UNIVERSITI TEKNIKAL MALAYSIA MELAKA

TRIBOLOGICAL BEHAVIOUR OF 3D-PRINTED POLY(LACTIC) ACID -POLYCARBONATE URETHANE POLYMER BLEND FOR ARTIFICIAL ARTICULAR CARTILAGE

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A thesis submitted
in fulfillment of the requirements for the degree of
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2024

DECLARATION

I declare that this thesis entitled "Tribological Behaviour of 3D-Printed Poly(Lactic) Acid - Polycarbonate Urethane Polymer Blend for Artificial Articular Cartilage" 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.

Signature	:
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Date	: 31st JULY 2024

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 Master of Science in Mechanical Engineering.

Signature	:
Supervisor Name	: PROF. DR. MOHD FADZLI ABDOLLAH
Date	: 31st JULY 2024

DEDICATION

To my dearest mother and aunty.

ABSTRACT

In order to better understand the tribological behaviour of a poly(lactic) acid (PLA)-polycarbonate urethane (PCU) blend for artificial articular cartilage applications, this study investigates the blend's composition, which is 90 wt.% PLA-10 wt.%PCU. Layer thicknesses of 0.10, 0.12, 0.14, and 0.16 mm were used when printing the samples. All the samples were put through a ball-on-disc tribo-test in which a normal load of 30, 50, and 70 N was applied. Ringer's lactate served as a lubricant and the simulating the environment in vivo. The hardness, contact angle, surface roughness, and surface morphology tests were also used to analyse the 3D-printed samples. Based on these tests, 3D-printed samples with 0.16 mm layer thickness outperform other samples with different viscosities of Ringer's lactate, regardless of the applied normal load during the tribo-test. The results showed that the PLA-PCU polymer blend was well suited for artificial articular cartilage applications due to its favourable tribological characteristics, including a lower friction coefficient of around 0.10 and wear rate of around $1x10^{-3}mm^3/Nm$ when tested with highest viscosity of Ringer's lactate of 1.52mPa.s. PLA's mechanical integrity and wear resistance were enhanced by the addition of PCU, increasing PLA's durability. Additionally, the addition of Ringer's lactate enhanced the polymer blend's tribological performance, indicating its compatibility with the natural joint environment. By shedding light on the tribological behaviour of PLA-PCU polymer blends 3D printed for artificial articular cartilage, this work paves the way for future developments in additive manufacturing and biomaterial design. The findings are a promising first step toward creating durable prosthetic joint implants that will enhance mobility and quality of life for individuals with joint disorders.

SIFAT TRIBOLOGI CETAKAN-3D CAMPURAN POLIMER ASID POLI(LAKTIK) - POLIKARBONAT URETENA BAGI APLIKASI RAWAN ARTIKULAR BUATAN

ABSTRAK

Untuk memahami dengan lebih baik perilaku tribologis campuran asid poli(lactik) (PLA)-polikarbonat uretena (PCU) untuk aplikasi tulang rawan artikular buatan, kajian ini menyelidiki komposisi campuran tersebut, yang terdiri daripada 90 wt.% PLA-10 wt.%PCU. Ketebalan lapisan 0.10, 0.12, 0.14, dan 0.16 mm digunakan semasa mencetak sampel. Semua sampel diuji dengan ujian tribo 'ball-on-disc' di mana beban 30, 50, dan 70 N digunakan. 'Ringer's lactate' berfungsi sebagai pelincir dan menselimulasikan persekitaran secara in vivo. Ujian kekerasan, sudut sentuh, kekasaran permukaan, dan analisis morfologi permukaan juga digunakan untuk menganalisis sampel yang dicetak 3D. Berdasarkan ujian ini, sampel yang dicetak 3D dengan ketebalan lapisan 0.16 mm menunjukkan prestasi yang lebih baik berbanding sampel lain, selanjutnya diuji dengan kelikatan 'Ringer's lactate' yang berbeza, tanpa mengira beban normal yang dikenakan semasa ujian tribo. Keputusan menunjukkan bahawa campuran polimer PLA-PCU sangat sesuai untuk aplikasi tulang rawan artikular buatan kerana ciri-ciri tribologisnya yang baik, termasuk pekali geseran sekitar 0.10 dan kadar haus sekitar $1x10^{-3}$ mm^3/Nm apabila diuji dengan kelikatan tertinggi Ringer's lactate iaitu 1.52 mPa.s. Integriti mekanikal dan ketahanan haus PLA ditingkatkan dengan penambahan PCU, meningkatkan ketahanan PLA. Selain itu, penambahan Ringer's lactate meningkatkan prestasi tribologis campuran polimer, menunjukkan keserasian dengan persekitaran sendi semula jadi. Dengan menjelaskan perilaku tribologis campuran polimer PLA-PCU yang dicetak 3D untuk tulang rawan artikular buatan, kajian ini membuka jalan untuk perkembangan masa depan dalam pembuatan tambahan dan reka bentuk biomaterial. Penemuan ini merupakan langkah pertama yang menjanjikan ke arah penciptaan implan sendi prostetik yang tahan lama yang akan meningkatkan mobiliti dan kualiti hidup bagi individu dengan gangguan sendi.

