

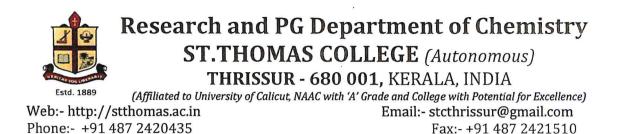
15-09-2022

CERTIFICATE

I hereby certify that, this is the revised version of the thesis entitled "Bismaleimide Nanocomposites for High Dielectric Applications" submitted by Ms. Savitha Unnikrishnan K under my guidance after incorporating the necessary corrections/suggestions made by the adjudicators.

Dr. Sunil Jose T

(Research Guide)



19-04-2022

CERTIFICATE

This is to certify that the thesis entitled "Bismaleimide Nanocomposites for High Dielectric Applications" is an authentic record of research work carried out by Ms. Savitha Unnikrishnan K under my supervision in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Chemistry of University of Calicut and further that no part thereof has been presented before for any other degree.

Dr. Sunil Jose T

(Research Guide)

DECLARATION

I hereby declare that the thesis entitled "Bismaleimide Nanocomposites for High Dielectric Applications" is the outcome of original research work undertaken and carried out by me at St. Thomas College (Autonomous), Thrissur, under the guidance of Dr. Sunil Jose T, Assistant Professor, Department of Chemistry, St. Thomas College (Autonomous), Thrissur, Kerala. I also declare that the material presented in this thesis is original and does not form the basis for the award of any other degree, diploma or other similar titles of any other university.

Laviller SAVITHA UNNIKRISHNAN K

19-04-2022

ACKNOWLEDGEMENT

I am extremely happy to acknowledge my sincere gratitude to my supervising guide Dr. Sunil Jose T, Assistant Professor, Department of Chemistry, St. Thomas College for his excellent guidance and encouragement throughout this work. I take this opportunity to extend my overwhelming thanks to my guide for his innovative ideas, inevitable suggestions and timely advice, without his general assistance, I would not have reached this point.

I am highly obliged to our Principal Rev. Fr. Dr. Martin Kolambrath and former Principals Dr. Joy K,L., Dr. Ignatius Antony and Dr. P.O. Jenson St. Thomas College, Thrissur and the management for permitting me to carry out my research work in this esteemed institution. I am thankful to Dr. C.L. Joshy, Head of the Department of Chemistry, Dr. Paulson Mathew, Dr. Jency Thomas, Dr. Jinish Antony.M, Dr. Reeja Johnson, Dr. Joseph Joly V. L, Prof. Aji. C. V and Dr. Sr. Jisha Joseph, Department of Chemistry, St. Thomas College for the help and support extended to me during my work. Special thanks to lab assistants Mr. Andrews and Mr. Pauljo for lending their help, especially whenever technical support is needed. I express my sincere thanks to Dr. Joby Thomas. K. Former Head of the Department of Chemistry, St. Thomas College for his scholarly comments and constant encouragement which have been of immense help to me in maintaining the excellence of my work. I express my genuine gratitude for his care and support.

I am grateful to Dr. Raina Jose, Assistant Professor, St. Aloysius College, Elthuruth, Thrissur for her help to initiate my research work, I acknowledge thanks for the support and encouragement of Dr. Anoop Anand, Scientist, DRDO, Pune and Dr. Arun K J, Assistant Professor, Sree Kerala Varma College, Thrissur. I express my sincere thanks to Dr. C. Rajesh, Principal, MES Keeveeyem College, Valanchery for permitting me to do part of my research work at MES college. I take immense pleasure in expressing my sincere thanks to Dr. Chacko V M, Research co-ordinator, St. Thomas College for his valuable guidance and suggestions while completing my Ph D course. Special thanks to Mr. Sanjo Jose, Librarian, for his generous help with library services and for providing information to improve academic writing skills. I would also like to thank the college office staff for their support and help with documentation processes. A special word of thanks to Dr. Prathibha, Dr Sreedevi. P. Chakiyar and Dr. Divia for their support and encouragement during my research work.

I sincerely acknowledge the help rendered by Ms. Memsy C. K, Assistant Professor, Mercy College, Palakkad, Dr. Siny Paul, Assistant Professor, Charley and Saji, M A College, Kothamangalam and Sajeev. I.V, Trade Instructor, Govt. Engineering College, Thrissur, during the characterization studies of samples. I also express my sincere thanks to Dr Subodh. G, Assistant Professor, Department of Physics, Kariavattom Campus, Vidya Lalan, Research scholar, Kariavattom Campus, Aswathy A, Project assistant, Kariavattom Campus, Aparna and Bhavya, NIIST, Thiruvananthapuram for the characterization studies. Words are insufficient to express my acknowledgement to Dr. Dinoop lal S, who was always willing to help and give his best suggestions throughout my research carrier. I sincerely thank senior researchers and fellow labmates Dr. Vinod P Raphael, Dr. Nimmy Kuriakose, Dr. Drishya Sashidharan, Dr. Sini Varghese, Dr. Binsi M Paulson, Mr. Ramesh N, Ms. Siji T B, Dr. Ragi K, Ms. Vidhya Thomas, Ms. Swathy T S, Ms. Raji, Ms. Anju Rose Puthukkara P, Mr. Martin Francis, Ms. Rohini Das K, Ms. Nithya, Ms. Neera, Ms. Cinu and Ms. Akhila for their co-operative and helpful attitude.

