PREPARATION AND CHARACTERIZATION OF STARCH-BASED COMPOSITE FOAMS



Ms. Dujdao Preechawong

A Thesis Submitted in Partial Fulfilment of the Requirements
for the Degree of Master of Science

The Petroleum and Petrochemical College, Chulalongkorn University
in Academic Partnership with

The University of Michigan, The University of Oklahoma,
and Case Western Reserve University

2001
ISBN 974-13-0734-9

Thesis Title: Preparation and Characterization of Starch-Based

Composite Foams

By: Ms.Dujdao Preechawong

Program: Polymer Science

Thesis Advisor: Assoc. Prof. David C. Martin

Dr. Ratana Rujiravanit

Dr. Pitt Supaphol

Accepted by the Petroleum and Petrochemical College, Chulalongkorn University, in partial fulfilment of the requirements for the Degree of Master of Science.

K. Bunya hint. College Director

(Assoc. Prof. Kunchana Bunyakiat)

Thesis Committee:

(Assoc. Prof. David C. Martin)

(Dr. Ratana Rujiravanit)

(Dr. Pitt Supaphol)

(Dr. Mahit Nithitanakul)

บทคัดย่อ

คุจคาว ปรีชาวงศ์ : การเตรียมและวิเคราะห์คุณสมบัติของคอมพอสิตโฟมที่มีแป้งเป็น ส่วนประกอบหลัก (Preparation and Characterization of Starch-Based Composite Foams) อ. ที่ปรึกษา : รศ. คร. เควิค ซี มาร์ติน (Assoc. Prof. David C. Martin) คร. รัตนา รุจิรวนิช และ คร.พิชญ์ ศุภผล 120 หน้า ISBN 974-13-0734-9

งานวิจัยนี้เป็นการเตรียมคอมพอสิต โฟม โดยวิธีเบคจากแป้งมันสำปะหลังและพอลิเมอร์ สังเคราะห์ที่ย่อยสลายได้ได้แก่ พอลิไวนิลแอลกอฮอล์ พอลิแลคติก เอสิกและพอลิกาโปรแลก โตน จากการศึกษาโดยการใช้กล้องสแกนนิ่งอิเล็กตรอนไมโครสโคป (Scanning Electron Microscope) พบว่าขอบบนและล่างของโฟมจะมีความหนาแน่นสูงในขณะที่ส่วนกลางของโฟมจะมีความหนา แน่นต่ำ ในงานวิจัยนี้ได้ทำการศึกษาผลกระทบของความชื้นสัมพัทธ์ เวลาในการเก็บ โฟม การเดิม พอลิเมอร์สังเคราะห์ที่ย่อยสลายได้ และ การเติมพลาสติไซเซอร์ที่มีต่อสมบัติเชิงกล ผลจากการศึกษาสมบัติเชิงกลพบว่า ค่าการทนต่อแรงดึง และค่าการทนต่อแรงโค้งงอจะให้ก่าสูงสุดที่สภาวะ ความชื้นสัมพัทธ์ 42 เปอร์เซ็นต์และใช้เวลาในการเก็บ 2 วัน และการเติมพอลิเมอร์สังเคราะห์ สามารถปรับปรุงค่าการทนต่อแรงดึง ค่าการทนต่อแรงโก้งงอ และค่าการยืดตัว ณ จุดขาดของโฟม ได้ ในขณะที่การเติมพลาสติไซเซอร์ทำให้ค่าการทนต่อแรงดึง และค่าการทนต่อแรงโค้งงอของ โฟมลดลงแต่เพิ่มค่าการยืดตัว ณ จุดขาดของโฟม นอกจากนี้การศึกษาสมบัติการดูดซับน้ำ แสดง ให้เห็นว่า การเติมพอลิเมอร์สังเคราะห์ที่ย่อยสลายได้สามารถลดการดูดซับน้ำของโฟมได้และจาก การศึกษาการย่อยสลายค้วยเอนไซม์อะไมเลสพบว่าพอลิเมอร์นี้มีผลน้อยมากต่อการย่อยสลายของ แป้ง

ABSTRACT

4272007063: POLYMER SCIENCE PROGRAM

Dujdao Preechawong: Preparation and characterization of starch-based composite foams. Thesis Advisors: Assoc. Prof. David C Martin, Dr. Ratana Rujiravanit, and Dr. Pitt Supaphol,

