CHARACTERISATION AND PROCESSING OF PLA/PEG/CURCUMIN MICROFIBER DRAWN VIA MELT SPINNING METHOD

BY

NUR ATIQAH BT MOHD AKHIR

A thesis submitted in fulfilment of the requirement for the degree of Master of Science (Materials Engineering)

Kulliyyah of Engineering
International Islamic University Malaysia

JANUARY 2022

ABSTRACT

Poly (lactic acid) (PLA) has been recognized as an excellent candidate to be used as bioplastic and biomaterial due to its biodegradability and biocompatibility with excellent tensile strength. However, PLA has inherent brittleness and has low percentage of elongation at break that may limit its suitability to be used for specific geometrical shape such as fibers for biomedical application. The addition of plasticizer to improve brittleness also results with decrease in strength. Hence, particulates are often added as reinforcement filler. The main objective of this research is to characterize the properties of various PLA/PEG and PLA/PEG/cur blends and investigate the resultant properties of the melt spun microfiber. This research has two main stages. The first stage involved in investigating the effect of polyethylene glycol (PEG) additions into PLA with increments of 5 wt. % up to 30 wt. % to improve the brittleness of PLA. These compositions were then prepared via two blending methods i.e. solvent cast and melt blend. These PLA/PEG blends were structurally and thermally characterized using Fourier-transform infrared spectroscopy (FTIR), differential scanning calorimeter (DSC) and thermogravimetric analysis (TGA). Results from the studies showed that as the incorporation of PEG (wt. %) into PLA increases, the IR spectra for O-H band stretching became broader and sharper proposing that hydrogen bonding interaction between the network chains of PEG and PLA. DSC thermograms showed that the incorporations of PEG (wt.%) into PLA blends led to significant decrease in the glass transition temperature (T_g) and the crystallization temperature (T_c). TGA thermograms indicated that the initial degradation temperature for all the PLA/PEG composition shifted systematically to lower temperature with further additions of PEG (wt.%). All PLA/PEG blends were then successfully drawn via an in-house built fiber drawing tower with diameter ranging from 15µm to 112µm. These fibers were further characterized using optical microscope (OM) and scanning electron microscopy (SEM). The images obtained showed that the surface of the PLA/PEG microfibers were bead-free and had uniformly circular cross-sections. The surface of the fiber transitioned from smooth to slightly rough with increasing PEG content (wt.%) regardless of the blending method postulated due to thermally induced phase separation of PLA and PEG. It was noted that PLA/PEG microfiber prepared via melt blending were more brittle and fractured easily. Thus, only fibers obtained from solvent cast PLA/PEG blends were further tested for single fiber tensile test (SFTT). The SFTT results revealed that adding PEG up to 25 wt.% resulted with microfibers having fair strength, modulus, and elongation properties, thus was selected to be added with curcumin particulates. In the second stage of the study, PLA/PEG/cur blends were thermally and structurally characterized using DSC, TGA, and FTIR. The incorporation of curcumin into the PLA/PEG blends resulted with noticeable shift in peaks for O-H stretching vibration. Thermal studies showed that the incorporation of curcumin (wt. %) into PLA/PEG blends did not affect the T_g and the final degradation temperature. SFTT for PLA/PEG/curcumin microfibers further curcumin loadings beyond 1wt.% had resulted with decreasing strength, Young's modulus and elongation (%) possibly due to particulate agglomeration and inhomogeneous dispersion in the polymer matrix. PLA/PEG/cur microfibers were successfully drawn using an in-house-built fiber drawing tower with average diameters of 31µm to 36µm. The OM images showed bead-free and, uniformly circular in cross section microfibers.

