



**PREPARATION AND CHARACTERIZATION OF RECYCLED  
HIGH-DENSITY POLYETHYLENE HYBRID COMPOSITES  
FOR WEATHERING AND THERMAL AGING  
PERFORMANCE**

**THINAKARAN A/L NARAYANAN**  
UNIVERSITI TEKNIKAL MALAYSIA MELAKA

**DOCTOR OF PHILOSOPHY**

**2025**



**Faculty of Industrial and Manufacturing Technology and  
Engineering**

**Preparation and Characterization of Recycled High-Density Polyethylene  
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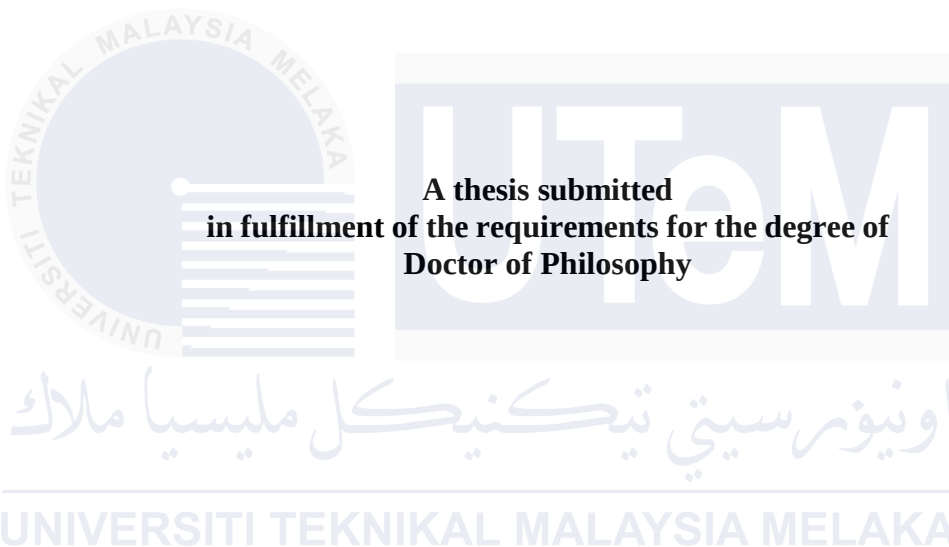
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**Thinakaran A/L Narayanan**  
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**Faculty of Industrial and Manufacturing Technology and Engineering**

**UNIVERSITI TEKNIKAL MALAYSIA MELAKA**

**2025**

## DECLARATION

I declare that this thesis entitled “Preparation and Characterization of Recycled High-Density Polyethylene Hybrid Composites for Weathering and Thermal Aging Performance “is the result of my own research except as cited in the references. The thesis has not been accepted to any degree and is not concurrently submitted in candidature of any other degree.



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Name : Ts. THINAKARAN A/L NARAYANAN

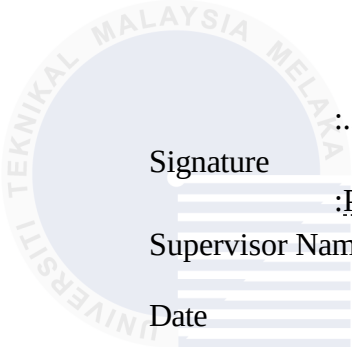
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## APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Doctor of Philosophy.



|                 |   |                                          |
|-----------------|---|------------------------------------------|
| Signature       | : | .....                                    |
| Supervisor Name | : | PM, Ir. Ts. Dr. JEEFFERIE BIN ABD. RAZAK |
| Date            | : | 25.07.2025                               |



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## DEDICATION

To my adored wife Thilagalakshmi Manogaran and wonderful children's, Daakshavarthan Thinakaran, Roshan Thinakaran, Tharunraj Thinakaran and Vahrn Thinakaran whose tireless efforts and unconditional love have been the pillars of my success. You have carried the weight of our family while I pursued this rigorous path, and for that, I am eternally grateful. This thesis is a tribute to your strength and sacrifice. It is a declaration of my love and appreciation, and a promise to continue honoring the legacy we build together.



## ABSTRACT

This research focuses on the preparation and characterization of recycled high-density polyethylene (rHDPE)/calcium carbonate ( $\text{CaCO}_3$ ) hybrid composites reinforced with fiberglass (FG) and waste rubber (WR), targeting structural applications in agricultural and outdoor environments. Objective 1 optimized the single-screw extrusion process using a two-level full factorial Design of Experiments (DOE), identifying optimal conditions as 260°C mixing temperature, 20 rpm screw speed, and an 80:20 wt% ratio of rHDPE to  $\text{CaCO}_3$ , achieving improved mechanical properties, tensile strength of 18.89 MPa, flexural strength of 48.89 MPa, and compressive strength of 10.43 MPa. Objective 2 evaluated the effects of hybrid fillers on mechanical, thermal, flammability, and physical properties, revealing that FG significantly enhanced structural strength with a tensile strength of 12.6 MPa, while WR improved impact resistance and toughness. UL 94 flammability tests showed that FG 7030 achieved the shortest burn times (17.24 s for 25 mm and 110.78 s for 100 mm), and Limiting Oxygen Index (LOI) values increased from 18.5% for pure rHDPE/ $\text{CaCO}_3$  to 37.78% for FG 6040, indicating enhanced flame retardancy. Thermogravimetric analysis (TGA) confirmed improved thermal stability with a decomposition onset temperature of 481.3°C, while DSC results showed good crystallinity retention, confirming minimal thermal degradation. FTIR analysis revealed chemical interactions between the matrix and fillers through carbonyl ( $\text{C=O}$ ) and silicate ( $\text{Si-O-Si}$ ) bonding, which improved interfacial adhesion. XRD patterns confirmed the preservation of crystallinity in the rHDPE matrix and effective integration of fillers without disrupting the lattice structure. Objective 3 assessed the outdoor performance under natural weathering and accelerated thermal conditions, where the selected formulation (70% rHDPE/ $\text{CaCO}_3$ , 21% FG, 9% WR) maintained its mechanical and thermal stability after 90 days of exposure, with only minor degradation observed in tensile strength (from 12.8 MPa to 12.6 MPa). FESEM analysis confirmed consistent filler dispersion and strong interfacial bonding. Overall, hybrid filler reinforcement significantly enhances the mechanical, thermal, and environmental resilience of rHDPE-based composites. By effectively utilizing recycled and industrial waste materials, this study offers a sustainable, high-performance alternative for structural use in construction, agriculture, and automotive industries.

