CHROMOPHORES MODIFIED POROUS CLAY HETEROSTRUCTURE FOR SMART PACKAGING FILMS



Supatcharee Boonruang

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

2012

Thesis Title: Chromophores M

Chromophores Modified Porous Clay Heterostructure for

Smart Packaging Films

By:

Supatcharee Boonruang

Program:

Polymer Science

Thesis Advisors:

Asst. Prof. Hathaikarn Manuspiya

Assoc. Prof. Rathanawan Magaraphan

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

...... College Dean

(Asst. Prof. Pomthong Malakul)

Thesis Committee:

Mathailian M (Asst. Prof. Hathaikarn Manuspiya)

(Assoc. Prof. Rathanawan Magaraphan)

, |

(Asst. Prof. Marit Nithitanakul)

(Asst. Prof. Kanogwan Seraypheap)

Tarinee N

(Asst. Prof. Tarinee Nampitch)

ABSTRACT

5372027063: Polymer Science Program

Supatcharee Boonruang: Chromophores Modified Porous Clay

Heterostructures for Smart Packaging Films.

Thesis Advisors: Asst. Prof. Hathaikarn Manuspiya, Assoc. Prof.

Rathanawan Magaraphan 105 pp.

Keywords: Porous clay heterostructure/ Chromophores/ Smart packaging

Smart packagings for detecting fish and climacteric fruit freshness were based on polypropylene/chromophores (methyl red) functionalized porous clay heterostructure (PCH) nanocomposite films and low polyethylene/chromophores (bromothymol blue) modified **PCH** nanocomposite films, respectively. The incorporation of chromophores in porous materials was investigated by N₂ adsorption-desorption, XRD and SEM. The nanaocomposite was prepared by twin screw extruder and fabricated into nanocomposite film by compression molding. The color change of PP/APPCH-MR nanocomposite films from red to light orange corresponded to the total volatile basic nitrogen releasing during fish spoilage. The color change of LDPE/PCH-BTB nanocomposite films from green to yellow correlated with standard CO₂ levels, which can be compared to CO₂ levels from respiration during fruit ripening. Porous clay improved the barrier properties of nanocomposite indicated by the reduction of oxygen transmission rate. Thus, PP/APPCH-MR nanocomposite films could be used to determine fish freshness and LDPE/PCH-BTB nanocomposite films can be applied for detecting the quality of climacteric fruit by color change. Moreover, both pH indicators can prolong the shelf-life of product by incorporated porous materials into the films.

บทคัดย่อ

สุภัจฉรี บุญเรื่อง: การพัฒนาวัสคุรูพรุนคัคแปรค้วยโครโมฟอร์สำหรับบรรจุภัณฑ์ฉลาค (Chrompohores Modified Porous Clay Heterostructure for Smart Packaging Films) อ. ที่ปรึกษา: ผศ.คร. หทัยกานต์ มนัสปียะ และ รศ.คร. รัตนวรรณ มกรพันธุ์ 105 หน้า

บรรจุภัณฑ์ฉลาคสำหรับบ่งบอกความสคของเนื้อปลาสามารถเตรียมได้โดยใช้โพลีพรอพิ ลีนร่วมกับแร่ดินเหนียวโครงสร้างรูพรุนที่มีหมู่ฟังก์ชั่นคัดแปรค้วยเมทธิลเรคนาโนคอมโพสิต และบรรจุภัณฑ์ฉลาดสำหรับบ่งบอกความสดของผลไม้ชนิด climacteric สามารถเตรียมได้โดย ใช้โพลีเอทิลีนความหนาแน่นต่ำร่วมกับแร่ดินเหนียวโครงสร้างรูพรูนที่คัดแปรด้วยโบรโมไธมอ ลบลูนาโนคอมโพสิต วัสคุรพรุนคัดแปรด้วยโครโมฟอร์สามารถตรวจวิเคราะห์ด้วยเทคนิคการคูด ซับในโตรเจน (N_2 adsorption-desorption) เทคนิค XRD และเทคนิค SEM วัสดุนาโนคอมโพ สิตที่ไวต่อการเปลี่ยนแปลงความเป็นกรค-เบสสามรถเครียมได้โคยใช้เครื่องอัครีคแบบเกลียวคู่ และขึ้นรูปเป็นแผ่นฟิล์มโคยใช้เครื่องขึ้นรูปแบบอัค ฟิล์มโพลีพรอพิลีนเคลย์นาโนคอมโพสิตถูก นำมาใช้ในการบ่งบอกความความสคของเนื้อปลาจนกระทั่งเนื้อปลาเกิดความเน่าเสีย เนื่องจากเมื่อ เนื้อปลาเกิดการเน่าเสียจะผลิตก๊าซที่ประกอบด้วยสารประกอบในโตรเจน (TVB-N) ทำให้ค่า ความเป็นกรค-เบสเพิ่มขึ้น และสีของเมทธิลเรคจะเปลี่ยนจากสีแคงป็นสีส้ม นอกจากนี้ฟิล์มโพลีเอ ทิลีนความหนาแน่นต่ำนาโนคอมโพสิตยังถูกนำมาประยุกต์ใช้ในการบอกความสดของผลไม้ชนิด climacteric เนื่องจากสีของโบรโมไธมอลบลูในนาโนคอมโพสิตฟิล์มจะเปลี่ยนจากสีเขียวเป็น เหลือง เมื่อสัมผัสกับก๊าซคาร์บอนไดออกไซค์และน้ำ ซึ่งสามารถนำไปเปรียบเทียบได้กับการ หายใจของผลไม้ชนิด climacteric และมีผลทำให้ค่าความเป็นกรด-เบสลดลง ดังนั้นฟิล์มนาโน คอมโพสิตอินดิเคเตอร์จึงสามารถใช้เป็นวัสคุที่ไวต่อการเปลี่ยนแปลงความเป็นกรค-เบส รวมทั้ง สามารถยึดอายุการเก็บรักษาเพื่อใช้ในบรรจุภัณฑ์ได้อย่างมีประสิทธิภาพอีกด้วย