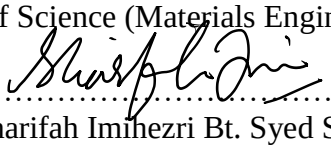
خلاصة البحث

يعد بولي-حمض اللاكتيك (PLA) عنصرًا متميزًا حيث يمكن استخدامه بوصفه بلاستيكًا ومواد حيوية نظرًا لقابليته للتحلل البيولوجي والتوافق الحيوي مع قوته الممتازة الشدية. وعلى الرغم من ذلك، فإن PLA لها هشاشة طبيعية وله نسبة منخفضة من الاستطالة عند الكسر مما قد يحد من ملاءمته للاستعمال في شكل هندسي محدد، من مثل: الألواح الرقيقة والألياف للتطبيق الطبي الأحيائي. وتسبّب إضافة الملدّنات لتحسين سرعة الانكسار في انخفاض القوة، وغالبًا ما تضاف فيه الجسيمات بصفتها أداة من أدوات الحشو والتعزيز. ويهدف هذا البحث خاصة إلى توصيف خصائص امتزاج PEG / PLA و cur / PEG / PLA ودراسة الخصائص الناتجة من الألياف الدقيقة الذائبة. وقد أجري هذا البحث بمرحلتين رئيستين. ففي المرحلة الأولى، يحاول هذا البحث الكشف عن تأثير إضافة الجلايكول متعدد الإثلين (PEG) في PLA بزيادات قدرها 5% بالوزن إلى أن تصل 30% بالوزن لتحسين هشاشة PLA. وتجهّز هذه التركيبات لاحقًا من خلال طريقتين للامتزاج، أولًا: صب المحلول في صبغة خاصة حتى يتبخر (Solvent cast)، وثانيًا: تسخين تركيبات PLA/PEG في خلاطة خاصة حتى تذوب (Melt blend). فهذه الخلطات التي تتكون منها PLA/PEG كانت تُصنَّف هيكليًا وحراريًا باستخدام مطياف فوريه المتحولة بالأشعة تحت الحمراء (FTIR)، ومسعر المسح التفاضلي (DSC)، والتحليل الحراري الوزني (TGA). وتوصلت الدراسة إلى أنه كلما يزداد دمج PEG مع PLA، أصبحت أطياف الأشعة تحت الحمراء لتمدد نطاق O-H أكثر سعة وحدة، وبالتالي، يشير إلى تفاعل ارتباط الهيدروجين بين سلاسل الشبكة لـ PEG وPLA. وأظهرت عمليات تصوير DSC الحرارية أن إدماج PEG (بالوزن%) في خلائط PLA أدى إلى انخفاض كبير في درجة حرارة التحول الزجاجي (Tg) ودرجة حرارة التبلور (Tc). وقد دلت مخططات TGA الحرارية على أن درجة الحرارة للانخفاض المبدئي لكل تركيبات PLA/PEG تحوّلت بانتظام إلى درجة حرارة أقل انخفاضًا مع زيادات أخرى لـ PEG (بالوزن%). وقد تم إعداد وإنشاء جميع خلائط PLA/PEG بنجاح عبر البرج الذي يُبنى خاصة لإنتاج الألياف بقطر يتراوح من 15 مايكروميتر إلى 112 مايكروميتر لتركيبات PLA/PEG المسخنة المختلطة. وتُصنّف هذه الألياف لاحقًا باستعمال المجهر الضوئي (OM) ومجهرية المسح الإلكتروني (SEM). وأشارت الصور التي حصلت عليها الدراسة الحالية إلى أن الألياف الصغرية