## ***Penyediaan dan Pencirian Komposit Hibrid Kitar Semula Polietilena Berketumpatan Tinggi untuk Prestasi Luluhawa dan Penuaan Haba***

### **ABSTRAK**

Penyelidikan ini memberi tumpuan kepada penyediaan dan pencirian komposit hibrid kitar semula polietilena berketumpatan tinggi (rHDPE)/kalsium karbonat ( $\text{CaCO}_3$ ) yang diperkukuh dengan gentian kaca (FG) dan getah sisa (WR), menyasarkan aplikasi struktur dalam persekitaran pertanian dan penggunaan luar. Objektif 1 mengoptimumkan proses penyemperitan skru tunggal menggunakan reka bentuk eksperimen (DOE) faktorial penuh dua peringkat, mengenal pasti keadaan optimum sebagai suhu pencampuran  $260^\circ\text{C}$ , kelajuan skru 20 rpm, dan nisbah 80:20% wt% rHDPE kepada  $\text{CaCO}_3$ , mencapai sifat mekanikal yang lebih baik, kekuatan tegangan 18.89 MPa, kekuatan lentur 48.89 MPa, dan kekuatan mampatan 10.43 MPa. Objektif 2 menilai kesan pengisi hibrid terhadap sifat mekanikal, haba, mudah terbakar dan fizikal, mendedahkan bahawa FG meningkatkan kekuatan struktur dengan ketara dengan kekuatan tegangan 12.6 MPa, manakala WR meningkatkan rintangan hentaman dan keliatan. Ujian mudah terbakar UL 94 menunjukkan bahawa FG 7030 mencapai masa pembakaran terpendek (17.24 s untuk 25 mm dan 110.78 s untuk 100 mm), dan nilai Indeks Oksigen Mengehadkan (LOI) meningkat daripada 18.5% untuk rHDPE/ $\text{CaCO}_3$  tulen kepada 37.78% untuk FG 6040, menunjukkan kalis api yang dipertingkatkan. Analisis termogravimetri (TGA) mengesahkan kestabilan haba yang lebih baik dengan suhu permulaan penguraian  $481.3^\circ\text{C}$ , manakala keputusan DSC menunjukkan pengekalan penghabluran yang baik, mengesahkan degradasi haba yang minimum. Analisis FTIR mendedahkan interaksi kimia antara matriks dan pengisi melalui ikatan karbonil ( $\text{C}=\text{O}$ ) dan silikat ( $\text{Si}-\text{O}-\text{Si}$ ), yang meningkatkan lekatan antara muka. Corak XRD mengesahkan pemeliharaan kehabluran dalam matriks rHDPE dan penyepaduan pengisi yang berkesan tanpa mengganggu struktur kekisi. Objektif 3 menilai prestasi luar di bawah luluhawa semula jadi dan keadaan haba dipercepatkan, di mana formulasi yang dipilih (70% rHDPE/ $\text{CaCO}_3$ , 21% FG, 9% WR) mengekalkan kestabilan mekanikal dan termalnya selepas 90 hari pendedahan, dengan hanya kemerosotan kecil yang diperhatikan dalam kekuatan tegangan (daripada 12.8 MPa kepada 12.6 MPa). Analisis FESEM mengesahkan penyebaran pengisi yang konsisten dan ikatan antara muka yang kuat. Secara keseluruhan, tetulang pengisi hibrid meningkatkan daya tahan mekanikal, haba dan alam sekitar komposit berasaskan rHDPE dengan ketara. Dengan menggunakan bahan buangan kitar semula dan industri dengan berkesan, kajian ini menawarkan alternatif yang mampan dan berprestasi tinggi untuk kegunaan struktur dalam industri pembinaan, pertanian dan automotif.



