

**EFFECT OF ONIUM ION STRUCTURE ON NANOCCLAY AND  
PP NANOCOMPOSITES**

Kittimon Jirakittidul

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,  
Case Western Reserve University and Institut Français du Pétrole

2006

ISBN 974-9937-92-9

**Thesis Title:** Effect of Onium Ion Structure on Nanoclay and PP  
Nanocomposites  
**By:** Kittimon Jirakittidul  
**Program:** Polymer Science  
**Thesis Advisors:** Assoc.Prof. Rathanawan Magaraphan  
Asst. Prof. Manit Nithitanakul  
Dr. Hathaikarn Manuspiya

---

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

..... *Nantaya Yanumet.* ..... College Director  
(Assoc. Prof. Nantaya Yanumet)

**Thesis Committee:**

..... *R. Magaraphan* .....  
(Assoc.Prof. Rathanawan Magaraphan)

..... *M. Nithitanakul* .....  
(Asst. Prof. Manit Nithitanakul)

..... *Hathaikarn Manuspiya* .....  
(Dr. Hathaikarn Manuspiya)

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

..... *Suparat R* .....  
(Asst. Prof. Suparat Rukchonlatee)

**ABSTRACT**

4772009063. Polymer Science Program  
Ms. Kittimon Jirakittidul: Effect of Onium Ion Structure on  
Nanoclay and PP Nanocomposites.  
Thesis Advisors: Assoc.Prof. Rathanawan Magaraphan, Asst. Prof.  
Manit Nithitanakul and Dr. Hathaikarn Manuspiya 63 pp. ISBN 974-  
9937-92-9
- Keywords: Polypropylene/ Bentonite/ Montmorillonite/ Co-intercalation  
monomer/ Nanocomposite

In this research, two types of nanoclays which were obtained from different location and had different CEC values, were modified with four types of alkylammonium ions via ion exchange reaction. The effect of the alkylammonium ion structures on organoclays was studied including the effect of the primary alkylammonium ion, tertiary alkylammonium ion, quaternary monoalkylammonium ion, and quaternary dialkylammonium ion. The effect of cationic surfactant on two different types of nanoclays between sodium activated bentonite from Thailand and sodium montmorillonite in Japan was compared. To improve dispersion of silicate clay layer in PP, there is a new way to prepare nanocomposites by using a co-intercalation monomer. Modified organoclays with the co-intercalation monomer have slightly larger interlayer spacing than the ordinary organoclays only modified by alkylammonium ions. PP was melted and blended with modified organoclays in twin screw extrusion to generate PP-graft-modified organoclays. Then, pure PP was mixed with PP-graft-modified organoclays to obtain PP/clay nanocomposites. Subsequently thermal and mechanical properties of PP/clay nanocomposites which were prepared by modified organoclays with a co-intercalation monomer were determined.

## บทคัดย่อ

นางสาวกิตติมนต์ จิระกิตติคุณย์: อิทธิพลของโครงสร้างไอเนียมไอออนต่อนาโนเคลย์และพอลิพรอพิลีนนาโนคอมพอสิต (Effect of Onium Ion Structure on Nanoclay and PP Nanocomposites) อ. ที่ปรึกษา: รศ.ดร.รัตนวรรณ มกรพันธุ์, ผศ.ดร.มานิตย์ นิธิธนากุล และ ดร.หทัยกานต์ มนัสปิยะ 63 หน้า ISBN 974-9937-92-9