ACKNOWLEDGEMENTS

The author would like to thank The Higher Education Research Promotion and National Research University Project of Thailand, Office of The Higher Education Commission (FW 0649A) and Ratchadaphiseksomphot Fund for supporting the thesis work. Partial funding was received from the Polymer Processing and Polymer Nanomaterials Research Unit, the Petroleum and Petrochemical College, Chulalongkorn University and the Center of Excellence on Petrochemical and Materials Technology (PETRO-MAT).

In addition, the author would like to thank Thai Nippon Chemical Industry Co, Ltd., for providing bentonite clay as raw materials.

The author would like to gratefully give the special thanks to Asst. Prof. Dr. Hathaikarn Manuspiya and Assoc. Prof. Dr. Rathanawan Magaraphan for their suggestions and vital help throughout this research. The author thanks Asst. Prof. Dr. Manit Nithitanakul, Asst. Prof. Dr. Kanogwan Seraypheap and Asst Prof. Dr. Tarinee Nampitch for serving on the thesis committee.

Finally, the author would like to thank my friends and my family for their assistance, cheerfulness, creative suggestions and encouragement.

TABLE OF CONTENTS

			PAGE
	Title	e Page	i
	Abst	eract (in English)	iii
	Abst	ract (in Thai)	iv
	Ackı	nowledgements	v
		e of Contents	vi
		of Tables	ix
			17
	List	of Figures	xi
CHA	PTER		
	I	INTRODUCTION	1
	II	LITERATURE REVIEW	3
	Ш	EXPERIMENTAL	27
	IV	SYNTHESIS OF CHROMOPHORES MODIFIED	
		POROUS CLAY HETEROSTRUCTURE	39
		4.1 Abstract	39
		4.2 Introduction	39
		4.3 Experimental	40
		4.4 Result and Discussion	43
		4.5 Conclusions	55
		4.6 Acknowledgements	55
		4.7 References	55

CHAPTER		PAGE
v	pH INDICATOR FILM BASED ON PLASTIC/	
	CHROMOPHORES MODIFIED PCH	
	NANOCOMPOSITE FILMS	57
	5.1 Abstract	57
	5.2 Introduction	57
	5.3 Experimental	59
	5.4 Result and Discussion	63
	5.5 Conclusions	78
	5.6 Acknowledgements	78
	5.7 References	79
VI	PHYSICAL PROPERTIES AND BARRIER	
	PROPERTIES OF pH INDICATOR	
	NANOCOMPOSITE FILMS	80
	6.1 Abstract	80
	6.2 Introduction	80
	6.3 Experimental	81
	6.4 Result and Discussion	83
	6.5 Conclusions	93
	6.6 Acknowledgements	93
	6.7 References	93
VII	CONCLUSIONS AND RECOMMENDATIONS	95
	REFERENCES	97
	APPENDICES	100
	Appendix A	100
	Appendix B	101
	Appendix C	102

