## Faculty of Manufacturing Engineering

# OPTIMIZATION OF TAPIOCA STARCH-MODIFIED NATURAL RUBBER COMPOSITES FOR BALLISTIC ENERGY DISSIPATION IN TRAUMA PACK

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**Doctor of Philosophy**

**2023**

**OPTIMIZATION OF TAPIOCA STARCH-MODIFIED NATURAL RUBBER COMPOSITES FOR BALLISTIC ENERGY DISSIPATION IN TRAUMA PACK**

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**A thesis submitted
in fulfillment of the requirements for the degree of
Doctor of Philosophy**

**Faculty of Manufacturing Engineering**

**UNIVERSITI TEKNIKAL MALAYSIA MELAKA**

**2023**

## DECLARATION

I declare that this thesis entitled “Optimization of Tapioca Starch-Modified Natural Rubber Composites for Ballistic Energy Dissipation in Trauma Pack” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

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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.

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Supervisor Name : Assoc. Prof. Dr. Noraiham Binti Mohamad

Date : 29 March 2023

# DEDICATION

To my beloved husband, father, mother & siblings.

# ABSTRACT

The requirement to lessen the blunt trauma of the shield's back against body armour wearers prompted the quest for novel materials with excellent energy dissipation, flexibility, and affordability. This study developed a natural rubber-modified starch (NRS) composite as a residual impact energy absorber in a ballistic trauma pack. NRS composite is made using a melt compounding method with an internal mixer. The typical ingredients were 100 parts per hundred (phr) of natural rubber (NR), various loadings of tapioca starch (TS) and filler materials, curing agents and additives. The NRS composites were vulcanized in a hot press at 160 °C. In Stage 1, the effect of tapioca starch loadings (0, 5, 10, 20, 40, 60 phr) on mechanical properties and cure characteristics were analysed. The NRS vulcanizate with 20 phr TS was selected for its maximum mechanical properties and processability. In Stage 2, Response Surface Methodology (RSM) was used to optimize the other formulation parameters with the help of Design Expert 6.0.10 software. Four formulation variables, 1) type of fillers (carbon black (CB) and ZrO2 nanoparticles), 2) glycerol and 3) silane coupling agent (3-aminopropyltriethoxysilane) were evaluated for their rebound resilience, tensile strength, and cure characteristics. The regression models for the responses were chosen by comparing the observational data with the software's predicted values. A result of $R^2$ close to unity from the analysis of variance indicates the model accuracy in representing the actual system. The samples were subjected to the Rheometer test, tensile test, hardness test, rebound resilience (RR) test, swelling test, compositional analysis using infrared Fourier transformation spectroscopy, morphological analysis via a Field Emission Scanning Electron Microscopy (FESEM), and Dynamic Mechanical Thermal Analysis (DMTA). Compared to vulcanizate without filler, TS at 20 phr showed the best compatibility with NR matrices due to enhanced cure characteristics, tensile energy absorption, hardness, and crosslink density. In Stage 3, the composites with the lowest RR (100 phr CB) and highest RR (50 phr CB) were chosen for the ballistic trauma test and tested against the effect of no. of layers (3 layers and 6 layers) and with (NRS composites) or without TS (NR composites). Using the Prototypa Universal Test Gun, NRS composites were subjected to the NIJ 0101.04 Level II Ballistic Resistance Test against 9 x 19 mm Full Metal Jacketed Round Nose (FMJ RN) bullet penetration. NR composites were integrated with mild steel plates to determine ballistic limit and back-face signature (BFS). Deformation patterns of the NR composites were observed and supported with morphological characteristics using FESEM to establish the failure mechanism. NRS composites manifested BFS of 4.55 (NRS-CB50) to 14.52 (NRS-CB100) for the range of energy dissipation between 507.00 to 562.50 J. NRS-CB50 with low RR value has depicted the highest potential to be used in trauma pack due to the enormous trauma reduction compared to the NRS-CB100 with high RR value. The presence of TS particles resulted in substantial chain mobility and improved the overall energy dissipation via viscous and elastic responses. The morphological characteristics of the deformed composite back face were in line with the BFS and energy adsorption of the composite under ballistic impact. The best NRS formulation and no. of layer for the trauma pack was selected to be at 100phr NR, 20phr TS, 50phr CB, 5phr glycerol and 6 layers.

