

**CHITINEOUS GEL VIA EPOXY GROUP INCORPORATION AND
ITS HYDROXYAPATITE FORMATION**



Ms. Jutatip Fungangwanwong

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

2003

ISBN 974-17-2324-5

3 121.8. 2551

Thesis Title: Chitineous Gel via Epoxy Group Incorporation and its Hydroxyapatite Formation
By: Jutatip Fungangwanwong
Program: Polymer Science
Thesis Advisors: Assoc. Prof. Suwabun Chirachanchai
Prof. Seiichi Tokura

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

K. Bunyakiat
..... College Director
(Assoc. Prof. Kunchana Bunyakiat)

Thesis Committee:

Suwabun Chirachanchai
.....
(Assoc. Prof. Suwabun Chirachanchai)

S. Tokura
.....
(Prof. Seiichi Tokura)

Nantaya Yanumet
.....
(Assoc. Prof. Nantaya Yanumet)

AVM. Somsak Naviroj
.....
(Dr. Somsak Naviroj, Air Vice Marshal)

บทคัดย่อ

จุฑาทิพย์ ฟังกังวาลวงศ์: การสร้างโคตินัสเจลด้วยหมู่อีพอกซี และการเกิดไฮดรอกซีอะพาไทต์ (Chitinous Gel via Epoxy Group Incorporation and its Hydroxyapatite Formation) อ. ที่ปรึกษา: รองศาสตราจารย์ ดร. สุวบุญ จิระกาญจชัย และ ศาสตราจารย์ ดร. เซอิจิ โทคุระ, 31 หน้า ISBN 974-17-2324-5

งานวิจัยนี้รายงานถึงการเตรียมอีพอกซี-ไคโตซานเจลกับไฮดรอกซีอะพาไทต์ ในขั้นแรก ความว่องไวต่อการเกิดปฏิกิริยา และคุณสมบัติการละลายของไคโตซานถูกปรับปรุงโดยการติดหมู่พทาโลอิวกับสายโซ่ไคโตซาน หมู่อีพอกซีถูกนำเข้าไปที่หมู่แอลกอฮอล์ตำแหน่ง C-6 โดยการทำให้หมู่ไฮดรอกซิลของพทาโลอิวเกิดปฏิกิริยากับพทาโลอิวไคโตซาน การทำปฏิกิริยากับไฮดรอกซีนั่น นอกจากจะทำให้หมู่ปกป้องพทาโลอิวถูกกำจัดแล้วยังเป็นการเปิดวงแหวนอีพอกซีด้วย ทำให้ได้ปฏิกิริยาการบ่มซึ่งสามารถตรวจวิเคราะห์ได้ด้วย FTIR หลังจากการกำจัดหมู่พทาโลอิวและปฏิกิริยาการบ่ม การจุ่มแบบสลับในสารละลายแคลเซียมกับฟอสเฟตถูกนำมาประยุกต์ใช้เพื่อให้เกิดไฮดรอกซีอะพาไทต์ในโครงร่างอีพอกซี-ไคโตซาน สารโคตินัสเจลและไฮดรอกซีอะพาไทต์ที่ก่อตัวขึ้นในโครงสร้าง ถูกตรวจวิเคราะห์ด้วย XRD, FTIR และ TGA

ABSTRACT

4472006063 : POLYMER SCIENCE PROGRAM

Jutatip Fungangwanwong: Chitineous Gel via Epoxy Group

Incorporation and its Hydroxyapatite Formation

Thesis Advisors: Assoc. Prof. Suwabun Chirachanchai,

Prof. Seiichi Tokura, 31 pp. ISBN 974-17-2324-5

Keywords : Epoxy-chitosan/ Hydroxyapatite/ Chitineous gel/ Alternate soaking

The preparation of epoxy-chitosan gel with hydroxyapatite is reported. Initially, the reactivity and solubility of chitosan is improved by conjugating phthaloyl groups with chitosan chains. The epoxy group is introduced to hydroxyl group at C-6 by reacting epichlorohydrin with *N*-phthaloyl-chitosan. The reaction with hydrazine will not only bring the dephthaloylation but also the ring opening of epoxy group to obtain the crosslinking as confirmed by FTIR. After dephthaloylation and crosslinking, the alternate soaking of calcium with phosphate solution is applied to establish hydroxyapatite formation in the epoxy-chitosan matrix. Chitineous gel and its hydroxyapatite formation are characterized by XRD, FTIR, and TGA.