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LIST OF ABBREVIATIONS

100PLA	-	100 wt.% PLA
3D	-	Three dimension
3HH	-	3-hydroxyhexanoate
3HP	-	3-hydroxypropionate
3HV	-	3-hydroxyvalerate
4D	-	Four dimension
4HB	-	4-hydroxybutyrat
90PLA_10PCU	-	90 wt.% PLA-10 wt.% PCU
ABS	-	Acrylonitrile butadiene styrene
ACL	-	Anterior cruciate ligament
Al_2O_3	-	Aluminium oxide
AM	-	Additive manufacturing
ASTM	-	American Society for Testing and Materials
B-O-D	-	Ball-on-disc
CAD	-	Computer-aided design
CH3CHOHCOOH	-	Lactic acid
COF	-	Coefficient of friction
COVID-19	-	Coronavirus disease
CT	-	Computer tomography
DLP	-	Digital light processing
DMLS	-	Direct metal laser sintering
EBM	-	Electron beam melting
FDM	-	Fused-deposition manufacturing
FFF	-	Fused filament fabrication
FIDEC	-	Fibre and Biocomposition Centre

HA	-	Hydroxyapatite
HB	-	Hydroxybutyrate
ISO	-	International Organisation for Standardisation
LMD	-	Laser metal deposition
LOM	-	Laminated object manufacturing
Mg	-	Magnesium
MIT	-	Massachusetts Insitute or Technology
MJM	-	Multi-jet modelling
MoDTC	-	Molybdenum dialkyl dithiocarbamate
MoS_2		Molybdenum disulfide
MRI	-	Magnetic resonance imaging
MTIB	-	Malaysian Timber Industry Boards
OA	-	Osteoarthritis
PA	-	Polyamide
PC	-	Polycarbonate
PCU	-	Polycarbonate urethane
PDA	-	Poly(dopamine)
PDIH	-	Powder bed and ink-jet head 3D-printing
PET	-	Polyethylene terephthalate
PFRR	-	Polymers from renewable resources
PGA	-	Polyglycolic acid
PHA	-	Polyhydroxyalkanoate
PLA	-	Poly(lactic) acid
PLDA	-	Poly(D, L-lactic) acid
PLGA	-	Poly(lactic-co-glycolic) acid
PLLA	-	Poly(L-lactic) acid
PP	-	Polypropylene

PP	-	Plaster-based 3D-printing
PS	-	Polystyrene
SEM	-	Scanning electron microscope
SHS	-	Selective heat sintering
SLA	-	Sclerose laterale amyothrophique
SLM	-	Selective laser melting
SLS	-	Selective laser sintering
SPECT/CT	-	Single proton emisson computer tomography
UC	-	Ultraviolet consolidation
UHMWPE	-	Ultra high molecular weight polyethylene
USA	-	United States of America
UTeM	-	Universiti Teknikal Malaysia Melaka
UV	-	Ultraviolet

LIST OF SYMBOLS

°C	-	Degree celcius
%	-	Percentage
g	-	Gram
kg	-	Kilogram
kg/cm^2	-	Kilogram per square centimetre
ml	-	Mililitre
mm	-	Milimetre
N	-	Newton
pH	-	Potential hydrogren
Ra	-	Surface roughness
rpm	-	Revolutions per minute
wt.%	-	Weight percentage
λ_c	-	Lambda c

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LIST OF PUBLICATIONS

JOURNAL PAPER

Shaharudin S., Abdollah, M. F. Bin, Amiruddin, H., Liza, S., and Ramli, F. R.. 2023. Applied normal load and printing layer thickness relationship on the tribological properties of novel 3D-printed PLA-PCU polymer blend. *Jurnal Tribologi 39*, pp.1-16, https://jurnaltribologi.mytribos.org/v39.html.

CONFERENCE ATTENDED

Shaharuddin S., Abdollah, M. F. Bin, Amiruddin, H., Liza, S., and Ramli, F. R.. 2022. Effect of sliding load on the tribological properties of 3D-printed PLA-PCU polymeric composite manufactured using fused filament fabrication. *Proceedings of SAKURA Symposium on Surface Technology and Engineering Material 2022*, pp.20-22.

CHAPTER 1

INTRODUCTION

1.1 Background and motivation

Articular cartilage, the smooth flexible tissue that covers the ends of bones in human joints, is essential for the smooth and pain-free movement of human joints. Because of its unique composition and structure, it has low friction and wear resistance, allowing joints to withstand the enormous mechanical stresses of daily activities (Kanca et al., 2018a). However, articular cartilage injuries and degenerative diseases, such as osteoarthritis, can cause severe pain, reduced mobility, and a lower quality of life for those who suffer from them (Hudelmaier et al., 2001).

Traditional treatments for damaged articular cartilage, such as total joint replacement, are effective but have drawbacks such as a short lifespan, a high risk of complications, and high costs (Kluyskens et al., 2022). As a result, there is an increasing demand for the creation of synthetic articular cartilage materials that can imitate the mechanical and tribological characteristics of natural cartilage while also being more durable and affordable.