## ACKNOWLEDGEMENT

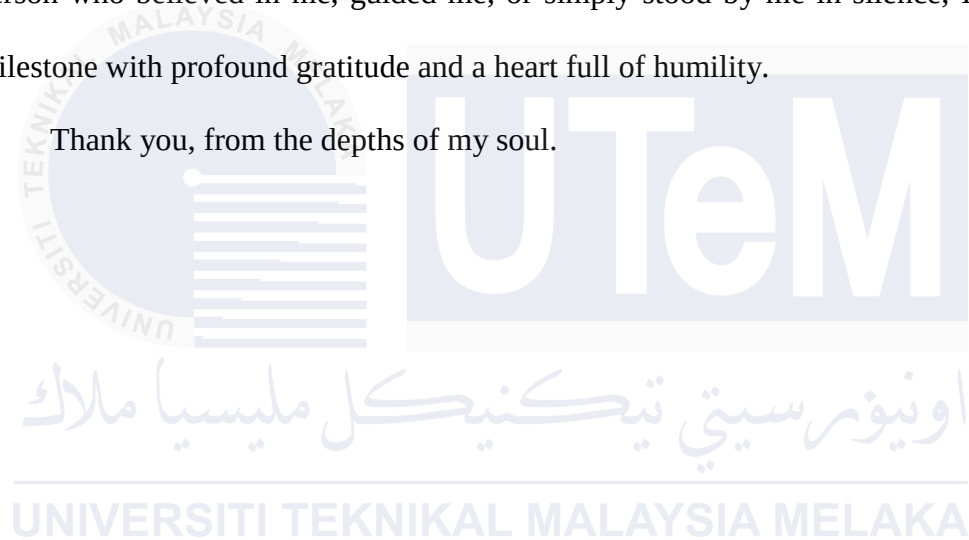
First and foremost, I express my deepest gratitude to my respected supervisor, AP Ir. Ts. Dr. Jeefferie Bin Abd Razak, whose invaluable guidance, unwavering support, and profound wisdom have been the foundation of my research journey. His patience, insightful critiques, and constant encouragement have not only shaped this thesis but have also nurtured my growth as a researcher and scholar. I am truly blessed to have been under his mentorship.

I would like to extend my sincere appreciation to the examination panel, whose expertise and thoughtful feedback greatly contributed to the refinement of this work. To the Chairman of the Examination Committee, Profesor Madya Ts. Dr. Rostam Affendi bin Hamzah, thank you for your leadership and professionalism throughout the process. To the External Examiner, Profesor Madya Dr. Poppy Puspitasari, I am deeply grateful for your meticulous review, constructive comments, and academic generosity. To the Internal Examiner, Profesor Madya Ir. Ts. Dr. Mohd Yuhazri bin Yaakob, thank you for your valuable insights and for upholding the highest standards of scholarly excellence.

My heartfelt thanks also go to the School of Graduate Studies, for your administrative support, guidance, and dedication in ensuring a smooth and meaningful academic journey. Your commitment to excellence has made a lasting difference in my experience as a postgraduate researcher. To my beloved family and cherished friends your understanding, patience, and unconditional love have been my anchor through every high and every challenge. In moments of doubt, your prayers and encouragement lifted my spirit and renewed my resolve. This achievement is as much yours as it is mine.

I am equally grateful to my dedicated colleagues at Institut Kemahiran Tinggi Belia Negara (IKTBN) Sepang and the Kementerian Belia dan Sukan (Ministry of Youth & Sports Malaysia). Your cooperation, motivation, and moral support have been a constant source of strength. Working alongside such committed and inspiring individuals has been both an honour and a privilege. This thesis is more than a culmination of research it reflects the collective effort, faith, and kindness of all who walked beside me, seen and unseen. To every person who believed in me, guided me, or simply stood by me in silence, I dedicate this milestone with profound gratitude and a heart full of humility.

Thank you, from the depths of my soul.



## TABLE OF CONTENTS

|                                                                             |             |
|-----------------------------------------------------------------------------|-------------|
| <b>DECLARATION</b>                                                          | <b>i</b>    |
| <b>APPROVAL</b>                                                             | <b>ii</b>   |
| <b>DEDICATION</b>                                                           | <b>iii</b>  |
| <b>ABSTRACT</b>                                                             | <b>iv</b>   |
| <b>ABSTRAK</b>                                                              | <b>v</b>    |
| <b>ACKNOWLEDGEMENT</b>                                                      | <b>vi</b>   |
| <b>TABLE OF CONTENTS</b>                                                    | <b>viii</b> |
| <b>LIST OF TABLES</b>                                                       | <b>xii</b>  |
| <b>LIST OF FIGURES</b>                                                      | <b>xv</b>   |
| <b>LIST OF ABBREVIATIONS</b>                                                | <b>xix</b>  |
| <b>LIST OF SYMBOLS</b>                                                      | <b>xxi</b>  |
| <b>LIST OF PUBLICATIONS</b>                                                 | <b>xxii</b> |
| <br><b>CHAPTER</b>                                                          |             |
| <b>1. INTRODUCTION</b>                                                      | <b>1</b>    |
| 1.1 Background of Study                                                     | 1           |
| 1.2 Problem Statement                                                       | 3           |
| 1.3 Objectives                                                              | 4           |
| 1.4 Scope of Study                                                          | 5           |
| 1.5 Significant of Study                                                    | 6           |
| 1.6 Thesis Outline                                                          | 7           |
| <br><b>2. LITERATURE REVIEW</b>                                             | <b>9</b>    |
| 2.1 Introduction                                                            | 9           |
| 2.2 Recycled High Density Polyethylene                                      | 9           |
| 2.3 Types and Classification of the r-HDPE                                  | 11          |
| 2.4 Physical and Mechanical Properties of HDPE and r-HDPE                   | 12          |
| 2.5 Thermal and Other Properties of HDPE and r-HDPE                         | 14          |
| 2.6 Composite Based on r-HDPE and Related Studies                           | 15          |
| 2.7 Calcium Carbonate                                                       | 17          |
| 2.8 Types, Chemical Properties and Structures of CaCO <sub>3</sub> Minerals | 19          |
| 2.8.1 Source and Synthesis of CaCO <sub>3</sub>                             | 22          |
| 2.8.2 Application and Polymer Composition Filled CaCO <sub>3</sub> Filler   | 24          |
| 2.9 Waste Rubber                                                            | 26          |
| 2.9.1 Current Issues on Waste Rubber                                        | 27          |
| 2.9.2 Potential Usage and Application of Waste Rubber                       | 28          |
| 2.9.3 Waste Rubber as a Filler in Polymer Composites                        | 30          |
| 2.9.4 Waste Rubber as Effective Damping Materials                           | 32          |
| 2.10 Fiberglass                                                             | 33          |
| 2.10.1 Types and Classification of Fiberglass                               | 33          |
| 2.10.2 Fiberglass as Potential Filler in Polymer Composites                 | 34          |
| 2.10.3 Performance and Applications of Fiberglass Filled Polymer Composites | 35          |