120 pp ISBN 974-13-0734-9

Keywords: Starch foams/ Composite foams/ Starch/ Poly(vinyl alcohol)/

Poly(lactic acid)/ Polycaprolactone

Starch-based composite foams were prepared by baking a mixture of starch and a synthetic biodegradable polymer (i.e., poly(vinyl alcohol), poly(lactic acid), and poly(ε-caprolactone)) in a hot mold. This process can be used to prepare a thinwalled object, such as a plate. Scanning electron micrographs of the cross-sectional view of the foams showed that the cellular size is very dense in the outer layer and less dense in the inner layer. The effects of relative humidity, storage time, the presence of synthetic biodegradable polymers, and the presence of plasticizers (i.e., glycerol, urea, and ammonium chloride) on tensile and flexural properties were investigated. For all formulations, the amount of relative humidity which gave the maximum value of the ultimate strength of the foams was 42%, while the storage time which gave the maximum value of the ultimate strength of the foams was 2 days (only tested for a fixed relative humidity of 42%). Addition of the synthetic biodegradable polymers improved the ultimate strength and the elongation at break of the foams. Increasing the plasticizer contents increased the elongation at break at the expense of the ultimate strength. Water absorption and biodegradability of the foams were also studied. Increasing the synthetic biodegradable polymer contents increased the water resistivity of the foams. Enzymatic degradation tests showed that the foams were degraded by enzyme α -amylase.

ACKNOWLEDGEMENTS

I would like to thank the Petroleum and Petrochemical College, Chulalongkorn University, where I has gained invaluable knowledge in Polymer Science program and for their kindness in providing her with a scholarship which enabled her to persue her master degree.

I would like to express my sincere gratitude to Assoc. Prof. David C. Martin, Dr. Ratana Rujiravanit, and Dr. Pitt Supaphol, for their guidance and encouragement during the course of this work.

I would like gives special thanks to the Siam Modified Starch Co., Ltd., East Asiatic Co., Ltd., and Coin Chemicals Co., Ltd. For the support of the raw materials and chemicals used throughout this work.

I would like to express the grateful appreciation to Mr. John W. Ellis for providing technical knowledge and helpful suggestion. Special thanks are due also to all Petroleum and Petrochemical College's staff.

Finally, I would like to thank my friends for their friendship, helpfulness, cheerfulness, suggestions, and encouragement. I am also greatly indebted to my parents for their support, understanding and patience during this pursuit.

TABLE OF CONTENTS

		PAGE
40	Title Page	i
	Abstract (in English)	iii
	Abstract (in Thai)	iv
	Acknowledgements	v
	Table of Contents	vi
	List of Tables	ix
	List of Figures	xvi
CHAPTER	L	
I	INTRODUCTION	1
II	LITERATURE SURVEY	17
II	EXPÉRIMENTAL	24
	3.1 Material	24
	3.1.1 Biodegradable Polymer	24
	3.1.2 Plasticizers	24
	3.1.3 Additives	24
	3.1.4 Diethyl Ether	25
	3.1.5 Salts	25
	3.1.6 Enzyme	25
	3.2 Experimental Procedure	25
	3.2.1 Preparation of Starch Composi	te Foams 25
	3.2.1.1 Tapioca Starch Prepara	ation 25
	3.2.1.2 Preparation of Starch I	Batter 26
	3.3 Humidity Testing	26

CHAPTER		PAGE
	3.3 Mechanical Properties	27
	3.3.1 Tensile Testing	27
	3.3.2 Flexural Testing	27
	3.4 Microstructure Charaterization	27
	3.5 Moisture Determination	28
	3.6 Water Absorption	28
	3.7 Enzymatic Degradation	28
IV	RESULTS AND DISCUSSION	
	4.1 Morphology	29
	4.2 Moisture Content	31
	4.2.1 Effect of Relative Humidity	32
	4.2.2 Effect of Storage Time	34
	4.2.3 Effect of Polymers	36
	4.2.4 Effect of Plasticizers	37
	4.3 Mechanical Properties	39
	4.3.2 Tensile Properties	40
	4.3.2.1 Effect of Relative Humidity	40
	4.3.2.2 Effect of Storage Time	43
	4.3.2.3 Effect of Polymers	46
	4.3.2.4 Effect of Plasticizers	48
	4.3.3 Flexural Properties	51
	4.3.3.1 Effect of Relative Humidity	51
	4.3.3.2 Effect of Storage Time	54
	4.3.3.3 Effect of Polymers	57
	4.3.3.4 Effect of Plasticizers	59
	4.4 Water Absorption	61
	4.5 Enzymatic Degradation	62