I also express my sincere gratitude to STIC-CUSAT, NIT, Kozhikkode, NIIST, Thiruvananthapuram, University of Kerala, Kariavattom Campus Thiruvananthapuram, CBPST-Kochi, MES Keeveeyem College, Valanchery, Mercy College, Palakkad, MA College, Kothamangalam, Christ College, Irinjalakuda, Govt. Engineering College, Thrissur and XRD unit-St. Thomas College, Thrissur for providing analytical data. I always remain thankful to Mr.Subhag for providing me facilities to do my work. I sincerely thank all the CHMK library staff, University of Calicut, and especially thank Dr. Vinod V M, Assistant Librarian, CHMK library, for conducting the plagiarism check of my thesis. I am also thankful to the Educare printing press, Thrissur, for their kind co-operation and help in many printings and documentation work during my research period. I sincerely acknowledge the help rendered by all the Teaching and Non-teaching staff of GHSS Malampuzha, Palakkad.

Finally, I am forever indebted to my family for their love, care, prayers and support, without which this thesis would not be a reality. Let me bow before the Eternal truth, Almighty God for being with me in every moment and giving me the strength to overcome all the hurdles.

With heartfelt gratitude

Savitha Unnikrishnan K

To My Husband

PREFACE

Being one of the most important high performance thermosetting resins, bismaleimide resin (BMI) has several applications in electronics, radar, capacitors, stealth technologies, circuit boards, microelectronics etc. Epoxies are widely accepted in aerospace industry for the manufacture of most important composite parts because of their excellent mechanical properties, ease of manufacture and suitable service temperature. BMI composites possess mechanical properties higher than epoxies and are more efficient than the corresponding epoxies in high temperature applications. In order to achieve both temperature performance of the BMI resin and the processing ease of epoxy resins, attempts have been made to prepare BMI-epoxy composites. The thermal, mechanical and dielectric properties of the polymer composites strongly depend on the polymer matrix, size and weight percentage of the filler materials. All these parameters are crucial for the fabrication of polymer composites and all these parameters should be optimized for the development of a novel polymer nanocomposite.

High dielectric permittivity materials have widespread applications in various fields like energy storage capacitors, microcapacitors in IC, sensors, printed circuit boards etc. The introduction of high dielectric permittivity materials on the nanoscale into the polymer matrix could increase the dielectric constant of the polymer nanocomposites. For high dielectric applications, the polymer composite should exhibit high dielectric permittivity, low dielectric loss and high breakdown strength. High dielectric permittivity is highly desired for the dielectric materials used in the embedded capacitors and energy storage devices. In order to enhance the dielectric properties of the BMI epoxy composites, suitable fillers with high dielectric constants are added.

In the present work a new class of BMI-epoxy composites reinforced with glass fiber and further performance enhancements made by the incorporation of a variety of nanofillers such as BaTiO₃, Rochelle salt crystals and hydroxylated BaTiO₃ nanoparticles were studied.

BMI-epoxy nanocomposites prepared using a variety of nanofillers such as BaTiO₃, Rochelle salt crystals and hydroxylated BaTiO₃ nanoparticles possess good thermo-mechanical and dielectric properties. Hence these composites stand as potential candidates for high dielectric applications.

The present thesis consists of eight chapters. **Chapter 1** includes a brief introduction of the polymer matrix used - BMI and epoxy along with structure and preparation of different nanofillers used. The specific objectives of the present research work are also detailed in this chapter.

Chapter 2 includes the review of available reports of polymer nanocomposites, mainly BMI-epoxy nanocomposites and polymer matrix composites with different fillers like BaTiO₃, Rochelle salt crystals and hydroxylated BaTiO₃ nanoparticles.

Chapter 3 describes the experimental techniques employed for the preparation and characterisation of both nanoparticles and BMI-epoxy nanocomposites related to the present work.

In **Chapter 4**, synthesis of BaTiO₃ nanoparticles (BT) by hydrothermal method and characterisation of BMI resin, BMI-epoxy composites, BaTiO₃ nanoparticles and BMI-epoxy BaTiO₃nanocomposites were included. The influence of BaTiO₃ nanoparticles on the thermo-mechanical and dielectric properties of BMI-epoxy composites reinforced with E glass fiber (EGF) and silane coated E glass fiber (SC-EGF) is also addressed.

Chapter 5 describes the effect of Rochelle salt crystals (RS) on various properties such as mechanical, thermal and dielectric properties of BMI-epoxy RS composites.

Chapter 6 focuses on the synthesis and characterisation of surface hydroxylated $BaTiO_3$ nanoparticles (BTOH). Effect of BTOH on various properties of BMI-epoxy composites is also described in this chapter.

Chapter 7 includes the effect of MWCNT on thermo-mechanical, electrical and EMI-SE of BMI-epoxy composites with different nanofillers such as BT, RS and BTOH.

Chapter 8 includes the summary, conclusion and future outlook of the study.

ABBREVIATIONS

BMI	Bismaleimide Resin
BT	Barium titanate
RS	Rochelle Salt
ВТОН	Surface hydroxylated Barium titanate
BDV	Breakdown Voltage
€r	Dielectric permittivity
FTIR	Fourier Transform Infrared Spectroscopy
XRD	X-ray Diffraction
SEM	Scanning Electron Microscopy
EDX / EDAX	Energy Dispersive X-ray
EGF	E Glass Fiber
SC-EGF	Silane Coated E Glass Fiber
DGEBA/DGEBP	Diglycidyl ether of bisphenol A
NP	Nanoparticle
TGA	Thermogravimetric analysis
EMI-SE	Electromagnetic interference-shielding effectiveness
NTCR	Negative Temperature Coefficient of Resistance
PTCR	Positive Temperature Coefficient of Resistance
MLCC	Multilayer Ceramic Chip Capacitor
ASTM	American Society for Testing and Materials
GHz	Gigahertz
SAXS	Small-angle X-ray scattering
ISM	Industrial, Scientific and Medical