CHAPTER		PAGE
	Appendix D	103
	Appendix E	104
	CURRICULUM VITAE	105

LIST OF TABLES

TABLE		PAGE
	CHAPTER II	
2.1	Examples of external and internal indicators and their	
	working principle or reacting compounds to be used in	
	intelligent packaging for quality control of packed food	3
2.2	Rate of respiration of green bananas at different temperatures	12
2.3	The times of respiration rise from pre-ripening phase	
	to peak value at different temperature	13
	CHAPTER IV	
4.1	Surface area, pore diameters and pore volume from nitrogen	
	adsorption- desorption	48
4.2	Element analysis result of APPCH	48
4.3	Adsorption of methyl red by APPCH and PCH	49
4.4	Surface area, pore diameters and pore volume from nitrogen	
	adsorption- desorption	50
	CHAPTER V	
5.1	Change in hunter color (L, a, b) and total color difference	
	(TCD) values of PP/APPCH-MR (10:1) nanocomposite films	
	after indirect contact with standard ammonia	64
5.2	Change in hunter color (L, a, b) and total color difference	
	(TCD) values of PP/APPCH-MR (20:1) nanocomposite films	
	after indirect contact with standard ammonia	64
5.3	Change in hunter color (L, a, b) and total color difference	
	(TCD) values of PP/APPCH-MR (30:1) nanocomposite films	
	after indirect contact with standard ammonia	65

TABLE		PAGE	
5.4	Change in hunter color (L, a, b) and total color difference		
	(TCD) values of PP/APPCH-MR (10:1) nanocomposite films		
	after in direct contact with fresh fish tissue	69	
5.5	Change in hunter color (L, a, b) and total color difference		
	(TCD) values of PP/APPCH-MR (20:1) nanocomposite films		
	after in direct contact with fresh fish tissue	70	
5.6	Change in hunter color (L, a, b) and total color difference		
	(TCD) values of PP/APPCH-MR (30:1) nanocomposite films		
	after in direct contact with fresh fish tissue	70	
5.7	Change in hunter color (L, a, b) and total color difference		
	(TCD) values of LDPE/PCH-BTB (10:1) nanocomposite films		
	after indirect contact with standard carbon dioxide and excess		
	water	72	
5.8	Change in hunter color (L, a, b) and total color difference		
	(TCD) values of LDPE/PCH-BTB (20:1) nanocomposite films		
	after indirect contact with standard carbon dioxide and excess		
	water	73	
5.9	Change in hunter color (L, a, b) and total color difference		
	(TCD) values of LDPE/PCH-BTB (20:1) nanocomposite films		
	after indirect contact with standard carbon dioxide and excess		
	water	73	
	CHAPTER VI		
6.1	Melting and Crystallization behavior	84	
6.2	Thermal behavior	85	
6.3	Oxygen gas transmission rate of PP and PP/APPCH-MR		
	nanocomposites	92	
6.4	Oxygen gas transmission rate of LDPE and LDPE/PCH-BTB		
	nanocomposites	93	

LIST OF FIGURES

FIGURE		PAGE	
	CHAPTER II		
2.1	Change in CO ₂ level in golden drop at 25°C with indicator		
	level which showed color change with time	6	
2.2	Correlation of sensor response (spin-coated at 1000 rpm)		
	and changes in bacterial population of fresh cod kept at		
	20°C over time	8	
2.3	Typical BCG sensor responses to a spoiling whiting sample	9	
2.4	Rate of production of carbon dioxide by bananas (initially unripe)		
	at different temperatures	13	
2.5	Heats of respiration of bananas which stored at 13, 17, 20		
	and 30 °C in ambient air and CAs containing 4% O_2 - 5% CO_2		
	and 4% O ₂ - 10% CO ₂	15	
2.6	O ₂ consumption rate of bananas which stored at 13, 17, 20		
	and 30 °C in ambient air and CAs containing 4% O_2 - 5% CO_2		
	and 4% O ₂ - 10% CO ₂	15	
2.7	CO ₂ evolution rate of bananas which stored at 13, 17, 20		
	and 30 °C in ambient air and CAs containing 4% O_2 - 5% CO_2		
	and 4% O ₂ - 10% CO ₂	16	
2.8	Respiration rate of unheated mango, heat treatment at 42		
	and 46°C for 85 and 75 min, respectively stored at 13°C	17	
2.9	Mechanism of methyl red indicator in yellow color (left)		
	and red color (right)	18	
2.10	Mechanism of bromoyhymol blue indicator in yellow color		
	(left), intermediate between yellow and blue (middle) and		
	blue color (right)	18	
2.11	Structure of 2:1 layer silicate	20	
2.12	Schematic diagrams for the adsorption of BBF by the acidified		
	APTES particles	22	