|           |                                                                                                                  |           |
|-----------|------------------------------------------------------------------------------------------------------------------|-----------|
| 2.11      | Polymer Composites with Hybrid Fillers                                                                           | 38        |
| 2.11.1    | Type and Classification of Hybrid Composites                                                                     | 39        |
| 2.11.2    | Theory on Hybrid Composite                                                                                       | 41        |
| 2.11.3    | Hybrid Fillers and Selection of Fillers                                                                          | 42        |
| 2.11.4    | Reinforcement Effects of The Hybrid Fillers                                                                      | 45        |
| 2.12      | Circular Economy in Polymer Recycling for Composite Manufacturing                                                | 56        |
| 2.13      | Design of Experiments                                                                                            | 57        |
| 2.13.1    | Two Level Full Factorial                                                                                         | 58        |
| 2.13.2    | Response Surface Methodology (RSM)                                                                               | 60        |
| 2.13.3    | Application of Design of Experiments in Polymer Composite Research                                               | 61        |
| 2.14      | Review of Research Gap                                                                                           | 64        |
| 2.15      | Summary                                                                                                          | 65        |
| <b>3.</b> | <b>METHODOLOGY</b>                                                                                               | <b>66</b> |
| 3.1       | Introduction                                                                                                     | 66        |
| 3.1.1     | Raw Materials                                                                                                    | 70        |
| 3.2       | Phase 1- Objective 1: Preparation of rHDPE/CaCO <sub>3</sub> Composite via Design of Experiments (DOE) Approach  | 74        |
| 3.2.1     | Design of Experiment (DOE)                                                                                       | 75        |
| 3.2.2     | The rHDPE/CaCO <sub>3</sub> Composites Preparation                                                               | 76        |
| 3.2.3     | Sample Testing and Parameter Optimization                                                                        | 78        |
| 3.3       | Mechanical Testing of rHDPE/CaCO <sub>3</sub> Composites                                                         | 79        |
| 3.3.1     | Tensile Testing of rHDPE/CaCO <sub>3</sub> Composites                                                            | 79        |
| 3.3.2     | Flexural Testing of rHDPE/CaCO <sub>3</sub> Composites                                                           | 80        |
| 3.3.3     | Compression Testing of rHDPE/CaCO <sub>3</sub> Composites                                                        | 80        |
| 3.4       | FESEM Fracture Morphological Observation of rHDPE/CaCO <sub>3</sub> Composites                                   | 81        |
| 3.5       | Phase 2-Objective 2: Hybrid Filler rHDPE/CaCO <sub>2</sub> Composites Filler Material Preparation                | 81        |
| 3.5.1     | The rHDPE/CaCO <sub>3</sub> hybrid composites filled with waste rubber (WR) hybrid composites                    | 82        |
| 3.5.2     | The Preparation of the rHDPE/CaCO <sub>3</sub> filled fiberglass (FG) Composites                                 | 84        |
| 3.6       | Characterization and Testing of rHDPE/CaCO <sub>3</sub> /WR and rHDPE/CaCO <sub>3</sub> /FG Hybrid Composites    | 85        |
| 3.6.1     | Tensile Testing of rHDPE/CaCO <sub>3</sub> /WR and rHDPE/CaCO <sub>3</sub> /FG Hybrid Composites                 | 85        |
| 3.6.2     | Density and Voids content Analysis rHDPE/CaCO <sub>3</sub> /WR and rHDPE/CaCO <sub>3</sub> /FG Hybrid Composites | 86        |
| 3.6.3     | Fourier Transform Infrared Spectroscopy (FTIR) analysis                                                          | 87        |
| 3.6.4     | X-ray diffraction (XRD)                                                                                          | 88        |
| 3.6.5     | Thermogravimetric analysis (TGA)                                                                                 | 89        |
| 3.6.6     | Underwriters Laboratories (UL94) for Flammability Testing                                                        | 90        |
| 3.6.7     | Limiting Oxygen Index (LOI)                                                                                      | 91        |