3D-printing has become known as a promising technology for manufacturing customized implants and prostheses, including artificial articular cartilage, in recent years (Ngo et al., 2018). Poly(lactic) acid (PLA) and polycarbonate urethane (PCU) have shown significant promise among the various materials available for 3D-printing due to their biocompatibility, mechanical properties, and ease of processing (Hamad et al.; Beckmann et al., 2018). Understanding the tribological behaviour of these 3D-printed PLA-PCU polymer blends, on the other hand, is critical for their successful use in artificial articular cartilage.

1.2 Problem statement

Poly(lactic) acid and its resulting composites have been extensively utilized in clinical applications, most notably for articular cartilage (DeStefano et al., 2020). This material is biocompatible, long-lasting, and wear-resistant. Due to lack of porosity, the existing formative manufacturing-created artificial cartilage implant is ineffective in preserving joint lubrication via the weeping mechanism. PLA has an enhanced elastic modulus than articular cartilage and is mechanically limited (Saini et al., 2016).

Given that its elastic modulus corresponds to that of articular cartilage, PCU is a promising candidate for artificial articular cartilage (Beckmann et al., 2016; Kanca et al., 2018). Because of its mechanical properties and biocompatibility, PCU is used in many implants, including orthopaedic prostheses (Beckmann et al., 2018) , and it has good wear and friction performance (Kanca et al., 2018a). Also, since different processing methods (such as extrusion and injection moulding) are frequently needed for different polymers. Securing a homogeneous mixture with the intended characteristics can present technological difficulties and financial inefficiencies. Hence, to ensure that PLA and PCU are distributed uniformly, extrusion can be utilized to thoroughly mix the two polymers. Extruders with twin screws work especially well for this.

Fused filament fabrication (FFF) is a form of AM, designed to minimize procedure time and steps. It is also cheaper, quicker, and simpler to apply than the other processes. Regardless, FFF samples have poor mechanical properties and rougher surfaces (Rouf et al., 2022). Although 3D printing technology is used to fabricate PCU-based products, due to the soft polymer properties, the manufacturing process demands the use of a high-end 3D printer with specific nozzles or techniques (Miller et al., 2017). A 3D-printed blend of PLA and other biodegradable and biocompatible polymers, such as PCU, may be able to address this issue.

As stand-alone substitutes for a natural articular cartilage implant, PLA and PCU are already excellent. However, the drawbacks of both materials could be compensated for by combining PLA with PCU to create an artificial articular cartilage material that is more dependable. Printing performance such as layer thickness, infill density, and printing temperature have been demonstrated in studies to influence tribology performance (Tanveer et al., 2022). The primary focus of the research is on how polymer blends with different layer thicknesses will affect the tribology properties with different applied normal load and the extent to which there will be an optimal printing parameter.

1.3 Research objectives

The main objectives of this thesis are to look into the tribological properties of 3D-printed PLA-PCU polymer blends as potential substitutes for artificial articular cartilage. The research specifically seeks to:

i. To analyse the synergistic effect of applied normal load during tribo-test and printed layer thickness on the tribological behaviour of 3D-printed PLA-PCU polymer blend.

ii. To analyse the tribological behaviour of 3D-printed PLA-PCU polymer blend with different Ringer's lactate viscosities.

1.4 Research scope

Scope of this research emphasises on:

i. PLA and PCU polymer blend; developed using fused filament fabrication; 3D printing and compression moulding;

ii. Ball-on-disc tribometer test as per ASTM G99 is performed under lactated Ringer's condition with applied normal load of 30, 50 and 70N;

iii. Additional testing like hardness, contact angle, surface roughness and surface morphology analysis also conducted.

1.5 Thesis Organization

This thesis is divided into eight chapters, each with a distinct role in the research process.

i. Chapter 1: Introduction - The introduction describes the study's problem, objectives, and importance of the study. It sets the tone for the following chapters by offering background knowledge and context.
ii. Chapter 2: Literature Review - The literature review analyses current study on the topic. It includes relevant theories, models, and results from experiments that guide and reinforce the current research.
iii. Chapter 3: Materials and Methodology - This chapter describes the research planning and techniques used in the research. It describes the data accumulation methods, instruments, and analysis techniques used to answer the research questions.
iv. Chapter 4: Results and Discussions - The results chapter unveils the study's findings. It consists of analysing and interpreting data, with a focus on the most significant findings and patterns.
v. Chapter 5: Conclusion and Recommendations - The discussion places the findings in the light of the objectives of the study. It investigates the consequences of the findings, discusses limitations, and suggests future research directions. Also in this chapter, the study is summed up, highlighting its importance and possible consequences. It also makes recommendations based on research findings.
vi. Chapter 6: References - This chapter lists all of the sources used in the thesis to ensures proper acknowledgement of the works cited throughout the study.
vii. Chapter 7: Appendices - The appendices contain additional resources such as unprocessed responses to surveys, and comprehensive methodological descriptions. These additional documents supplement the main text and offer additional insights.