



UNIVERSITI PUTRA MALAYSIA

***PREPARATION AND CHARACTERIZATION OF
POLYLACTIDE/POLYCAPROLACTONE/FATTY HYDRAZIDE
AND OCTADECYLAMINE-MODIFIED CLAY NANOCOMPOSITE***

SITI ZULAIHA BINTI HAIRALDIN

FS 2012 61

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By

SITI ZULAIHA BINTI HAIRALDIN

**This Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in
fulfilment of the Requirement for degree of Master of Science**

December 2012

This thesis is especially dedicated to:

*My mother Saadiah Brahim, My father Hairaldin Senawi, and
My siblings, who are infinitely precious to me,*

&

*My husband Shaiful Amri Mohd Som,
My daughter Nuradryana Amani, who has filled my life with joy and
happiness,*

&

My friends, who were there for me

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science

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December 2012

Chairman : Nor Azowa Ibrahim, PhD

Faculty : Science

In this study, two organically modified montmorillonite (OMMT) clay were prepared via ion exchange reaction. One was fatty hydrazides synthesized from palm oil functions was use to modify the nature of montmorillonite (Na-MMT). The other was ODA which is obtained from the industry. FH-MMT and ODA-MMT organoclay were successfully prepared by intercalation of the alkylammonium chains into the gallery of MMT via ion exchanged reaction. The basal spacing of FH-MMT and ODA-MMT has increased from the original Na-MMT of 11.62Å to 13.10 Å 29.90 Å respectively. The shifting of the basal peak position indicates successfully intercalation of alkylammonium ion into the modified clay. Fourier Transform Infrared (FTIR) spectra of the FH-MMT and ODA-MMT organoclay indicated that the presence of alkylammonium ion group resulting from modification reaction.

The 90/10 of PLA/PCL ratio nanocomposites was chosen to produce PLA/PCL nanocomposite in the internal mixer. This was chosen due to the highest tensile strength among PLA/PCL blends besides severe loss in elongation at break. Furthermore, TGA result indicated ratio 90/10 increase about 27 °C and 72 °C of maximum thermal degradation temperature (T_{max}) and decomposition temperature (T_d) compared to neat PLA. Two types of nanocomposites were prepared by melt blending technique and characterized. The X-ray diffraction (XRD) technique was used to analyze the degree of expansion of the prepared clays. XRD analysis indicated that PLA/PCL containing 1, 3, 5, 7, and 10% FH-MMT exhibits interlayer distance of 13.26, 13.80, 13.93, 14.31, and 14.06 Å respectively. Meanwhile, the d_{001} diffraction for PLA/PCL containing 1, 3, 5, 7% ODA-MMT exhibits interlayer distance of 30.87, 31.14, 32.24 and 32.34 Å respectively.

The transmission electron microscopy (TEM) was used to confirm the presence of the clay. The presence of intercalated and partially exfoliated structure for nanocomposites was observed. The clay was dispersed however the agglomeration in the TEM micrograph was still exist. The thermal stability of PLA/PCL improved after addition of FH-MMT and ODA-MMT. Presence of 1% of FH-MMT in PLA/PCL improved about 24 °C and 17 °C compared to neat PLA/PCL in term of the maximum thermal degradation temperature (T_{max}) and initial degradation temperature (T_{on}) respectively.

Tensile test showed different effects on the strength, modulus and elongation of the PLA/PCL nanocomposites. The morphology of etched samples was investigated by scanning electron microscopy (SEM), which showed addition of OMMT reduces the diameter of black hole of PLA/PCL. The diameter of spherulites which indicated phase separation in fractured surface samples also reduced after addition of FH-MMT and ODA-MMT. TEM analysis confirmed that the prepared PLA/PCL/FH-MMT and PLA/PCL/ODA-MMT nanocomposites are intercalated and exfoliated types.