ในงานวิจัยนี้ได้ทำการดัดแปลงนาโนเคลย์ ๒ ชนิดที่มีแหล่งกำเนิดและค่า CEC ที่ต่างกันด้วยแอลคิลแอมโมเนียมไอออน ๔ ชนิดโดยผ่านปฏิกิริยาแลกเปลี่ยนไอออน ศึกษาถึงอิทธิพลของโครงสร้างแอลคิลแอมโมเนียมไอออน ออร์กาโนเคลย์ โดยเปรียบเทียบระหว่างแอลคิลแอมโมเนียมไอออนชนิดปฐมภูมิ, ชนิดทุติยภูมิ, ชนิดจตุรภูมิแบบมอนอแอลคิลและชนิดจตุรภูมิแบบไดแอลคิล ทั้งยังเปรียบเทียบอิทธิพลของสารดัดแปลงต่อนาโนเคลย์ที่ต่างชนิดกันคือเบนโทไนท์จากประเทศไทยและโซเดียมมอนท์มอริโลไนท์ในประเทศญี่ปุ่น เพื่อช่วยปรับปรุงการกระจายตัวของชั้นซิลิเกตในพอลิพรอพิลีนได้นำเอาวิธีใหม่มาใช้เตรียมนาโนคอมพอสิตซึ่งก็คือการใช้อินเตอร์คาเลชันมอนอเมอร์ ออร์กาโนเคลย์ที่ถูกดัดแปลงด้วยอินเตอร์คาเลชันมอนอเมอร์จะทำให้เกิดระยะห่างระหว่างชั้นซิลิเกตที่กว้างกว่าออร์กาโนเคลย์ที่ไม่ทำการดัดแปลงเล็กน้อย พอลิพรอพิลีนหลอมเหลวจะถูกผสมกับออร์กาโนเคลย์ที่ถูกดัดแปลงในเครื่องอัดรีดแบบเกลียวคู่จนได้พอลิพรอพิลีนกราฟท์ออร์กาโนเคลย์ที่ถูกดัดแปลง หลังจากนั้นนำเอาพอลิพรอพิลีนไปผสมกับพอลิพรอพิลีนกราฟท์ออร์กาโนเคลย์ที่ถูกดัดแปลงจะได้พอลิพรอพิลีน/เคลย์นาโนคอมพอสิต จากนั้นศึกษาสมบัติทางความร้อนและสมบัติเชิงกลของพอลิพรอพิลีน/เคลย์นาโนคอมพอสิตที่เตรียมโดยใช้ออร์กาโนเคลย์ที่ถูกดัดแปลงด้วยอินเตอร์คาเลชันมอนอเมอร์

## ACKNOWLEDGEMENTS

This work would not have been possible without the assistance of the following individuals.

The author gratefully acknowledges the partial scholarship and partial funding of the thesis work provided by Postgraduate Education and Research Programs in Petroleum and Petrochemical Technology (PPT Consortium).

This thesis work is funded by National Research Council of Thailand, Polymer Processing and Polymer Nanomaterials Research Units. The author would also like to thank Kunimine Industries Co,Ltd in Japan, Thai Nippon Chemical Industry Co,Ltd., HMC polymer company limited, and Kao Industrial Co,Ltd in Thailand for providing the raw materials to carry out in this research work.

The author would like to gratefully give special thanks to her advisors, Associated Professor Rathawan Magaraphan, Assistant Professor Nithitanakul and Dr. Hathaikarn Manuspiya for their intensive suggestions, valuable guidance and vital help throughout this research work. The author deeply thanks to Assoc. Prof. Nantaya Yanumet and Asst. Prof. Suparat Rukchonlatee for serving on her thesis committee

Special thanks go to all of the Petroleum and Petrochemical College's faculties who have tendered invaluable knowledge and go to the college staffs who give me invaluable assistance.

In addition, the author would like to thank Mr. Jirawut Junkasem for his suggestions and assistance the author would like to take this opportunity to thank all her PPC friends for their friendly assistance, cheerfulness, creative suggestions, and encouragement.

Finally, the author is greatly indebted to her mother and her family for their support, love and understanding. Without them, this work would have been successful.