|           |                                                                                                                                              |           |
|-----------|----------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| 3.7       | Phase 3 – Objective 3: Degradation Analysis of rHDPE/CaCO <sub>3</sub> /FG/WR Hybrid Composites                                              | 92        |
| 3.7.1     | Mechanical Strength Degradation under the Natural Weathering Environmental Conditions                                                        | 93        |
| 3.7.2     | Thermal Degradation under Controlled Laboratory Conditions                                                                                   | 94        |
| 3.8       | Summary                                                                                                                                      | 96        |
| <b>4.</b> | <b>RESULT AND DISCUSSION</b>                                                                                                                 | <b>97</b> |
| 4.1       | Introduction                                                                                                                                 | 97        |
| 4.2       | Design of E                                                                                                                                  | 98        |
| 4.3       | Analysis of Main Response for rHDPE/CaCO <sub>3</sub> filled Composites                                                                      | 100       |
| 4.3.1     | Tensile Strength of rHDPE/CaCO <sub>3</sub> Composites                                                                                       | 100       |
| 4.3.2     | Compression Strength of rHDPE/CaCO <sub>3</sub> Composites                                                                                   | 110       |
| 4.3.3     | Flexural Strength of rHDPE/CaCO <sub>3</sub> Composites                                                                                      | 120       |
| 4.4       | Mechanical Strength Performance Analysis for rHDPE/CaCO <sub>3</sub> Composites                                                              | 130       |
| 4.5       | Morphological Observation using Field Emission Scanning Electron Microscope (FESEM) of rHDPE/CaCO <sub>3</sub> composites                    | 132       |
| 4.6       | Density and Specific Gravity Analysis of rHDPE/CaCO <sub>3</sub> Composites                                                                  | 134       |
| 4.7       | Thermal Gravity Analysis                                                                                                                     | 141       |
| 4.7.1     | Thermal Degradation of rHDPE/CaCO <sub>3</sub> Composites                                                                                    | 141       |
| 4.7.2     | Thermal Degradation rHDPE/CaCO <sub>3</sub> /WR Hybrid Composite                                                                             | 142       |
| 4.7.3     | Thermal Degradation rHPDE/CaCO <sub>3</sub> /FG Hybrid Composite                                                                             | 144       |
| 4.7.4     | Comparative Analysis and Discussion                                                                                                          | 146       |
| 4.8       | Differential Scanning Calorimetry                                                                                                            | 147       |
| 4.8.1     | Differential Scanning Calorimetry rHDPE/CaCO <sub>3</sub> Composite                                                                          | 147       |
| 4.8.2     | Differential Scanning Calorimetry rHDPE/CaCO <sub>3</sub> /FG Hybrid Composites                                                              | 149       |
| 4.8.3     | Differential Scanning Calorimetry rHDPE/CaCO <sub>3</sub> /WR Hybrid Composite                                                               | 152       |
| 4.9       | Flammability Test Results and Analysis for UL 94                                                                                             | 154       |
| 4.10      | Limiting Oxygen Index (LOI)                                                                                                                  | 157       |
| 4.11      | X-Ray Diffraction Analysis                                                                                                                   | 159       |
| 4.12      | Fourier Transform Infrared Analysis for rHDPE/CaCO <sub>3</sub> , 70+30FG and 70+30WR Composites                                             | 162       |
| 4.13      | Mechanical Strength Performance Analysis for rHDPE/CaCO <sub>3</sub> /FG and rHDPE/CaCO <sub>3</sub> /WR Hybrid Composites                   | 168       |
| 4.14      | Analysis of Degradation Behavior in rHDPE/CaCO <sub>3</sub> / FG and rHDPE/CaCO <sub>3</sub> /WR Hybrid Composites                           | 173       |
| 4.14.1    | Degradation study of rHDPE/CaCO <sub>3</sub> /FG and rHDPE/CaCO <sub>3</sub> /WR hybrid composites for stability and decomposition analysis  | 174       |
| 4.14.2    | Performance Evaluation of rHDPE/CaCO <sub>3</sub> Composite with Waste Rubber and Fiberglass after Environmental Natural Weathering Exposure | 177       |
| 4.15      | FESEM Analysis of rHDPE/CaCO <sub>3</sub> Hybrid Composite Filled with Waste Rubber and Fiberglass after Environmental Natural Weathering    |           |

|                                                              |            |
|--------------------------------------------------------------|------------|
| Exposure                                                     | 180        |
| 4.16 Summary                                                 | 181        |
| <b>5. CONCLUSION AND RECOMMENDATIONS FOR FUTURE RESEARCH</b> | <b>184</b> |
| 5.1 Conclusion                                               | 186        |
| 5.2 Research Contributions                                   | 184        |
| 5.3 Recommendation for Future Research                       | 186        |
| <b>REFERENCES</b>                                            | <b>189</b> |



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## LIST OF TABLES

| <b>TABLE</b> | <b>TITLE</b>                                                                                                       | <b>PAGE</b> |
|--------------|--------------------------------------------------------------------------------------------------------------------|-------------|
| Table 2.1    | Comparison Table of Mechanical Properties between the HDPE and rHDPE                                               | 13          |
| Table 2.2    | Effects of filler additions on mechanical properties of HDPE and r-HDPE composites                                 | 17          |
| Table 2.3    | Summary of studies on calcium carbonate reinforcement in polymer composites                                        | 19          |
| Table 2.4    | Summary of studies on the application of waste polymers and rubber in sustainable material development             | 31          |
| Table 2.5    | Summary of recent studies on composite materials and their fabrication methods                                     | 35          |
| Table 2.6    | Summary of research outcomes on composite materials and machining technique                                        | 38          |
| Table 2.7    | Summary of research findings on hybrid fillers in polymer composites                                               | 47          |
| Table 2.8    | Summary of research results on performance polymer composites with hybrid fillers in thermal properties            | 48          |
| Table 2.9:   | Summary of research results on hybrid fillers in polymer composites for biodegradability and mechanical properties | 50          |
| Table 2.10:  | Summary of research results on hybrid fillers in polymer composites for enhanced properties.                       | 52          |
| Table 2.11:  | Summary of thermal and weather degradation effects on polymer hybrid composites.                                   | 54          |
| Table 2.12:  | Summary of hybrid fillers in polymer composite for structural application used in agriculture industry.            | 55          |
| Table 2.13:  | Summary of waste material recycling in plastic industry circular economy                                           | 57          |
| Table 2.14:  | Summary of design of experiments (DOE) studies in structural composites manufacturing and characterization         | 63          |