FIGURE		PAGE
2.13	Structure of surlyn [®]	24
	CHAPTER III	
3.1	The color of boric solution changed from pink to green	35
3.2	The color changed back to pink after titrated with 0.01 N HCl	35
	CHAPTER IV	
4.1	(a) Na-BTN, (b) OBTN, (c) PCH and (d) APPCH	43
4.2	The XRD patterns of (a) Na-BTN, (b) OBTN (CTAB) and	
	(c) OBTN (CTAC)	44
4.3	Fourier transform infrared spectroscopy spectra of (a) Na-BTN,	
	(b) OBTN, (c) PCH and (d) APPCH	45
4.4	Scanning Electron Microscope images of (a) Na-BTN, (b) PCH	
	and (c) APPCH	47
4.5	Adsorption of methyl red by (a) APPCH and (b) PCH	49
4.6	(a) methyl red modified APPCH and (b) bromothymol blue	
	modified PCH at various weight ratio of clay and pH dye;	
	10:1, 20:1 and 30:1	51
4.7	The XRD patterns of (a) APPCH, (b) APPCH-MR 10:1,	
	(c) APPCH-MR 20:1 and (d) APPCH-MR 30:1	51
4.8	The XRD patterns of (a) PCH, (b) PCH-BTB 10:1,	
	(c) PCH-BTB 20:1 and (d) PCH-BTB 30:1	52
4.9	SEM images of (a) APPCH-MR 10:1, (b) APPCH-MR 20:1	
	and (c) APPCH-MR 30:1	53
4.10	SEM images of (a) PCH-BTB 10:1, (b) PCH-BTB 20:1	
	and (c) PCH-BTB 30:1	54
	CHAPTER V	
5.1	Changes in TCD values of the pH indicator films after indirect	
	contact with standard ammonia during storage at room temperature	65

FIGURE		PAGE	
5.2	Changes in pH of standard ammonia	66	
5.3	Color changes of the pH indicator films (a) before and		
	(b) after indirect contact with 25 ppm standard ammonia		
	during storage at room temperature	66	
5.4	Changes in total volatile basic nitrogen (TVB-N) of fresh fish		
	during storage at room temperature	67	
5.5	Color changes of PP/APPCH-MR (30:1) nanocomposite films		
	during fish storage at room temperature	68	
5.6	Changes in pH of total volatile basic nitrogen (TVB-N) of		
	fresh fish during storage at room temperature	69	
5.7	Changes in total color difference values (ΔE) of pH indicator		
	film at various weight ratio of APPCH: MR (a) 10:1 (b) 20:1		
	and (c) 30:1 during fish storage at room temperature	71	
5.8	Changes in total color difference values (ΔE) of pH indicator film		
	at various weight ratio of PCH: BTB (a) 10:1 (b) 20:1 and (c) 30:1	74	
5.9	Color changes of LDPE/PCH-BTB (10:1) nanocomposite films		
	after test with standard carbon dioxide at various concentrations		
	(a) 0 ppm (b) 30 ppm (c) 60 ppm (d) 90 ppm (e) 120 ppm and		
	(f) 150 ppm	74	
5.10	Changes in pH of fresh banana during storage at room temperature	75	
5.11	Reference bananas ripening at room temperature	75	
5.12	Color change of LDPE/PCH-BTB (10:1) nanocomposite film		
	during banana ripening	76	
5.13	The leakage of methyl red from the PP/APPCH-MR		
	nanocomposite films	77	
5.14	The leakage of bromothymol blue from LDPE/PCH-BTB		
	nanocomposite films	78	

FIGURE		PAGE	
	CHAPTER VI		
6.1	DSC thermograms of PP/APPCH-MR nanocomposites		
	(a) crystallization temperature and (b) melting temperature	86	
6.2	DSC thermograms of LDPE/PCH-BTB nanocomposites		
	(a) crystallization temperature and (b) melting temperature	87	
6.3	TG curves of PP/APPCH-MR nanocomposites	88	
6.4	TG curves of LDPE/PCH-BTB nanocomposites	88	
6.5	Young's Modulus of PP and PP/APPCH-MR nanocomposite films	89	
6.6	Tensile Strength of PP and PP/APPCH-MR nanocomposite films	90	
6.7	% Elongation at yield of PP and PP/APPCH-MR		
	nanocomposite films	90	
6.8	Young's Modulus of LDPE and LDPE/PCH-BTB		
	nanocomposite films	91	
6.9	Tensile strength of LDPE and LDPE/PCH-BTB		
	nanocomposite films	91	
6.10	%Elongation at yield of LDPE and LDPE/PCH-BTB		
	nanocomposite films	92	