لــ PLA/PEG كانت واضحة وخالية من أية خرزة ولها مقاطع عرضية بنمط موحد. وينتقل سطح الألياف من أملس إلى أخشن بنسبة طفيفة مع زيادة مضمون PEG (بالوزن%) بصرف النظر عن طريقة الامتزاج بسبب انفصال المرحلة المستحث حراريًا لــ PLA/PEG. والجدير بالذكر أن الألياف التي تم الحصول عليها من تركيبات PLA/PEG المسخنة المختلطة أو Melt blend أكثر تشتتًا وتكسرًا بسهولة. ولذلك، لقد تم فقط اختبار الألياف المستمدة من خلائط PLA/PEG المصبوبة المتبخرة Solvent castمستعينًا باختبار الشد لألياف فردية أو ما يسمى بــ (SFTT). وأكدت نتائج لاختبار SFTT على أن إضافة PEG بقدر يصل إلى 25% بالوزن أدت إلى أن تصبح الألياف الصغرية عناصر ذات قوة معتدلة، وتصبح مُعاملًا وخاصية من خصائص الاستطالة، وبالتالي، تم إضافتها مع جسيمات الكركمين cur. وفي المرحلة الثانية من الدراسة، تم تمييز خلطات PLA/PEG/cur حراريًا وتركيبيًا من خلال هذه الأدوات الثلاث المذكورة سابقًا: DSC، وTGA، وFTIR. ويؤدي امتزاج الكركمين في خلائط PLA/PEG إلى حدوث تحوُّل ملحوظ في نسبته العالية لاهتزاز التمدد O-H. وأشارت مخططات DSC الحرارية إلى أن عملية إدماج الكركمين (بالوزن%) مع خلائط PLA/PEG/cur ليس لها تأثير على T_g ودرجة الحرارة للتحلل النهائية. كما كشف اختبار SFTT للألياف الصغرية PLA/PEG/cur عن أن إضافة الكركمين أكثر من 1% بالوزن قد سبب في انخفاض القوة، وكذا انخفاض المعامل والاستطالة عند يونغ (Young)؛ ويعود ذلك إلى تكتُّل الجسيمات والتشتُّت غير المتجانس في مصفوفة البوليمر. وقد أُنتجت الألياف الصغرية PLA/PEG/cur بنجاح مستعينة ببرج يُصمَّم خاصة لإنتاج الألياف بأقطار متوسطة تتراوح ما بين 31 مايكروميتر إلى 36 مايكروميتر. وأشارت الصور التي تم الحصول عليها بالمجهر الضوئي OM إلى خلو العينات من الخرز وأن شكلها دائري بنمط موحد في المقاطع العرضية للألياف الصغرية.

APPROVAL PAGE

I certify that I have supervised and read this study and that in my opinion, it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science (Materials Engineering).



…….
Sharifah Imihezri Bt. Syed Shaharuddin
Supervisor

……
Yose Fachmi Buys
Co-Supervisor

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a thesis for the degree of Master of Science (Materials Engineering).

…….
Dzun Noraini Jimat
Internal Examiner

…….
Mariatti Jaafar @ Mustapha
External Examiner

This thesis was submitted to the Department of Manufacturing and Materials Engineering and is accepted as a fulfilment of the requirement for the degree of Master of Science (Materials Engineering).

……
Ahmad Zahirani Bin Ahmad Azhar
Head, Department of Manufacturing and Materials Engineering

This thesis was submitted to the Kulliyyah of Engineering and is accepted as a fulfilment of the requirement for the degree of Master of Science (Materials Engineering).

……
Sany Izan Ihsan
Dean, Kulliyyah of Engineering

DECLARATION

I hereby declare that this thesis is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at IIUM or other institutions.

Nur Atiqah Binti Mohd Akhir

Signature ..... Date .....

INTERNATIONAL ISLAMIC UNIVERSITY MALAYSIA

DECLARATION OF COPYRIGHT AND AFFIRMATION OF FAIR USE OF UNPUBLISHED RESEARCH

CHARACTERISATION AND PROCESSING OF PLA/PEG/CURCUMIN MICROFIBER DRAWN VIA MELT SPINNING METHOD

I declare that the copyright holders of this thesis are jointly owned by the student and IIUM.

By signing this form, I acknowledged that I have read and understand the IIUM Intellectual Property Right and Commercialization policy.

Affirmed by Nur Atiqah Bt Mohd Akhir

……..…….. ……..
Signature Date

ACKNOWLEDGEMENTS

In the name of Allah, the Most Gracious, Most Merciful, Praise Almighty for the blessed and peace upon Prophet Muhammad S.A.W.

Alhamdulillah, I had completed my thesis for Master of Science (Manufacturing Engineering). First and foremost, I would like to express my highly gratitude towards Allah S.W.T who gives me great mind and amazing health to accomplish my research for Master degree. The completion of the task gives me a great feeling of achievement and pleasure.

I would like to express my sincere gratitude to my supervisor, Dr. Sharifah Imihezri Binti Syed Shaharuddin, for giving valuable guides by sharing useful knowledge regarding this project and determined support in completing this project. Second, I would like to thank the lab assistance of Department of MME, IIUM for assisting me through the completion of the project. I am also thankful that this project was being carried out easily with the financial assistance, equipment and work spaces provided by the Kuliyyah Engineering.

