UNIVERSITI PUTRA MALAYSIA

EFFECTS OF ANNEALING TEMPERATURE AND TIME ON PROPERTIES OF COMPOSITES BASED ON POLY(LACTIC ACID), MICROCRYSTALLINE CELLULOSE AND KENAF FIBER

AMIR ALIZADEHMONIR

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By

AMIR ALIZADEHMONIR

Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fulfilment of Requirements for the Degree of Master of Science

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To my beloved wife, daughter,

And my sweetie twin,

My family members and friends.

Thanks for your encouragement, patience and loving support.

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the Degree Master of Science.

EFFECTS OF ANNEALING TEMPERATURE AND TIME ON PROPERTIES OF COMPOSITES BASED ON POLY(LACTIC ACID), MICROCRYSTALLINE CELLULOSE AND KENAF FIBER

By

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January 2018

Chair: Associate Professor Dr. Rosnita A. Talib, PhD

Faculty: Engineering

The aim of this study was to produce PLA composites having a range of HDT above 130 °C. This was achieved by investigating the effect of heating rate, annealing conditions (temperature and time) and an addition of natural fillers namely microcrystalline cellulose (MCC) and kenaf fiber (KF) on the crystallinity and HDT of PLA. The ratio of PLA:filler was fixed to 70:30 (%w/w). The PLA/KF composites were melt-processed using a counter rotating twin screw extruder, whilst the PLA/MCC composites were produced using an internal mixer. Test specimens of PLA and PLA composites were compression moulded by a hot press machine. Differential scanning calorimetry (DSC) analysis of PLA sheet showed a marked crystallisation effect subjected to various heating rates as compared to that of as-received PLA resin. A heating rate of 10 °C/min had shown an intense crystallisation in the PLA sheet with a larger crystallisation peak and a double crystallisation melting peak. Crystallisation of PLA sheets was depended by both the annealing temperature and time, as observed in XRD patterns. A more intense and occurrence of multiple crystalline phases were achieved in the PLA sheets at a higher temperature and time.

XRD was also used to calculate %crystallinity content, crystal phase and crystal size. POM-HS micrographs were utilized to provide evidence of crystallisation in the PLA and its composites. Annealed PLA composites were selected for HDT test and compared with their crystallinity. Annealed PLA/30%KF composite at 90 °C for 60 minutes was shown to have a higher HDT than PLA and PLA/30%MCC composites. By increasing annealing time, HDT decreased

because extending time caused to create lots of petty crystals. The highest HDT of annealed PLA was obtained after heated at 110 °C for 60 minutes (71.2 °C). The maximum %crystallinity was attained in PLA/30%MCC annealed at 90 °C for 30 minutes (79.66%). The PLA/30%KF composite annealed at 110 °C for 60 minutes had the smallest crystallite size among all PLA composites and the maximum %crystallinity reached when PLA/30%KF annealed at 90 °C for 60 minutes (70.65%), demonstrating the highest HDT of 147.9 °C.

This result shows that the presence of MCC and KF as a filler in PLA composites provides better HDT values than annealed neat PLA. The KF was shown to have a better nucleating ability than MCC based on the XRD and polarised optical microscopy studies. As a conclusion, sufficient annealing temperature and time, as well as effective filler, play the significant role in enhancing the crystallinity and HDT values in this study.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia Sebagai memenuhi keperluan untuk Ijazah Master Sains

KESAN-KESAN SUHU DAN MASA PENYEPUHLINDAPAN KE ATAS SIFAT-SIFAT KOMPOSIT BERASASKAN POLI(ASID LAKTIK), MIKROKRISTAL SELULOSA DAN GENTIAN KENAF