|                                                                                                                                |     |
|--------------------------------------------------------------------------------------------------------------------------------|-----|
| Table 2.15: Overview of the Existing Research Deficiencies in The Domain of Hybrid Fillers Within Polymer Composite Materials. | 64  |
| Table 3.1: Summary of raw material                                                                                             | 73  |
| Table 3.2: Factors and levels for rHDPE/CaCO <sub>3</sub> composite preparation using full factorial DOE                       | 74  |
| Table 3.3: Experimental run combinations for rHDPE/CaCO <sub>3</sub> composite fabrication                                     | 76  |
| Table 3.4: Specimens configuration and dimensions for respective mechanical testing based on each respective ASTM standards    | 78  |
| Table 3.5: Weight percentage of waste rubber (WR) in rHDPE/CaCO <sub>3</sub> /WR composites                                    | 82  |
| Table 3.6: Percentage of fibreglass (FG) weight in different samples                                                           | 84  |
| Table 4.1: Parametric combination for rHDPE/CaCO <sub>3</sub> polymer composites preparation and their responses values.       | 99  |
| Table 4.2: Selected level of variables for rHDPE/CaCO <sub>3</sub> composite preparation                                       | 99  |
| Table 4.3: The effect list of tensile strength model terms for rHDPE/CaCO <sub>3</sub> composites                              | 103 |
| Table 4.4: Analysis of Variance (ANOVA) for the Tensile Strength response of rHDPE/CaCO <sub>3</sub> Composites                | 104 |
| Table 4.5: Coefficients of the Regression Equation for Predicting Tensile Strength Response                                    | 106 |
| Table 4.6: The effect list of model terms for rHDPE/CaCO <sub>3</sub> composites for compression strength response             | 113 |
| Table 4.7: Analysis of variance (ANOVA) for the compression strength of rHDPE/CaCO <sub>3</sub> composites                     | 115 |
| Table 4.8: Coefficients of the regression equation for predicting compression strength response                                | 117 |
| Table 4.9: The effect list of for rHDPE/CaCO <sub>3</sub> Composite (flexural strength response)                               | 123 |
| Table 4.10: Analysis of variance (ANOVA) for the mechanical flexural strength properties of rHDPE/CaCO <sub>3</sub> composites | 124 |



|                                                                                                                                             |     |
|---------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Table 4.11: Coefficients of the regression equation for predicting flexural strength                                                        | 125 |
| Table 4.12: Optimization results of RSM on rHDPE/CaCO <sub>3</sub> hybrid composites                                                        | 127 |
| Table 4.13: Optimization solutions recommendation of rHDPE/ CaCO <sub>3</sub> hybrids composite                                             | 128 |
| Table 4.14: Experimental parameter combinations                                                                                             | 130 |
| Table 4.15: Experimental design matrix and mechanical properties of rHDPE/CaCO <sub>3</sub> composites                                      | 131 |
| Table 4.16: Density and specific gravity measurements for rHDPE/CaCO <sub>3</sub> composite samples                                         | 134 |
| Table 4.17: Density and specific gravity measurements for rHDPE/ CaCO <sub>3</sub> /WR hybrid composite samples                             | 136 |
| Table 4.18: Density and specific gravity measurements for rHDPE/CaCO <sub>3</sub> /FG hybrid composite                                      | 138 |
| Table 4.19: Average Burn Times for 25mm and 100mm Specimens of waste rubber (WR), fibreglass (FG) filled rHDPE/CaCO <sub>3</sub> composites | 156 |
| Table 4.20: Limiting oxygen index (LOI) values for rHDPE, waste rubber (WR), and fibreglass (FG) filled rHDPE/CaCO <sub>3</sub> composites  | 158 |
| Table 4.21: Tensile strength of rHDPE/CaCO <sub>3</sub> composites with WR 70+30 and FG 70+30                                               | 169 |

## LIST OF FIGURES

| FIGURE       | TITLE                                                                                                                               | PAGE |
|--------------|-------------------------------------------------------------------------------------------------------------------------------------|------|
| Figure 2.1:  | Recycled HDPE Process (Lange, 2021)                                                                                                 | 11   |
| Figure 2.2:  | Types of $\text{CaCO}_3$ (a) aragonite, (b) calcite, and (c) vaterite (Wakayama et al., 2020)                                       | 20   |
| Figure 2.3:  | (a) Carbonate ions and (b) carbonic acid (Lu, Y. et al., 2021)                                                                      | 21   |
| Figure 2.4:  | Natural sources of calcium carbonate include (a) limestone, (b) marble, and (c) chalk                                               | 22   |
| Figure 2.5:  | Schematic diagram of calcium carbonate ( $\text{CaCO}_3$ ) precipitation in the pore space of the soil matrix (Rahman et al., 2020) | 23   |
| Figure 2.6:  | (a) polymer and (b) $\text{CaCO}_3$ molecular structure (Niu et al., 2022)                                                          | 24   |
| Figure 2.7:  | Environmental Impact of Waste Tire Dumping (Allseas Global, 2023)                                                                   | 27   |
| Figure 2.8:  | Rubberizing Road Sustainability (Marini and Lanotte, 2021)                                                                          | 28   |
| Figure 2.9:  | Revolutionizing Safety and Sustainability with Rubberized Surfaces (Chittella et al., 2021)                                         | 29   |
| Figure 2.10: | Life cycle of tire (Akbas and Yuhana, 2021)                                                                                         | 32   |
| Figure 3.1:  | Overall Research Flow-Chart                                                                                                         | 70   |
| Figure 3.2:  | Process flow of rHDPE/ $\text{CaCO}_3$ Composite Preparation                                                                        | 75   |
| Figure 3.3:  | Universal Testing Machine (UTM)                                                                                                     | 77   |
| Figure 3.4:  | Field Emission Scanning Electron Microscope (FE-SEM)                                                                                | 79   |
| Figure 3.5:  | (a) rHDPE polymer matrix and (b) $\text{CaCO}_3$ filler                                                                             | 80   |
| Figure 3.6:  | Crushed waste rubber (WR) as filler                                                                                                 | 81   |
| Figure 3.7:  | Process flow of WR filled rHDPE/ $\text{CaCO}_3$ hybrids composite fabrication                                                      | 81   |
| Figure 3.8:  | Crushed fiberglass (FG) filler                                                                                                      | 82   |
| Figure 3.9:  | Densimeter                                                                                                                          | 84   |