9.13

CHAPTER		PAGE
V	CONCLUSIONS	64
	REFERENCES	65
	APPENDICES	68
	CURRICULUM VITAE	114

LIST OF TABLES

TABLE		PAGE	
1.1	Advantages and disadvantages of foamed versus		
	non-foamed plastics	5	
1.2	Effect of starch type on mechanical properties		
	of films cast from aqueous solution	8	
1.3	Physical properties of poly(vinyl alcohol)	10	
1.4	Effect of stereochemistry and crystallinity on		
	mechanical properties of poly(lactic acid)	11	
1.5	Physical properties of polycaprolactone	12	
Al	Moisture content of starch foams as a function of		
	relative humidity	67	
A2	Moisture content of starch-10% PVA composite		
	foams as a function of relative humidity	67	
A3	Moisture content of starch-30% PVA composite		
	foams as a function of relative humidity	68	
A4	Moisture content of starch-10% PLA composite		
	foams as a function of relative humidity	68	
A5	Moisture content of starch-30% PLA composite		
	foams as a function of relative humidity	69	
A6	Moisture content of starch-10% PCL composite		
	foams as a function of relative humidity	69	
A7	Moisture content of starch-30% PCL composite		
	foams as a function of relative humidity	70	
A8	Moisture content of starch foams as a function of		
	storage time	70	

TABLI	TABLE		
4.0	No. in the contract of the con		
A9	Moisture content of starch-10% PVA composite	7.1	
	foams as a function of storage time	71	
A10	Moisture content of starch-30% PVA composite		
	foams as a function of storage time	71	
A11	Moisture content of starch-10% PLA composite		
	foams as a function of storage time	72	
A12	Moisture content of starch-30% PLA composite		
	foams as a function of storage time	72	
A13	Moisture content of starch-10% PCL composite		
	foams as a function of storage time	73	
A14	Moisture content of starch-30% PCL composite		
	foams as a function of storage time	73	
B1	Tensile strength of starch foams as a function of		
	relative humidity	74	
B2	Tensile strength of starch-10% PVA composite		
	foams as a function of relative humidity	74	
В3	Tensile strength of starch-30% PVA composite		
	foams as a function of relative humidity	75	
B4	Tensile strength of starch-10% PLA composite		
	foams as a function of relative humidity	75	
B5	Tensile strength of starch-30% PLA composite		
	foams as a function of relative humidity	76	
В6	Tensile strength of starch-10% PCL composite		
	foams as a function of relative humidity	76	
В7	Tensile strength of starch-30% PCL composite		
Di	foams as a function of relative humidity	77	

TABLI	TABLE		
В8	Tensile strength of starch foams as a function		
	of storage time	77	
В9	Tensile strength of starch-10% PVA composite		
	foams as a function of storage time	78	
B10	Tensile strength of starch-30% PVA composite		
	foams as a function of storage time	78	
B11	Tensile strength of starch-10% PLA composite		
	foams as a function of storage time	79	
B12	Tensile strength of starch-30% PLA composite		
	foams as a function of storage time	79	
B13	Tensile strength of starch-10% PCL composite		
	foams as a function of storage time	80	
B14	Tensile strength of starch-30% PCL composite		
	foams as a function of storage time	80	
B15	Tensile strength of starch foams containing glycerol		
	as a plasticizer	81	
B16	Tensile strength of starch foams containing urea		
	as a plasticizer	81	
B17	Tensile strength of starch foams containing		
	ammonium chloride as a plasticizer	82	
C1	Elongation at break of starch foams as a function		
	of relative humidity	83	
C2	Elongation at break of starch-10% PVA		
	composite foams as a function of relative humidity	83	
C3	Elongation at break of starch-30% PVA		
	composite foams as a function of relative humidity	84	