ACKNOWLEDGEMENTS

The author would like to give special thanks to her Thai advisor, Associate Professor Suwabun Chirachanchai, who not only originated this work, but also gave intensive suggestions, invaluable guidance, constructive criticisms, constant encouragements, inspirations and vital helps throughout this research work. She also would like to express her thanks to Japanese advisor, Professor Seiichi Tokura for recommendations on the research.

She also gratefully thanks Associate Professor Nantaya Yanumet and Air Vice Marshall Dr. Somsak Naviroj for their valuable comments and discussions in the reading of the thesis book.

She greatly appreciates all Professors who have tendered invaluable knowledge to her at the Petroleum and Petrochemical College, Chulalongkorn University.

She would like to thank Seafresh Chitosan (Lab) Company Limited, Thailand, for supporting chitosan starting materials and Dr. Rath Pichyangkura, Biochemistry Department, Faculty of Science, Chulalongkorn University, for advice and some chemicals.

In addition, she wishes to thank her seniors, Ms. Rangrong Yoksan and Ms. Sutinun Phongtamrug for invaluable guidance, suggestions and encouragements throughout this research work. She also would like to thank the college staff members, and all her best friends at the Petroleum and Petrochemical College.

This thesis work is partially funded by Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PPT Consortium).

Finally, she wishes to express her gratitude to her family for their love, understanding, encouragement and financial support.

TABLE OF CONTENTS

	PAGE
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of Contents	vi
List of Schemes	viii
List of Figures	ix
 CHAPTER	
I INTRODUCTION	1
 II LITERATURE REVIEW	 3
2.1 Bone Therapy: The Current Situation	3
2.2 Tissue Engineering of Bone	4
2.3 Biomaterials	5
2.4 Chitin-Chitosan: Specific Properties for Bone Therapy	6
2.5 Motivation of the Present Work	7
 III EXPERIMENTAL	 8
3.1 Materials	8
3.2 Equipment	8
3.3 Methodology	9
 IV CHITINEOUS GEL VIA EPOXY GROUP INCORPORATION AND ITS HYDROXYAPATITE FORMATION	 11
Abstract	11
Introduction	12
Experimental	13

CHAPTER	PAGE
Results and Discussion	15
Conclusions	18
Acknowledgements	18
References	18
III CONCLUSIONS	28
REFERENCES	29
CURRICULUM VITAE	31

LIST OF SCHEMES

SCHEME		PAGE
CHAPTER I		
1	Scheme I	3
2	Scheme II	4
3	Scheme III	5
4	Scheme IV	6
CHAPTER IV		
1	Scheme I	19

LIST OF FIGURES

FIGURE		PAGE
CHAPTER IV		
1	FTIR spectra of: (a) 1 , (b) 2 , (c) 3 , (d) 4 , and (e) epoxy-chitosan/HA composite	21
2	X-ray diffractograms of: (a) 1 , (b) 2 , (c) 3 , (d) 4 , and (e) epoxy-chitosan/HA composite	22
3	TGA diagrams of: (a) 1 , (b) 2 , (c) 3 , and (d) 4	23
4	FTIR spectra and curve fitting of 3 with hydrazine monohydrate under the curing at room temperature: (a) 4 minutes, (b) 12 minutes, (c) 20 minutes, and (d) 28 minutes	24
5	FTIR curve fitting of 3 with hydrazine monohydrate using intensity of the oxirane peak at 907 cm^{-1} and pyranose ring peak at 1026 cm^{-1} with various times	25
6	DSC diagrams of: (a) curing of 3 , (b) after curing of 3	26
7	TGA diagrams of epoxy-chitosan/HA composite after (a) 1 cycle, (b) 2 cycles, (c) 3 cycles, and (d) 4 cycles of alternate soaking of calcium and phosphate solution	27