Abstrak thesis yang dikemukakan kepada senat Universiti Putra Malaysia
sebagai memenuhi keperluan untuk ijazah Master Sains

**PENYEDIAAN DAN PENCIRIAN NANOKOMPOSIT
POLILAKTIK/POLIKAPROLAKTON/ TANAH LIAT TERUBAHSUAI
-LEMAK HIDRAZIDA DAN OKTADESILAMIN**

Oleh

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Dalam kajian ini, dua tanah liat organik terubahsuai montmorilonit (OMMT) telah disediakan melalui tindak balas pertukaran ion. OMMT yang pertama disediakan menggunakan hidrazides lemak yang disintesis daripada minyak sawit untuk mengubahsuai sifat montmorilonit (Na-MMT). OMM kedua pula menggunakan ODA yang diperolehi daripada industri. Tanah liat Organo FH-MMT dan ODA-MMT telah berjaya disediakan melalui interkalasi rantaian alkylammonium ke dalam galeri MMT melalui tindakbalas pertukaran ion. Hasilnya, jarak basal FH-MMT dan ODA-MMT telah meningkat dari jarak asal Na-MMT iaitu 11.62Å kepada 13.10 Å 29.90 Å. Peralihan kedudukan puncak basal menunjukkan interkalasi OMMT ke dalam tanah liat yang diubahsuai telah berjaya. Spectrum IR (FTIR) FH-MMT dan ODA-MMT menunjukkan kehadiran kumpulan ion alkilammonia selepas tindakbalas pengubahsuaian.

Nisbah 90/10 daripada PLA/PCL telah dipilih untuk menghasilkan nanokomposit PLA/PCL dalam pencampur dalaman. Nisbah ini telah dipilih kerana menghasilkan kekuatan tegangan tertinggi diantara nisbah campuran PLA/PCL tanpa kerugian teruk dalam sifat pemanjangan. Tambahan pula, keputusan TGA menunjukkan nisbah campuran 90/10 menghasilkan peningkatan masing-masing sebanyak 27 °C dan 72 °C bagi suhu degradasi terma maksimum (T_{max}) dan suhu penguraian (T_d) berbanding PLA. Dua jenis nanokomposit telah disediakan oleh teknik pengadunan leburan dan dicirikan. Pembelauan sinar-X (XRD) teknik telah digunakan untuk menganalisis tahap pengembangan tanah liat yang disediakan. XRD analisis menunjukkan bahawa PLA/PCL yang mengandungi 1, 3, 5, 7, dan 10% FH-MMT memberi jarak antara lapisan masing-masing sebanyak 13.26, 13.80, 13.93, 14.31, dan 14.06 Å. Sementara itu, pembelauan d_{001} untuk PLA/PCL yang mengandungi 1, 3, 5, 7% ODA-MMT pula menghasilkan jarak antara lapisan masing-masing sebanyak 30.87, 31.14, 32.24 dan 32.34 Å.

Transmisi mikroskopi elektron (TEM) telah digunakan untuk mengesahkan kehadiran tanah liat. Kehadiran struktur interkalasi dan sebahagiannya exfoliasi nanokomposit telah diperhatikan. Walaupun tanah liat telah tersebar, namun masih terdapat agglomerasi di dalam sempel. Kestabilan terma PLA/PCL telah ditambahbaik selepas penambahan FH-MMT dan ODA-MMT. Dengan Kehadiran 1% FH-MMT sahaja, suhu degradasi maksimum haba (T_{max}) dan suhu degradasi awal (T_{on}) nanokomposit PLA/PCL masing-masing telah meningkat sebanyak 24 °C dan 17 °C berbanding dengan PLA/PCL.