Ał	BLE		PAGE
C	:4	Elongation at break of starch-10% PLA	
		composite foams as a function of relative humidity	84
C	25	Elongation at break of starch-30% PLA	
		composite foams as a function of relative humidity	85
C	6	Elongation at break of starch-10% PCL	
		composite foams as a function of relative humidity	85
C	27	Elongation at break of starch-30% PCL	
		composite foams as a function of relative humidity	86
C	8	Elongation at break of starch foams as a function	
		of storage time	86
C	9	Elongation at break of starch-10% PVA	
		composite foams as a function of storage time	87
C	210	Elongation at break of starch-30% PVA	
		composite foams as a function of storage time	87
C	211	Elongation at break of starch-10% PLA	
		composite foams as a function of storage time	88
C	212	Elongation at break of starch-30% PLA	
		composite foams as a function of storage time	88
C	213	Elongation at break of starch-10% PCL	
		composite foams as a function of storage time	89
C	214	Elongation at break of starch-30% PCL	
		composite foams as a function of storage time	89
C	215	Elongation at break of starch foams containing	
		glycerol as a plasticizer	90
C	216	Elongation at break of starch foams containing	
		urea as a plasticizer	90

Γ.	FABLE		
	C17	Elongation at break of starch foams containing	
		Ammonium chloride as a plasticizer	91
	D1	Flexural strength of starch foams as a function	
		of relative humidity	92
	D2	Flexural strength of starch-10% PVA	
		composite foams as a function of relative humidity	92
	D3	Flexural strength of starch-30% PVA	
		composite foams as a function of relative humidity	93
	D4	Flexural strength of starch-10% PLA	
		composite foams as a function of relative humidity	93
	D5	Flexural strength of starch-30% PLA	
		composite foams as a function of relative humidity	94
	D6	Flexural strength of starch-10% PCL	
		composite foams as a function of relative humidity	94
	D7	Flexural strength of starch-30% PCL	
		composite foams as a function of relative humidity	95
	D8	Flexural strength of starch foams as a function	
		of storage time	95
	D9	Flexural strength of starch-10% PVA	
		composite foams as a function of storage time	96
	D10	Flexural strength of starch-30% PVA	
		composite foams as a function of storage time	96
	D11	Flexural strength of starch-10% PLA	
		composite foams as a function of storage time	97
	D12	Flexural strength of starch-30% PLA	
		composite foams as a function of storage time	97

Γ	TABLE		
	D13	Flexural strength of starch-10% PCL	
		composite foams as a function of storage time	98
	D14	Flexural strength of starch-30% PCL	
		composite foams as a function of storage time	98
	D15	Flexural strength of starch foams containing	
		glycerol as a plasticizer	99
	D16	Flexural strength of starch foams containing	
		urea as a plasticizer	99
	D17	Flexural strength of starch foams containing	
		ammonium chloride as a plasticizer	100
	E1	Maximum strain of starch foams as a function	
		of relative humidity	101
	E2	Maximum strain of starch-10% PVA	
		composite foams as a function of relative humidity	101
	E3	Maximum strain of starch-30% PVA	
		composite foams as a function of relative humidity	102
	E4	Maximum strain of starch-10% PLA	
		composite foams as a function of relative humidity	102
	E5	Maximum strain of starch-30% PLA	
		composite foams as a function of relative humidity	103
	E6	Maximum strain of starch-10% PCL	
		composite foams as a function of relative humidity	103
	E7	Maximum strain of starch-30% PCL	
		composite foams as a function of relative humidity	104
	E8	Maximum strain of starch foams as a function	
		of storage time	104

TABLE		PAGE
E9	Maximum strain of starch-10% PVA	
	composite foams as a function of storage time	105
E10	Maximum strain of starch-30% PVA	
	composite foams as a function of storage time	105
E11	Maximum strain of starch-10% PLA	
	composite foams as a function of storage time	106
E12	Maximum strain of starch-30% PLA	
	composite foams as a function of storage time	106
E13	Maximum strain of starch-10% PCL	
	composite foams as a function of storage time	107
E14	Maximum strain of starch-30% PCL	
	composite foams as a function of storage time	107
E15	Maximum strain of starch foams containing	
	glycerol as a plasticizer	108
E16	Maximum strain of starch foams containing	
	urea as a plasticizer	108
E17	Maximum strain of starch foams containing	
	ammonium chloride as a plasticizer	109
F1	Water absorption of starch-based composite foams	110
G1	Weight loss of enzymatic degradation of	
	starch-based composite foams	111
H1	Density of starch-based composite foams	112

