्कोपी (एसईएम) और ऊर्जा फैलाव विश्लेषण ने कंपोजिट में हैप और सिलिका fillers के समान फैलाव और वितरण का खुलासा किया। गतिशील यांत्रिक गुणों ने कार्नर समीकरण का उपयोग करके अनुमानित पॉलिमर नेटवर्क से संबंधित सुदृढ़ीकरण प्रभावशीलता का खुलासा किया। हैप भरे हुए कंपोजिट्स की तुलना में सिलिका / हैप संयोजन से भरे कंपोजिट्स ने अधिक व्यास तन्यता ताकत (डीटीएस) दिखाया। साइटोटोक्सिसिटी अध्ययनों से पता चला है कि निर्मित कंपोजिट्स गैर-विषाक्त पाए गए थे और इसलिए एक अनुकूल जैविक व्यवहार प्रदर्शित किया, जिससे यह दंत ऊतक इंजीनियरिंग अनुप्रयोगों में एक आशाजनक फॉर्मूलेशन बना।

Conditional fracture toughness (K_Q) मानों को तीन-बिंदु-झुकने वाले परीक्षण (मोड-I फ्रैक्चर) में प्री-क्रैक किए गए सिंगल-एज-पायच-बीम (एसईएनबी) नमूने का उपयोग करके निर्धारित किया गया था। सिलिका / हैप भरे हुए पुनर्स्थापनात्मक कंपोजिट्स ने फ्रैक्चर क्रूरता मान दिखाए जो हाप भरे दंत कंपोजिट्स के तुलनीय थे। भराव या उनके संयोजन की प्रकृति के बावजूद, 20 wt% के साथ composites % fillers ने K_Q का अधिकतम मूल्य दिखाया जबकि 50 wt % filler ने K_Q का न्यूनतम मूल्य दिखाया। Fracture toughness (K_Q) मानों का प्रयोग प्रायोगिक रूप से माइक्रोमैकेनिकल मॉडलिंग से सैद्धांतिक भविष्यवाणियों

की तुलना में किया गया था, जिसमें पता चला कि इन कंपोजिट्स के K_Q मुख्य रूप से क्रैक-टिप शील्डिंग तंत्र के लिए जिम्मेदार हैं।

पिन-ऑन-डिस्क सेट-अप पर कंपोजिट्स के स्लाइडिंग पहनने का मूल्यांकन लागू-लोड, स्लाइडिंग-अवधि और स्लाइडिंग-वेग के कार्य के रूप में किया गया था। टैगुची विश्लेषण से यह निष्कर्ष निकाला गया कि कारकों A5 (25 N), B2 (20 %), C2 (0.05 m/s), D5 (25 min) (शुष्क स्लाइडिंग स्थितियों के तहत) और A5 (25 N), B4 (40 %), C4 (0.07 m/s), D3 (23 min) (पानी स्नेहक स्थिति के तहत) न्यूनतम पहनने की पेशकश करते हैं। यह देखा गया था कि भार कारक पहनने की दर ($P = 0.001$, हैप भरे हुए कंपोजिट्स और सिलिका / हैप भरे हुए कंपोजिट्स, सूखे के साथ-साथ स्नेहक स्थिति) पर अधिक प्रभाव डालता है। 30-40 wt% filler-loading के साथ डेंटल कंपोजिट्स स्थिर राज्य पहनने के दौरान उच्चतम पहनने के प्रतिरोध दिखाते हैं। Worn सतह morphology 50 wt% filler के साथ composites के मामले में गहन कर्षण अंक पता चला। Brittleness पैरामीटर (B) और fracture toughness और wear behaviour के बीच एक सूचक सहसंबंध संकेत दिया कि अत्यधिक भरे composites poor आयामी स्थिरता प्रदर्शित करने के लिए अधिक प्रवण हैं।

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List of abbreviations and symbols

ANOVA	Analysis of Variance
Bis- GMA	Bisphenol A glycidyl methacrylate
BPA	Bisphenol A
CS	Compressive Strength
CQ	Camphorquinone
DEJ	Dentin-Enamel Junction
DMAEMA	N,N-Dimethylaminoethyl Methacrylate
DMA	Dynamic Mechanical Analysis
DOE	Design of Experiment
DTS	Diametral Tensile Strength
DSC	Differential Scanning Calorimetry
EGDMA	Ethylene Glycol Dimethacrylate
EDX	Energy Dispersive Analysis of X-ray
EVF	Effective Volume Fraction
FPZ	Fracture-Process-Zone
FTIR	Fourier-Transformed Infrared
FS	Flexural Strength
hMSCs	human-Derived Mesenchymal Stromal Cells
HAP	Hydroxyapatite
IMVF	Immobilized Volume Fraction of Polymer Chain
LED	Light Emitting Diode
RBCs	Resin Based Composites
SEM	Scanning Electron Microscopy
SEN	Single-Edge-Notched
SENB	Single-Edge-Notch-Beam
TEGDMA	Triethylene Glycol Dimethacrylate
TGA	Thermo-Gravimetric Analysis
UDMA	Urethane Dimethyl Acrylates
XRD	X-Ray Diffraction
XTT	2,3-bis-(2-methoxy-4-nitro-5-sulfophenyl)-2H-tetrazolium-5-carboxanilide
YTZP	Tetragonal Zirconia Polycrystals Stabilized By Zirconia
α_{tl}	Constant related to toughening by tilt-induced crack-deflection
α_{ds}	Constant related to deflected-crack increase in disseminated spacing
δm	Weight loss
σ_{Mu}	Ultimate tensile strength of the matrix
σ_{Cu}	Ultimate tensile strength of the composites
ρ	Density
φ	Immobilized volume fraction
v_e	Entanglement density
ν_m	Matrix Poisson ratio
C	Reinforcement effectiveness
E_c	Elastic moduli of the composite
E_m	Elastic moduli of the the resin matrix

E'_g	Storage modulus values in the glassy region
E'_r	Storage modulus values in the rubbery region
E'	Storage Modulus
E''	Loss Modulus
H/E	Hardness to Modulus
K_C	Critical stress intensity factors (fracture toughness) of the composite
K_{in}	Critical stress intensity factors (fracture toughness) of the interface
K_m	Critical stress intensity factors (fracture toughness) of the matrix
K_Q	Fracture Toughness
M_e	Molecular weight between entanglement nodes
N_a	Avogadro's Number
R	Universal Gas Constant
S/N	Signal to Noise
T_g	Glass Transition Temperature
V_f	Volume fraction of the particles
V_p	Filler volume fraction
V_{pc}	Experimental filler volume fraction
V_{pt}	Estimated filler volume fraction
W_s	Specific Wear Rate