Ujian tegangan menunjukkan kesan yang berbeza terhadap modulus kekuatan dan pemanjangan nanokomposit PLA/PCL. Keadaan morfologi sampel terukir telah disiasat oleh imbasan mikroskop elektron (SEM), yang menunjukkan dengan penambahan OMMT telah mengurangkan diameter lubang hitam yang hadir dalam sampel PLA/PCL. Diameter spherulite yang menunjukkan pemisahan fasa antara polimer PLA dan PCL dalam sampel permukaan patah menjadi lebih kecil selepas penambahan FH-MMT dan ODA-MMT. Analisis TEM mengesahkan bahawa nanokomposit PLA/PCL/FH-MMT dan PLA/PCL/ODA-MMT adalah dari jenis interkalasi dan jenis ekfoliasi.

ACKNOWLEDGEMENTS

بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

In the name of Allah, Most Gracious, and Most Merciful. Praise be to Allah. May the blessings and peace of Allah be upon our prophet Muhammad bin Abdullah (peace be upon him), upon his families and upon his companions. I wish to express my gratitude to my supervisor, Dr. Nor Azowa Ibrahim, and my co-supervisors, Dr Norhazlin Zainuddin and Prof. Dato' Dr Wan Md Zin Wan Yunus. This thesis would not have been realized without their support, encouragement, guidance and supervision throughout this work. I would also like to convey thanks to Universiti Putra Malaysia for providing the financial support under Graduate Research Fellowship (GRF) scheme. To the staff of Chemistry Department thank you for the help and co-operation. My sincere thanks are to all my friends. This thesis may not be completed without your help and friendship, you are all great friends.

I would like to thank my parent, Saadiyah Brahim and Hairaldin Senawi who raised me with lots of love, thank you for supporting me throughout my long education. And special thanks with heart full of love to my husband, Shaiful Amri Mohd Som for his love, encouragement, patience, and understanding. Allah has granted our prayer and this triumph is yours as much as it is mine. So really and true, Allah's promise that after every hardship there is relief. May Allah in His infinite mercy continue to be with us and lead us to success in this life, life after, and in the heaven. Amin.

I certify that an Examination Committee has met on **18 December 2013** to conduct the final examination of **Siti Zulaiha Hairaldin** on her **Master Degree of Science** thesis entitled “**Preparation and Characterization of Polylactide/Polycaprolactone/Fatty Hydrazide and Octadecylamine-Modified Clay Nanocomposite**” in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the student be awarded the Master of Science. Members of the Examination Committee were as follows:

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DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been fully acknowledged. I also declare that it has not been previously, and is not concurrently, submitted for any other degree at Universiti Putra Malaysia.