LIST OF FIGURES

FIGURE		
1.1	Structure of amylose	7
1.2	Structure of amylopectin	7
1.3	Structure of poly(vinyl alcohol)	9
1.4	Structure of poly(lactic acid)	10
1.5	Structure of polycaprolactone	11
1.6	Types of flexural testing equipment	15
4.1	Scanning electron micrograph of cross sections of	
	(A) starch foam, (B) starch-30% PVA,	
	(C) starch-30% PLA, and (D) starch-30% PCL.	30
4.2	Moisture contents of starch-based composite foams	
	as a function of relative humidity at 25°C for 7 days of	
	(A) starch-PVA foams, (B) starch-PLA foams, and	
	(C) starch-PCL foams.	33
4.3	Moisture contents of starch-based composite foams	
	as a function of storage time at 42% RH and 25°C of	
	(A) starch-PVA foams, (B) starch-PLA foams, and	
	(C) starch-PCL foams.	35
4.4	Effect of polymers on moisture contents of starch-based	
	composite foams at 42% RH for 2 days.	36
4.5	Effect of plasticizers on moisture contents of starch-based	
	composite foams at 42% RH for 2 days.	37
4.6	Tensile strength of starch-based composite foams as	
	a function of relative humidity at 25°C for 7 days of	
	(A) starch-PVA foams, (B) starch-PLA foams, and	
	(C) starch-PCL foams.	41

F	FIGURE		
	4.7	Elongation at break of starch-based composite foams as	
		a function of relative humidity at 25°C for 7 days of	
		(B) starch-PVA foams, (B) starch-PLA foams, and	
		(C) starch-PCL foams.	42
	4.8	Tensile strength of starch-based composite foams as	
		a function of storage time at 42% RH and 25°C of	
		(C) starch-PVA foams, (B) starch-PLA foams, and	
		(C) starch-PCL foams.	44
	4.9	Elongation at break of starch-based composite foams as	
		a function of relative humidity at 25°C for 7 days of	
		(D) starch-PVA foams, (B) starch-PLA foams, and	
		(C) starch-PCL foams.	45
	4.10	Effect of polymers on tensile strength of starch-based	
		composite foams at 42% RH for 2 days.	46
	4.11	Effect of polymers on elongation at break of starch-based	
		composite foams at 42% RH for 2 days.	47
	4.12	Effect of plasticizers on tensile strength of starch-based	
		composite foams at 42% RH for 2 days.	48
	4.13	Effect of plasticizers on elongation at break of starch-based	
		composite foams at 42% RH for 2 days.	49
	4.14	Tensile strength of starch-based composite foams as	
		a function of relative humidity at 25°C for 7 days of	
		(E) starch-PVA foams, (B) starch-PLA foams, and	
		(C) starch-PCL foams.	52

FIGURE	PAGE
4.15 Maximum strain of starch-based composite foams as	
a function of relative humidity at 25°C for 7 days of	
(F) starch-PVA foams, (B) starch-PLA foams, and	
(C) starch-PCL foams.	53
4.16 Tensile strength of starch-based composite foams as	
a function of storage time at 42% RH and 25°C of	
(G) starch-PVA foams, (B) starch-PLA foams, and	
(C) starch-PCL foams.	55
4.17 Maximum strain of starch-based composite foams as	
a function of storage time at 42% RH and 25°C of	
(H) starch-PVA foams, (B) starch-PLA foams, and	
(C) starch-PCL foams.	56
4.18 Effect of polymers on flexural strength of starch-based	
composite foams at 42% RH for 2 days.	57
4.19 Effect of polymers on maximum strain of starch-based	
composite foams at 42% RH for 2 days.	58
4.20 Effect of plasticizers on flexural strength of starch-based	
composite foams at 42% RH for 2 days.	59
4.21 Effect of plasticizers on maximum strain of starch-based	
composite foams at 42% RH for 2 days.	60
4.22 Water absorption of starch-based composite foams.	61
4.23 Enzymatic degradation of starch-based composite foams	
by α -amylase at 55°C.	62