|                                                                                                                                                     |     |
|-----------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 3.10: FTIR Analyzer                                                                                                                          | 85  |
| Figure 3.11: XRD Analyzer                                                                                                                           | 86  |
| Figure 3.12: UL94 vertical flammability test                                                                                                        | 87  |
| Figure 3.13: FESEM                                                                                                                                  | 89  |
| Figure 3.14: Specimen under natural weathering exposure                                                                                             | 90  |
| Figure 3.15: Lab control exposure process                                                                                                           | 91  |
| Figure 4.1: Half Normal Plot for tensile strength main response                                                                                     | 97  |
| Figure 4.2: Plot of residuals versus predicted tensile strength response for rHDPE/CaCO <sub>3</sub> composites                                     | 98  |
| Figure 4.3: Response surface plots of tensile strength response of rHDPE/CaCO <sub>3</sub> composites with (a) BC interaction; (b) AB interaction   | 104 |
| Figure 4.4: Optimization result of tensile strength response rHDPE/CaCO <sub>3</sub> composites in ramps graphical view                             | 106 |
| Figure 4.5: Optimization result of tensile strength for rHDPE/CaCO <sub>3</sub> in histogram graphical view                                         | 106 |
| Figure 4.6: Half normal plot of the compression strength response for rHDPE/CaCO <sub>3</sub> Composites                                            | 107 |
| Figure 4.7: Plot of residuals versus predicted compression strength response for rHDPE/CaCO <sub>3</sub> composite                                  | 109 |
| Figure 4.8: Response surface plots of compression strength response of rHDPE/CaCO <sub>3</sub> with (a) AB interaction; (b) AC interaction          | 115 |
| Figure 4.9: Optimization result of compression strength response for rHDPE/CaCO <sub>3</sub> composites in ramps graphical view                     | 117 |
| Figure 4.10: Optimization result of compression strength for rHDPE/CaCO <sub>3</sub> composites in histogram graphical view                         | 117 |
| Figure 4.11: Half normal plot for flexural strength of rHDPE/CaCO <sub>3</sub> composites                                                           | 118 |
| Figure 4.12: Response surface plots of flexural strength response of rHDPE/CaCO <sub>3</sub> composites with (a) AB interaction; (b) AC interaction | 123 |

|                                                                                                                                                                       |     |
|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 4.13: Optimization result of rHDPE/CaCO <sub>3</sub> composites in ramps graphical view                                                                        | 126 |
| Figure 4.14: Optimization result of rHDPE/CaCO <sub>3</sub> composites in histogram graphical view                                                                    | 126 |
| Figure 4.15: (a) denotes R10, (b) signifies R7, and (c) corresponds to R1, all pertaining to the composite of rHDPE and CaCO <sub>3</sub>                             | 131 |
| Figure 4.16: Mass and specific gravity of rHDPE/CaCO <sub>3</sub> composite samples                                                                                   | 132 |
| Figure 4.17: Mass and specific gravity of rHDPE/ CaCO <sub>3</sub> /WR hybrid composite                                                                               | 134 |
| Figure 4.18: Mass and specific gravity of rHDPE/CaCO <sub>3</sub> /FG hybrid composite                                                                                | 136 |
| Figure 4.19: Density analysis value for sample rHDPE/CaCO <sub>3</sub>                                                                                                | 137 |
| Figure 4.20: TGA of rHDPE/CaCO <sub>3</sub> composites                                                                                                                | 139 |
| Figure 4.21: TGA for rHDPE/CaCO <sub>3</sub> /WR composite                                                                                                            | 141 |
| Figure 4.22: TGA for rHDPE/CaCO <sub>3</sub> /FG composite                                                                                                            | 144 |
| Figure 4.23: DSC analysis of rHDPE/CaCO <sub>3</sub> composites                                                                                                       | 147 |
| Figure 4.24: DSC analysis of rHDPE/CaCO <sub>3</sub> /FG composite                                                                                                    | 150 |
| Figure 4.25: DSC analysis of rHDPE/CaCO <sub>3</sub> /WR composite                                                                                                    | 153 |
| Figure 4.27: Burn Time Comparison of waste rubber (WR) fibreglass (FG) filled rHDPE/CaCO <sub>3</sub> composites for 25mm and 100mm Specimens in Flammability Testing | 154 |
| Figure 4.28: Comparison of LOI (%) for various rHDPE, waste rubber (WR), and fibreglass (FG) filled rHDPE/CaCO <sub>3</sub> composite samples                         | 157 |
| Figure 4.29: XRD Patterns of rHDPE/CaCO <sub>3</sub> , 70+30FG, and 70+30WR hybrid composites highlighting crystallinity and phase composition                        | 159 |
| Figure 4.30: FTIR Spectrum of Showing Characteristic Peaks of rHDPE/CaCO <sub>3</sub> Composite                                                                       | 162 |
| Figure 4.31: FTIR spectrum of rHDPE/CaCO <sub>3</sub> (70%) and fiberglass (30%) composite                                                                            | 164 |
| Figure 4.32: FTIR spectrum of rHDPE/CaCO <sub>3</sub> (70%) and waste rubber (30%) composite                                                                          | 166 |