SITI ZULAIHA HAIRALDIN

Date: 18 December 2012

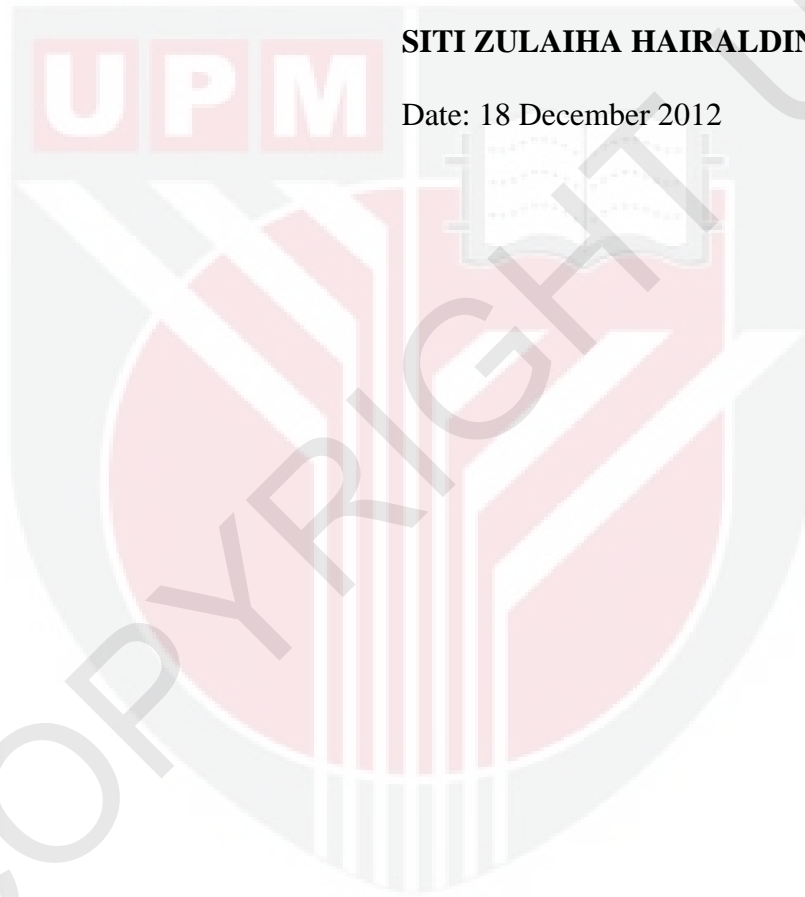


TABLE OF CONTENTS

		Page
	ABSTRACT	i
	ABSTRAK	iv
	ACKNOWLEDGEMENTS	vii
	APPROVAL	viii
	DECLARATION	x
	LIST OF TABLES	xiii
	LIST OF FIGURES	xiv
	LIST OF SCHEMES	xvii
	LIST OF ABBREVIATIONS	xviii
	LIST OF SYMBOLS	xx
	CHAPTER	
1.0	INTRODUCTION	
	Polymer nanocomposite	1
	Significance of study	3
	Scope of study	4
	Objectives of study	5
2.0	LITERATURE REVIEW	
	Poly lactide (PLA)	6
	Polycaprolactone (PCL)	7
	Application of PLA and PCL	8
	Fatty hydrazides	9
	Structure of layered silicates	11
	Montmorillonite	13
	Nanocomposites	14
	Modification of Montmorillonite	15
	Modification of Montmorillonite with Fatty Hydrazides and Octadecylamine	17
	Types of nanocomposite	19
	Preparation of nanocomposites	22
	Previous study	28
3.0	METHODOLOGY	
	Materials	34
	Synthesis of fatty hydrazide	35
	Preparation of fatty hydrazides modified clay (FH-MMT)	35
	Preparation of octadecylamine modified clay (ODA-MMT)	36
	Preparation of PLA/PCL polymer blend	37

Preparation of PLA/PCL organoclay nanocomposites	37
Characterization	38
Fourier Transforms Infrared (FTIR) analysis	38
X-ray diffraction (XRD) analysis	38
Thermal gravimetric analysis (TGA)	39
Tensile Measurement	39
Scanning Electron Microscopy (SEM)	40
Transmission Electron Microscopy (TEM)	40
4.0 RESULTS	
Characterization of organoclay	41
Fourier Transform Infrared analysis	41
X-Ray Diffraction Analysis	45
Thermal gravimetric analysis	46
Characterization of PLA and PCL polymer blend	52
Tensile properties of PLA/PCL polymer blend	52
Fourier Transform Infrared analysis of PLA and PCL	57
Thermal Properties Analysis of PLA/PCL polymer blend	58
Characterization of PLA/PCL clay nanocomposite	61
X-Ray Diffraction Analysis of nanocomposites	61
Tensile Properties for PLA/PCL with addition of NaMMT, FHMMT and ODAMMT	66
Thermal properties of analysis of PLA/PCL clay Nanocomposite	69
SEM analysis of PCL dispersion in PLA/PCL nanocomposite	73
SEM analysis of PLA/PCL nanocomposites of fractured samples	79
Transmission electron Microscopy analysis of PLA/PCL clay nanocomposite	85
5.0 CONCLUSIONS	89
Recommendation for Future Studies	90
REFERENCES	91
APPENDICES	98
BIODATA OF STUDENT	101
LIST OF PUBLICATIONS	102