## TABLE OF CONTENTS

	<b>PAGE</b>
Title Page	i
Abstract (in English)	iii
Abstract (in Thai)	iv
Acknowledgements	v
Table of contents	vi
List of Tables	viii
List of Figures	ix
 <b>CHAPTER</b>	
<b>I INTRODUCTION</b>	<b>1</b>
1.1 Structure of Silicate Clays	1
1.2 Bentonites	3
1.3 Organomodification of Silicate Clays	4
1.4 Nanocomposites Structure	4
1.5 Nanocomposite Preparation	6
1.4 Scope of Research Work	7
 <b>II LITERATURE SURVEY</b>	 <b>8</b>
 <b>III EXPERIMENTAL</b>	 <b>14</b>
3.1 Materials	14
3.2 Instruments	14
3.3 Methodology	16
3.3.1 Organomodification of Nanoclays	16
3.3.2 Characterization of Organoclays	16
3.3.3 Modified Organoclays	16
3.3.3 Characterization of Modified Organoclays	17
3.3.4 Preparation of PP/Clays Nanocomposites	17

<b>CHAPTER</b>	<b>PAGE</b>
3.3.5 Characterization of PP/Clays Nanocomposites	17
<b>IV RESULTS AND DISCUSSION</b>	<b>18</b>
4.1 Characterization of Organoclays	18
4.1.1 The Intercalation Effect of Alkylammoniumions Structure	18
4.1.2 Thermogravimetric Analysis	20
4.2 Characterization of Modified Organoclays	23
4.2.1 The Intercalation Effect of Co-Intercalation Monomer	23
4.2.2 Thermogravimetric Analysis	26
4.3 Characterization of PP/Clays Nanocomposites	27
4.3.1 Dispersion of Silicate Layer Structure	27
4.3.2 Thermogravimetric Analysis	30
4.3.3 Crystallization of PP/clays Nanocomposites	31
4.3.4 Melt Flow Index of PP/Clays Nanocomposites	37
4.3.5 Mechanical Properties of PP/Clays Nanocompsites	38
<b>V CONCLUSIONS</b>	<b>42</b>
<b>REFERENCES</b>	<b>43</b>
<b>APPENDICES</b>	<b>45</b>
<b>Appendix A</b> CEC Values of Nanoclays	45
<b>Appendix B</b> XRD Patterns of Nanoclays	46
<b>Appendix C</b> Calculation	48
<b>Appendix D</b> Condition of Ion Exchange Reaction	50
<b>Appendix E</b> Properties of PP and PP-PP/DCP	51
<b>Appendix F</b> Raw Data	52
<b>CURRICULUM VITAE</b>	<b>63</b>



## LIST OF TABLES

TABLE		PAGE
1.1	Chemical formula and characteristic parameter of commonly used 2:1 phyllosilicates	3
4.1	Thermogravimetric analysis of MMT, BEN, organoclays (MMT, BEN) for various surfactants	21
4.2	The exchanged molar content of surfactants in organo-MMTs	22
4.3	The exchanged molar content of surfactants in organo-BENs	22
4.4	Decomposition temperatures of surfactants and MAA	23
4.5	The basal spacing of modified organo-MMTs	26
4.6	The basal spacing of modified organo-BENs	26
4.7	Thermogravimetric analysis of MMT, BEN, organoclays (MMT, BEN) and modified organoclays (MMT, BEN) for various surfactants	27
4.8	The basal spacing of modified organo-MMTs and-PP/clays nanocomposites	29
4.9	The basal spacing of modified organo-BENs and PP/clays nanocomposites	30
4.10	Decomposition temperatures of PP/clays nanocomposites	31
4.11	%Crystallinity of PP/clays nanocomposites	37