***PENGOPTIMUMAN KOMPOSIT GETAH ASLI TERUBAHSUAI KANJI UBI KAYU UNTUK PELESAPAN TENAGA BALISTIK DALAM BUNGKUS TRAUMA***

## ABSTRAK

*Keperluan untuk mengurangkan trauma pukulan tumpul terhadap pemakai perisai jasad mendorong pencarian bahan baru dengan penyerapan tenaga yang baik, fleksibiliti, dan kebolehmampuan. Komposit getah asli terubahsuai kanji (NRS) dikembangkan dalam kajian ini sebagai penyerap tenaga hentaman sisa dalam pek trauma balistik. Komposit NRS dibuat menggunakan kaedah penyebatian lebur menggunakan alat pengadun dalaman. Formula umum adalah 100 bahagian per ratus (phr) getah asli (NR), kanji ubikayu (TS) dan bahan pengisi berbeza pembebanan, agen pematangan dan bahan tambah. Komposit NRS divulkanisasi dalam penekan panas pada suhu 160 ° C. Dalam Peringkat 1, pengaruh pembebanan kanji ubikayu (0, 5, 10, 20, 40, 60 phr) terhadap sifat mekanikal dan ciri pematangan dianalisa. Vulkanizat NRS dengan 20 phr TS dipilih kerana sifat mekanikal maksimum dan kebolehprosesan. Dalam Peringkat 2, Metodologi Permukaan Sambutan (RSM) digunakan untuk mengoptimumkan parameter formulasi lain dengan bantuan perisian Design Expert 6.0.10. Empat pemboleh ubah formulasi 1) jenis pengisi (hitam karbon (CB) dan nanopartikel ZrO2), 2) gliserol dan 3) agen gandingan silana (3-aminopropyltriethoxysilane) dinilai untuk kebingkasan pantulan, kekuatan tegangan, dan ciri pematangan. Model regresi untuk respons dipilih berdasarkan perbandingan data pengamatan dengan nilai yang dijangka oleh perisian. Hasil* $R^2$ *yang menghampiri kesatuan dari analisis varians menunjukkan ketepatan model untuk mewakili sistem yang sebenarnya. Sampel NRS dikenakan dengan Ujian Rheometer, Ujian tegangan, Uji Kekerasan, Ujian kebingkasan pantulan (RR), Ujian pengampulan, Analisis Komposisi menggunakan Spektroskopi Transformasi Fourier Inframerah, Analisis Morfologi Melalui Mikroskopi Elektron Imbasan Pelepasan Medan (FESEM) dan Analisis Termal Mekanikal Dinamik (DMTA). Jika dibandingkan dengan vulcanizat tanpa pengisi, TS pada 20 phr menunjukkan keserasian terbaik dengan matriks NR kerana ciri pematangan, penyerapan tenaga tegangan, kekerasan, dan ketumpatan silang yang dipertingkatkan. Dalam Peringkat 3, komposit dengan RR terendah (100 phr CB) dan RR tertinggi (50 phr CB) dipilih untuk ujian trauma balistik dan diuji terhadap kesan bilangan lapisan (3 lapisan dan 6 lapisan) dan dengan (komposit NRS) atau tanpa TS (komposit NR). Dengan menggunakan Senapang Ujian Semesta Prototypa, panel komposit dikenakan Ujian Rintangan Balistik Tahap II NIJ 0101.04 terhadap penembusan peluru 9 x 19 mm Full Metal Jacketed Round Nose (FMJ RN). Komposit NR disatukan dengan plat keluli ringan, untuk penentuan had balistik dan tanda muka belakang (BFS). Corak ubah bentuk komposit NR diperhatikan dan disokong dengan ciri morfologi menggunakan FESEM untuk mewujudkan mekanisme kegagalan. Komposit NRS memanifestasikan BFS dari 4.55 (NRS-CB50) hingga 14.52 (NRS-CB100) untuk julat penyerapan tenaga antara 507.00 hingga 562.50 J. NRS-CB50 dengan nilai RR rendah telah menggambarkan potensi tertinggi untuk digunakan dalam pek trauma kerana pengurangan trauma yang sangat besar berbanding NRS-CB100 dengan nilai RR yang tinggi. Kehadiran zarah TS menghasilkan mobiliti rantaian yang besar dan meningkatkan pelesapan tenaga secara keseluruhan melalui tindak balas likat dan elastik. Ciri-ciri morfologi muka belakang komposit yang cacat adalah selaras dengan BFS dan penjerapan tenaga komposit di bawah kesan balistik. Formulasi NRS dan bilangan lapisan terbaik untuk pek trauma dipilih adalah 100phr NR, 20phr TS, 50phr CB, 5phr gliserol dan 6 lapisan.*