Oleh

Amir AlizadehMonir

January 2018

Pengerusi: Profesor Madya Dr. Rosnita A. Talib, PhD
Fakulti: Kejuruteraan

Tujuan kajian ini adalah untuk menghasilkan komposit PLA mempunyai satu julat HDT atas 130 °C. Ini telah dicapai dengan menyiasat kesan pemanasan, keadaan annealing/penyepuhlindapan (suhu dan masa), penambahan pengisi asli seperti mikrokristal sellulose (MCC) dan gentian kenaf (KF) terhadap kristaliniti dan HDT bagi PLA. Nisbah bagi PLA:pengisis telah ditetapkan kepada 70:30 (%w/w). Komposit PLA/KF telah diproses-cair menggunakan satu penyemperit berlawanan berputar skru berkembar, mamakala komposit PLA/MCC telah dihasilkan menggunakan satu pemutar dalaman. Specimen ujian PLA dan kompositnya telah diacu mampatan oleh satu mesin mampatan panas. Analisis kalorimetri pengimbasan pembezaan (DSC) bagi kepingan PLA menunjukkan kesan penghabluran yang ketara dikenakan kadar pemanasan yang pelbagai berbanding kepada PLA resin seperti yang diterima. Satu kadar pemanasan 10 °C/min telah menunjukkan satu penghabluran yang tinggi dalam kepingan PLA dengan puncak penghaburan yang lebih besar dan satu puncak penghabluran pencairan berkembar. Penghabluran bagi kepingan PLA adalah bergantung oleh kedua-dua suhu dan masa penyepuhlindapan, seperti yang dilihat dalam corak XRD. Satu kehadiran fasa multiple kristal yang lebih ketara telah dicapai dalam kepingan PLA pada suhu dan masa yang lebih tinggi.

XRD telah digunakan untuk mengira kandungan kristaliniti (%), fasa kristal dan saiz kristal. Mikrograf POM-HS telah digunakan untuk memberikan bukti bagi penghabluran dalam PLA dan kompositnya. Penyepuhlindap komposit PLA/30%KF pada 90 °C untuk 90 minit telah menunjukkan mempunyai satu HDT yang lebih tinggi dari PLA dan komposit PLA/30%MCC. Dengan meningkatkan masa penyepuhlindapan, HDP telah menurun disebabkan melanjutkan masa telah menyebabkan terhasil krital kecil yang banyak. HDT yang tertinggi bagi PLA. %kristaliniti maksima dimiliki dalam PLA/30%MCC penyepuhlindap pada 90 °C untuk 30 minit (79.66%). Komposit

PLA/30%KF penyepuhlindap pada 110 °C untuk 60 minit mempunyai saiz krital terkecil di antara komposit PLA dan maksima %kristaliniti dicapai apabila PLA/30%KF penyepuhlindap pada 90 °C untuk 60 minit (70.65%), menunjukkan HDT tertinggi pada 147.9 °C.

Keputusan ini menunjukkan bahawa penambahan MCC dan KF sebagai satu pengisi dalam komposit PLA memberikan HDT lebih tinggi dari penyepuhlindap PLA. KF telah menunjukkan mempunyai keboleupayaan penukleusan yang lebih baik dari MCC berdasarkan kepada XRD dan kajian mikroscopi terpolarisi optikal. Sebagai kesimpulan, suhu dan masa penyepuhlindapan mencukupi, termasuk pengisi yang efektif, memainkan peranan penting dalam meningkatkan kristaliniti dan nilai HDT dalam kajian ini.

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I certify that a Thesis Examination Committee has met on 30 January 2018 to conduct the final examination of Amir AlizadehMonir on his thesis entitled ("EFFECTS OF ANNEALING TEMPERATURE AND TIME ON PROPERTIES OF COMPOSITES BASED ON POLY(LACTIC ACID), MICROCRYSTALLINE CELLULOSE AND KENAF FIBER") in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student be awarded the Master of Science degree).

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ASTM	American Society of Testing and Materials
DMA	Dynamic Mechanical Analysis
DP	Degree of Polymerization
DSC	Differential scanning calorimetry
ESEM	Environmental Scanning Electron Microscope
FTIR	Fourier Transform Infrared
HDPE	High Density Polyethylene
HDT	Heat Deflection Temperature
INTROP	Institute of Tropical Forestry and Forest Product
J	Joule
KBF	Kenaf Bast Fibre
LDPE	Low Density Polyethylene
LLDPE	Linear Low Density Polyethylene
MCC	Microcrystalline Cellulose
MFC	Microfibrillated Cellulose
MNKTB	Malaysian National Kenaf & Tobacco Board
MPa	Mega Pascal
PE	Polyethylene
PEG	Poly(ethylene glycol)
PET	Polyethylene terphthalate
PHB	Poly(hydroxyl butyrate)
PHBV	Polyhydroxybutyrate valerate
PLA	Polylactic acid
PP	Polypropylene
p-PLA	Plasticized Poly(lactic) Acid
PS	Polystyrene
PVC	polyvinyl carbonate
RHP	Rice Husk Powder
SBP	Sugar Beet Pulp
SEM	Scanning Electron Microscope
Tan δ	Tangent Delta