My sincere gratitude is also to all.my family members; My Suami Dunia Akhirat, Mama & Abah, Shafira the BFF, Kakak & Abang Nas, Angah, Ome & Kak fyra for giving me tremendous support till the very end of my project. To my daughter Hani Imani, thank you for being there in my master journey from the day I know you are existing till you are born in this world, mommy loves you. Last but not least, this acknowledgement goes to, COG for their moral and emotional support that ensure the realization and success of this project.

Thank You

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials
CaP	calcium phosphate
CoCrMo	cobalt-chromium-molybdenum
C=O	compound containing carbonyl group
C-O-C	compound containing ether group compound
CH_3	compound containing methyl group
C-H	compound containing alkane group
C-O	compound containing oxygen group
DSC	differential scanning calorimetry
et al.	(et alia): and others
FTIR	fourier-transform infrared spectroscopy
FDA	food and drug association
i.e	(id est): that is
IPN	interpenetrating polymer networks
LDPE	low density polyethylene
Mg	Magnesium
NiTi	nickel titanium
OM	optical microscope
O-H	compound containing hydroxyl group
PLA	polylactic acid
PEG	polyethylene Glycol
PE	Polyethylene

PP	Polypropylene
PLGA	copoly(lactic–glycolic acid)
PEO	polyethylene oxide
PS	Polystyrene
PET	polyethylene terephthalate
PCL	Polycaprolactam
PVA	polyvinyl alcohol
PBS	poly (butylene succinate)
PMMA	poly(methyl methacrylate)
pH	potential of hydrogen
SEM	scanning electron microscope
SFTT	single fiber tensile testing
TGA	thermogravimetric analyzer
Ti	Titanium
TPU	thermoplastic polyurethane
Ta	tantalum-tungsten
WPLA	weight percent of PLA
X_c	percentage of crystallinity
Y-TZP	Yttria-stabilized tetragonal zirconia polycrystal
ΔH_m	melting enthalpy
ΔH_c	crystallization enthalpy
ΔH_0	enthalpy compound
T_i	initial degradation temperature
T_f	final degradation temperature

T_g	glass transition temperature
T_c	crystallization temperature
T_m	melting temperature

LIST OF SYMBOLS

µM	microMolarity
±	plus minus
%	percentage
°	degree
°C	degree celsius
°C/min	degree celsius per min
cm^{-1}	reciprocal centimeters
g/day	gram per day
g/mol	gram per mol
kN	kilonewton
kV	kilovoltan
Mpa	megapascal
ml	mm
mg	milligram
mL/min	mililiter per min
mm/min	millimeter per minute
mm	milimeter
N	newton
Pa	pascal
rpm	revolutions per minute
wt. %	weight percent

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND OF THE STUDY

Polylactic acid (PLA) has outstanding properties such as biodegradability and biocompatibility (Hossain et al., 2014) due to its aliphatic polyester structure that represents an important family of biodegradable polymers (Baiardo et al., 2003). This makes PLA promising biodegradable polymers for biomedical applications (Hossain et al., 2014). PLA can be absorbed by the body and has been studied due to its potential roles in drug delivery systems (Gupta & Kumar, 2007; Lou et al., 2008; Ramakrishna et al., 2001).

Despite its many advantages, PLA also has several drawbacks. The brittle nature of PLA restricts the material's potential applications (K Sungsanit et al., 2012). Other drawbacks of PLA include uncontrollable hydrolysis rate, poor hydrophilicity and, crystallinity. This limitation of PLA leads to the idea to improve the low toughness by incorporating PLA with a plasticizer. Plasticizers are widely used in the plastics industry to improve the processability, flexibility, and ductility of glassy polymers like PLA (Baiardo et al., 2003).

Polyethylene glycol (PEG) is one of the efficient plasticizers used for polymers since it offers a broad range of molecular weights. PEG is reported to be nontoxic and biodegradable (Li et al., 2018). The addition of polyethylene glycol (PEG) as a plasticizing agent, into PLA, has also been reported to lead to overall increased flexibility and ductility of the blend (Busolo et al., 2009) which increases its processability into the finished product.