## ACKNOWLEDGEMENTS

***In the name of Allah, the Most Gracious and the Most Merciful.***

Alhamdulillah to Allah S.W.T for His bounty and guidance. I have successfully completed this scholarly training. This thesis is the result of my hard work for almost four years. This effort would not have been possible without the strong support of Associate Professor Dr. Noraiham Binti Mohamad as the main supervisor at the Fakulti Kejuruteraan Pembuatan (FKP), Universiti Teknikal Malaysia Melaka (UTeM), Melaka. She has guided my steps in both experimental and writing up while studying. I convey millions of thanks for her sincere efforts, thoughts and guidance intellectually and emotionally throughout my journey to complete this thesis. I am also not forgetting Professor Ir. Dr. Mohd Asyadi'Azam Bin Mohd Abid, who is very dedicated to carrying out his duty as co-supervisor.

Thousands of thanks are also extended to all the lecturers, officers, engineers, administrative staff, laboratory assistants, and technical staff who helped me a lot, whether at UTeM, Malaysian Nuclear Agency (MINT), Lembaga Getah Malaysia (LGM), and Ministry of Defence (STRIDE). Their excellent service is invaluable and will not be forgotten for a lifetime.

I would also like to thank my colleagues in the postgraduate room of the Fakulti Kejuruteraan Pembuatan (FKP), UTeM, who shared many thoughts and grief during my time at UTeM. I am not also forgetting my close friend at UTeM, Associate Profesor Ts. Dr. Jeefferie Abd Razak. He often gives me words of encouragement and support in times of need. Finally, a special appreciation goes to my dear family, who have continually provided support and encouragement and have strengthened me throughout my daily life journey. My gratitude is addressed especially to my beloved husband, Mohd Mef'at Bin Hamdan. Indeed, your love and understanding are great and meaningful and will be remembered until the end of my life. Thank you.

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## LIST OF ABBREVIATIONS

| | | |
|---|---|---|
| ANOVA | - | Analysis of Variance |
| ASTM | - | American Society for Testing and Materials |
| BABT | - | Behind Armour Blunt Trauma |
| BS | - | British Standards |
| C | - | Carbon |
| CB | - | Carbon Black |
| CH | - | Hydrocarbon |
| COOH | - | Carboxylic Group |
| CP | - | Complete Penetration |
| CV | - | Conventional Vulcanization |
| CBS | - | N-cyclohexylbenthiazyl sulphonamide |
| DMTA | - | Dynamic Mechanical Thermal Analysis |
| $E_{abs}$ | - | Energy absorption |
| EB | - | Elongation of brake |
| FESEM | - | Field Emission Scanning Electron Microscope |
| FTIR | - | Fourier-transform infrared spectroscopy |
| FMJ RN | - | Full Metal Jacketed Round Nose |
| EV | - | Efficient vulcanization system |
| LGM | - | Malaysian Rubber Board |
| MINT | - | Malaysian Institute for Nuclear Technology Research |
| M100 | - | Modulus at 100% elongation |
| M300 | - | Modulus at 300% elongation |
| NR | - | Natural rubber |
| OH | - | Hydroxyl Group |
| PHR | - | Part Per Hundred |

| | | |
|---|---|---|
| RPM | - | Revolutions per minute |
| RRIM | - | Rubber Research Institute of Malaysia |
| RSM | - | Response Surface Methodology |
| SCA | - | 3-aminopropyltriethoxysilane |
| STRIDE | - | Science Technolology Research Institute for Defence |
| SEM | - | Scanning Electron Microscope |
| S | - | Sulfur |
| SEMI-EV | - | Semi-effective Vulcanization |
| SMR | - | Standard Malaysin Rubber |
| SMR 20 | - | Standard Malaysin Rubber Grade 20 |
| TMTD | - | Tetramethylthiuram disulphide |
| TS | - | Tensile Strength |
| T2 | - | Scoorch Time |
| T90 | - | Cure Time |
| Tg | - | Glass Trasition Temperature |
| USA, US | - | United States |
| V0 | - | Initial Velocity |
| V50 | - | Ballistic limit |
| XRD | - | X-Ray Diffraction |
| ZnO | - | Zinc Oxide |
| ZrO2 | - | Zirconia |
| 6PPD | - | *n*-(1,3-dimenthyl)-*n'*-phenyl-p-phenylenediamine |

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