T_g	Glass Transition Temperature
T_m	Melting Temperature
TGA	Thermogravimetric Analysis
vol%	Volume Fraction
WF	Wood Flour
WP	Wood Pulp
wt%	Weight Fraction
α-cellulose	Alpha-Cellulose
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Research overview and Problem Statements

Bio-based thermoplastic poly(lactic acid) plastics, also known as PLA, offers an attractive alternative than traditional petroleum-based plastics due to its excellent mechanical and barrier properties as well as it's thermoformability and potential renewability. Despite many advantages of biodegradable thermoplastic PLA such as high tensile strength and modulus; its poor impact strength and elongation at break and also low heat distortion temperature (HDT) of around 55 to 60 °C has limited the practical applications of PLA in food packaging. For example, in the case of hot filling product operation, which typically involves product filling at an elevated temperature ranging from 80 to 90 °C, whereas for hot beverage service temperature product heat resistance may be above 130 °C. PLA can be moulded into disposable dishware and automotive components by melt processing technologies such as thermoforming and injection moulding. However, as moulded PLA products or parts usually are low of crystallinity due to a very slow crystallisation of PLA at a high cooling rate (Liu and Zhang, 2011). The low crystallinity of moulded product will not provide sufficient stiffness for it to be removed from the cold moulds without being distorted.

It is generally known that increasing crystallinity of PLA can enhance its heat resistance and mechanical performance (Shi, et al., 2017). Hence, in the current study, firstly, the crystallinity in the PLA resin was investigated by varying the heating rate during DSC heating scan that may accelerate the crystallisation in PLA resin and hot-pressed moulded PLA sheet. It is also known that crystallisation in melt-processed PLA polymer can emerge during DSC heating scan. Then, the PLA and PLA composites exposed to heat treatment, i.e. annealing to determine how much their crystallinity can be further enhanced. The annealing can be defined as a secondary process where the PLA composites were heated to a certain temperature (75, 90 and 110 °C were chosen in the current study), held for a specified time (10, 30 and 60 min, respectively) and then cooled to room temperature. The annealing of a polymer can change the crystal phase, the degree of crystallinity, the size and orientation of the crystallites, structural morphology, and a number of the chains between the crystallites (Hobbs and Pratt, 1975).

Subsequently, two type of naturally occurring fillers namely, micro crystalline cellulose (MCC) and kenaf fiber (KF) were utilized as nucleating agents for achieving significant improvements of crystallinity and HDT in PLA bio-composites. It has been reported that an addition of fillers into PLA has shown remarkable improvements of crystallinity and HDT of bio-composites (Li et al., 2015; Wootthikanokkhan et al., 2013; Mathew et al., 2006).

The primary reasons for choosing MCC and KF in the current study is that these materials are natural and renewable resources, safe, stable and physiologically inert. Incorporation of these fillers into the biopolymer PLA will produce completely biodegradable and environmentally friendly bio-composites.

Thus, it is hypothesised that a wide range of high HDT, above 130 °C can be achieved by incorporating MCC and KF, respectively, as the nucleating agents in the PLA composites coupled with applying sufficient annealing temperature and time to obtain high crystalline bio-composites.

1.2 Research Aim and Objectives

Thus, the aim of this study is to enhance the HDT of PLA bio-composites above 130 °C by increasing their crystallinity to widen their potential applications in hot filling and service temperature packaging products of foods and beverages.

To accomplish the aim of this study, two research objectives have been set as follows:

1. To investigate the effect of heating rate on thermal properties of the as-received PLA resin and PLA sheets
2. To compare the effects of annealing temperature and time on the thermal properties, crystalline structure and HDT of PLA sheets and PLA bio-composites
3. To evaluate the effects of adding different fillers on the thermal properties, crystalline structure and HDT of PLA sheets and PLA bio-composites

1.3 Outline of the Thesis

This thesis comprises five chapters. Chapter 1 introduces a research overview, problem statements, hypothesis, and a set of objectives to achieve the aim of this research. A literature review of PLA, PLA composites, cellulose, annealing, crystallinity, differential scanning calorimetry (DSC), x-ray diffraction (XRD) and heat deflection temperature (HDT) is elaborated in Chapter 2. Chapter 3 explains in details of materials and methods used in this research work. Chapter 4 presents the results and discussion in PLA resin and PLA composites experiments to investigate the effect of various heating rate, annealing condition and natural fillers on the crystallisation and HDT properties. Finally, Chapter 5 draws the conclusions of this research work and suggests several recommendations for future work.

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