|                                                                                                                                                                                    |     |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 4.33: Tensile strength analysis of rHDPE/CaCO <sub>3</sub> , WR70+30 and FG70+30 composites                                                                                 | 169 |
| Figure 4.34: TG and DTG curves showing thermal degradation and decomposition behavior of the hybrid composites material under nitrogen and oxygen atmospheres                      | 173 |
| Figure 4.35: Comparison of tensile strength and elongation percentages for composite samples after 90 days of outdoor exposure                                                     | 176 |
| Figure 4.36: Image (a) and (b) illustrating the presence of rHDPE/CaCO <sub>3</sub> , waste rubber, and fiberglass in the rHDPE/CaCO <sub>3</sub> /FG/WR hybrid composite material | 177 |



## LIST OF ABBREVIATIONS

|                   |   |                                                           |
|-------------------|---|-----------------------------------------------------------|
| UTeM              | - | Universiti Teknikal Malaysia Melaka                       |
| FTKIP             | - | Fakulti Teknologi dan Kejuruteraan Industri dan Pembuatan |
| IKTBN             | - | Institut Kemahiran Tinggi Belia Negara                    |
| HDPE              | - | High Density Polyethylene                                 |
| rHDPE             | - | Recycled High Density Polyethylene                        |
| CaCO <sub>3</sub> | - | Calcium Carbonate                                         |
| WR                | - | Waste Rubber                                              |
| FG                | - | Fiberglass                                                |
| FTIR              | - | Fourier Transform Infrared                                |
| XRD               | - | X-ray diffraction                                         |
| DOE               | - | Design of Experiment                                      |
| FESEM             | - | Field Emission Scanning Electron Microscope               |
| DSC               | - | Differential Scanning Calorimetry                         |
| TGA               | - | Thermogravimetric analysis                                |
| RSM               | - | Response surface methodology                              |
| WC                | - | Waste Carpet                                              |
| PVC               | - | Polyvinyl Chloride                                        |
| UV                | - | Ultraviolet                                               |
| HDT               | - | Heat Deflection Temperature                               |
| CTE               | - | Coefficient of Thermal Expansion                          |
| OPE               | - | Oxidized Polyethylene                                     |
| MICP              | - | Microbial-Induced Calcium Carbonate Precipitation         |
| ANOVA             | - | Analysis of Variance                                      |
| IM                | - | Injection Molding                                         |
| ASTM              | - | American Standard Testing Method                          |

|                |   |                                      |
|----------------|---|--------------------------------------|
| UTM            | - | Universal Testing Machine            |
| UL 94          | - | Underwriters Laboratories 94         |
| LOI            | - | Limiting Oxygen Index                |
| BBD            | - | Box–Behnken Design                   |
| HPC            | - | Hybrid Polymer Composites            |
| PMC            | - | Polymer matrix composites            |
| RH             | - | Rice Husk                            |
| RTPW           | - | recycled thermosetting polymer waste |
| FRP            | - | Fibre Reinforced Polymer             |
| GFRP           | - | Glass Fibre Reinforced Polymer       |
| rpm            | - | Revolutions per Minute               |
| wt. %          | - | Weight Percentage                    |
| MPa            | - | Mega Pascal                          |
| GYP            | - | waste gypsum                         |
| SS             | - | Soapstone                            |
| BRF            | - | Banana Rachis fibers                 |
| WF             | - | Wood flour                           |
| WSF            | - | Walnut Shell Flour                   |
| RHF            | - | Rice husk flour                      |
| DIY            | - | Do it yourself                       |
| mm             | - | Millimeter                           |
| min            | - | Minute                               |
| kN             | - | Kilo Newton                          |
| KJ             | - | Kilo Joule                           |
| m <sup>2</sup> | - | Square meter                         |
| m              | - | Mass                                 |
| v              | - | Volume                               |

## LIST OF SYMBOLS

|                                  |   |                            |
|----------------------------------|---|----------------------------|
| $\text{Ca}^{2+}$                 | - | calcium ions               |
| $^{\circ}\text{C}$               | - | Degree Celsius             |
| %                                | - | Percentage                 |
| et. al                           | - | et alia                    |
| $\text{g}/\text{cm}^3$           | - | grams per cubic centimeter |
| $\text{W}/\text{m}\cdot\text{K}$ | - | Watts per meter-Kelvin     |
| $\text{CO}_3^{2-}$               | - | carbonate ions             |
| $\text{H}^+$                     | - | hydrogen ions              |
| $\sigma$                         | - | Sigma                      |
| $\alpha$                         | - | Alpha                      |
| $\phi$                           | - | volume fraction            |
| wt. %                            | - | Weightage percentile       |
| mm/min                           | - | millimeters per minute     |
| :                                | - | Ratio                      |
| $\rho$                           | - | rho                        |