## LIST OF FIGURES

FIGURE	PAGE
1.1 Structure of 2:1 phyllosilicates	2
1.2 Scheme of different types of composite arising from the interaction of layered silicates and polymers: (a) phase separated microcomposite; (b) intercalated nanocomposite; and (c) exfoliated nanocomposite	5
2.1 Alkyl chain aggregation in layered silicates: a) lateral monolayer; b) lateral bilayer	9
2.2 Schematic representation of the dispersion process of the organized clay in the PP matrix with the aid of PPMAs	11
3.1 Chemical structures of surfactants	14
4.1 XRD patterns of organo-MMTs and unmodified-MMT: a) MMT, b) MMT-SA, c) MMT-DMS, d) MMT-TMS, and e) MMT-DMDS	19
4.2 XRD patterns of organo-BENs and unmodified-BEN: a) BEN, b) BEN-SA, c) BEN-DMS, d) BEN-TMS, and e) BEN-DMDS	20
4.3 XRD patterns of organo-MMTs and modified organo-MMTs: a) MMT-SA, b) MMT-SA/MAA, c) MMT-DMS, d) MMT-DMS/MAA, e) MMT-TMS, f) MMT-TMS/MAA, g) MMT-DMDS, and h) MMT-DMDS/MAA	24
4.4 XRD patterns of organo-BENs and modified organo-BENs: a) BEN-SA, b) BEN-SA/MAA, c) BEN-DMS, d) BEN-DMS/MAA, e) BEN-TMS, f) BEN-TMS/MAA, g) BEN-DMDS, and h) BEN-DMDS/MAA	25

FIGURE	PAGE
4.5 XRD patterns of PP/MMT nanocomposites: a) PP-PP/DCP, b) PP-MMT-SA/MAA 3%, c) PP-MMT-DMS/MAA 3%, d) PP-MMT-TMS/MAA 3%, and e) PP-MMT-DMDS/MAA 3%	28
4.6 XRD patterns of PP/BEN nanocomposites: a) PP-PP/DCP, b) PP-BEN-SA/MAA 3%, c) PP-BEN-DMS/MAA 3%, d) PP-BEN-TMS/MAA 3%, and e) PP-BEN-DMDS/MAA 3%	29
4.7 DSC cooling scan thermograms of PP/MMT nanocomposites: a) PP-PP/DCP, b) PP-MMT-SA/MAA 3%, c) PP-MMT-DMS/MAA 3%, d) PP-MMT-TMS/MAA 3%, and e) PP-MMT-DMDS/MAA 3%	32
4.8 DSC cooling scan thermograms of PP/BEN nanocomposites: a) PP-PP/DCP, b) PP-BEN-SA/MAA 3%, c) PP-BEN-DMS/MAA 3%, d) BEN-TMS/MAA 3%, and e) PP-BEN-DMDS/MAA 3%	33
4.9 Crystal structures of PP/MMT nanocomposites: a) PP-PP/DCP, b) PP-MMT-SA/MAA 3%, c) PP-MMT-DMS/MAA 3%, d) PP-MMT-TMS/MAA 3%, and e) PP-MMT-DMDS/MAA 3%	34
4.10 Crystal structures of PP/BEN nanocomposites: a) PP-PP/DCP, b) PP-BEN-SA/MAA 3%, c) PP-BEN-DMS/MAA 3%, d) PP-BEN-TMS/MAA 3%, and d) PP-BEN-DMDS/MAA 3%	34
4.11 DSC heating scan thermograms of PP/MMT nanocomposites: a) PP-PP/DCP, b) PP-MMT-SA/MAA 3%, c) PP-MMT-DMS/MAA 3%, d) PP-MMT-TMS/MAA 3%, and e) PP-MMT-DMDS/MAA 3%	35

<b>FIGURE</b>		<b>PAGE</b>
4.12	DSC heating scan thermograms of PP/BEN nanocomposites: a) PP-PP/DCP, b) PP-BEN-SA/MAA 3%, c) PP-BEN- DMS/MAA 3%, d) PP-BEN-TMS/MAA 3%, and e) PP- BEN-DMDS/MAA 3%	36
4.13	MFI of PP/clays nanocomposites	38
4.14	Tensile strengths of PP/clays nanocomposites	40
4.15	Tensile modulus of PP/clays nanocomposites	40
4.16	Strains at break of PP/clays nanocomposites	41