Curcuma longa (turmeric), has received considerable attention due to its multiple biological and pharmaceutical activities (Jayaprakasha et al., 2005; Priyadarsini, 2013). Curcumin is located in the rhizomes of turmeric has pharmacological effect such as anti-inflammation, anti-oxidant, anti-microbial and, anti-cancer activities (Thong et al., 2014). Curcumin is non-toxic and has been classified as safe by the National Cancer Institute (Leu & Maa, 2002). Schneider et al. (2015) reported that investigation towards the therapeutic potential of curcumin (diferuloylmethane) on wound healing has increased over past years. Bava et al. (2005) study on curcumin revealed that curcumin can demonstrate good anti-cancer activity and non-toxic effect on normal cells even with a high concentration of up to 50 µM. Despite the excellent pharmacological properties, curcumin application as wound healing is limited due to its hydrophobic property in nature (Perumal et al., 2017). However, there is a novel approach to overcome this problem, Greiner & Wendorff (2007) proposed the blending of curcumin with biodegradable polymer in the form of fiber.

PLA can be processed into nanofiber and microfiber using the electro-spun method (Chen et al., 2010; Busolo et al., 2009) and melt-spun method (Yuan et al., 2001; Padee et al., 2013). The process of fabricating nano fibers from PLA/PEG blends has been studied by Lee et al. (2013) and Javadian et al. (2012) using PLA/PEG electro-spun method resulting in small-scale production. In comparison to the electro-spun method, the melt-spun technique allows for the mass production of PLA/PEG microfibers at a low production cost.

The material combination PLA/PEG has been studied and reported based on their thermal (Wang et al., 2018), structural (Li et al., 2018) and tensile via solvent

casting (Septevani & Bhakri, 2017) and melt blend (Hashim et al., 2015). PLA/PEG nanofibers has been produced via electrospinning (Nazari & Garmabi, 2018). However, it was observed that studies that compares the resulting thermal properties and the obtained melt spun fiber prepared using both solvent cast and melt spun method has not been documented in literature. The effect of curcumin additions into PLA/PEG blends has been characterized (thermal and tensile) and produced via electrospinning approach resulting with PLA/PEG/cur nanofibers (Yakub et al., 2014). It is to the author's knowledge that studies on manufacturing of PLA/PEG/cur via melt spun approach and the structural and tensile evaluation of the obtained microfiber has not been reported in literature.

1.2 STATEMENT OF THE PROBLEM

Poly (lactic acid) (PLA) has been recognized as an excellent candidate to be developed as the future bioplastic and biomaterial due to its biodegradability and biocompatibility with excellent tensile strength. However, PLA has inherent brittleness and has low percentage of elongation at break that may limit its suitability to be used for specific geometrical shape such as fiber for biomedical application. Thus, to improve these lacking properties of PLA, plasticizer such as PEG was added incrementally. Hypothetically, the blending method used in polymer blend preparation may also affect the quality of the resultant fiber.

Production of polymeric fiber via melt spinning has been a challenge as the processing temperature is near the polymer's melting temperature and affects the stability of continuous fiber production. For instance, if the processing temperature is too low (hence high viscosity), this will induce melt fracture, non-uniform flow and hampers the processability into fiber. The melt spinning process offers simple, low cost

and mass production of fibers and is commonly used to produce polyamides, polyesters and polyolefins fibers. In comparison, the production of PLA based microfibers using this technique has not been systematically explored in prior literature studies. The addition of particulate filler such as curcumin which function as reinforcement or to impart certain properties is highly desirable. However, filler additions in the polymer blend pose a challenge in the fiber production phase as it decreases the ease of spinnability into continuous fiber due to particulate agglomeration and inhomogeneous distribution.

1.3 RESEARCH OBJECTIVES

The main objective of this research is to characterise the properties of various PLA/PEG and PLA/PEG/cur blends and investigate the resultant properties of the melt spun microfiber. In order to achieve this key objective, there are some explicit objectives that need to be addressed as follows:

1. To identify the effect of PEG additions on the thermal and structural properties of PLA/PEG compositions blended using solvent cast and melt blend method.
2. To investigate the effect of PEG additions and blending method used on the tensile properties of the resultant melt spun PLA/PEG fiber.
3. To identify the effect of curcumin additions on the thermal and structural properties of the PLA/PEG/cur blends.
4. To investigate the effect of curcumin additions on the tensile properties of the resultant melt spun PLA/PEG fiber