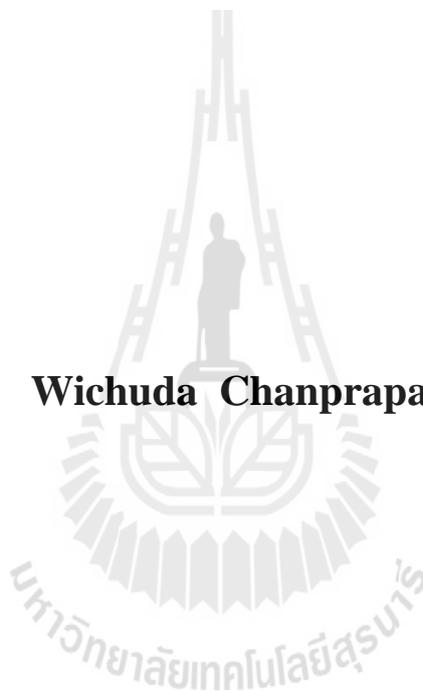


**EFFECT OF ORGANOCCLAYS ON PHYSICAL PROPERTIES
OF POLYPROPYLENE/SISAL FIBER COMPOSITES**

Wichuda Chanprapanon



**A Thesis Submitted in Partial Fulfillment of the Requirements for the
Degree of Master of Engineering in Polymer Engineering**

Suranaree University of Technology

Academic Year 2011

ผลของออร์กาโนเคลย์ต่อสมบัติทางกายภาพของพอลิเมอร์เชิงประกอบ
ระหว่างพอลิพรพิลีนกับเส้นใยป่านศรนารายณ์

นางสาววิชุดา จันทร์ประภานนท์



วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมพอลิเมอร์
มหาวิทยาลัยเทคโนโลยีสุรนารี
ปีการศึกษา 2554

EFFECT OF ORGANOCCLAYS ON PHYSICAL PROPERTIES OF POLYPROPYLENE/SISAL FIBER COMPOSITES

Suranaree University of Technology has approved this thesis submitted in partial fulfillment of the requirements for a Master's Degree.

Thesis Examining Committee

(Asst. Prof. Dr. Wimonlak Sutapan)

Chairperson

(Asst. Prof. Dr. Kasama Jarukumjorn)

Member (Thesis Advisor)

(Asst. Prof. Dr. Nitinat Suppakarn)

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วิชา จันทร์ประภานนท์ : ผลของออร์กาโนเคลย์ต่อสมบัติทางกายภาพของพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยป่านศรนารายณ์ (EFFECT OF ORGANOCCLAYS ON PHYSICAL PROPERTIES OF POLYPROPYLENE/SISAL FIBER COMPOSITES)

อาจารย์ที่ปรึกษา : ผู้ช่วยศาสตราจารย์ ดร.กษมา จารุกัจจร, 116 หน้า.

วิทยานิพนธ์นี้มีจุดมุ่งหมายเพื่อศึกษาผลของออร์กาโนเคลย์ต่อลักษณะโครงสร้างของออร์กาโนเคลย์ สมบัติทางกล สมบัติทางกระแสไฟฟ้า สมบัติทางความร้อน และสมบัติการต้านการติดไฟของพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยป่านศรนารายณ์ ปริมาณเส้นใยป่านศรนารายณ์ คือ 30 ส่วนใน 100 ส่วนของพอลิโพรพิลีน พอลิเมอร์เชิงประกอบถูกเตรียมโดยใช้เครื่องบดผสมภายใน และชิ้นงานทดสอบถูกขึ้นรูปด้วยเครื่องฉีดขึ้นรูป นอกจากนี้ พอลิโพรพิลีนกราฟท์ด้วยมาเลอิกแอนไฮไดรด์ถูกใช้เพื่อเพิ่มการยึดติดพื้นผิวระหว่างพอลิโพรพิลีนและเส้นใยป่านศรนารายณ์ รวมทั้งช่วยปรับปรุงการแตกตัวของออร์กาโนเคลย์ในพอลิโพรพิลีน

ออร์กาโนเคลย์ทางการค้าสามชนิด ได้แก่ คลอไซท์ 15 เอ คลอไซท์ 20 เอ และคลอไซท์ 30 บี ถูกเติมในพอลิโพรพิลีนและพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยป่านศรนารายณ์ เมื่อเติมออร์กาโนเคลย์ ค่าการทนต่อแรงดึงและค่าการทนต่อแรงดัดโค้งของพอลิโพรพิลีนเพิ่มขึ้น นอกจากนี้ การมีออร์กาโนเคลย์ยังปรับปรุงความเสถียรทางความร้อนของพอลิโพรพิลีน พอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับออร์กาโนเคลย์ชนิดคลอไซท์ 30 บี แสดงความเสถียรทางความร้อนและการต้านการติดไฟที่สูงที่สุด รูปแบบจากเทคนิคการเลี้ยวเบนของรังสีเอ็กซ์แสดงว่า พอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับออร์กาโนเคลย์ชนิดคลอไซท์ 15 เอ และพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับออร์กาโนเคลย์ชนิดคลอไซท์ 20 เอ มีลักษณะโครงสร้างแบบมีการขยายชั้นของออร์กาโนเคลย์ ในขณะที่พอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนที่มีการเติมด้วยออร์กาโนเคลย์ชนิดคลอไซท์ 30 บี มีลักษณะโครงสร้างแบบการแตกชั้นของออร์กาโนเคลย์

การเติมออร์กาโนเคลย์ในพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยป่านศรนารายณ์ลดค่าการทนต่อแรงดึงและค่าการทนต่อแรงดัดโค้งของพอลิโพรพิลีน แต่ค่าความต้านทานต่อแรงกระแทกและดัชนีการไหลของพอลิเมอร์เชิงประกอบไม่เปลี่ยนแปลง พอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยป่านศรนารายณ์และออร์กาโนเคลย์ชนิดคลอไซท์ 30 บี แสดงสมบัติทางกล สมบัติทางความร้อน และสมบัติการต้านการติดไฟที่สูงที่สุด รูปแบบจากเทคนิคการเลี้ยวเบนของรังสีเอ็กซ์แสดงลักษณะโครงสร้างแบบมีการแตกชั้นของออร์กาโนเคลย์สำหรับพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยป่านศรนารายณ์และออร์กาโนเคลย์

ชนิดคลอไรต์ 30 ปี ในขณะที่แสดงลักษณะโครงสร้างแบบการขยายชั้นของออร์กาโนเคลย์สำหรับพอลิเมอร์เชิงประกอบที่มีออร์กาโนเคลย์ชนิดคลอไรต์ 15 เอ และออร์กาโนเคลย์ชนิดคลอไรต์ 20 เอ

การเพิ่มปริมาณออร์กาโนเคลย์ชนิดคลอไรต์ 30 ปีไม่ส่งผลกระทบต่อสมบัติทางกล และดัชนีการไหลของพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยป่านศรนารายณ์ แต่ปรับปรุงความเสถียรทางความร้อนและการต้านการตีไฟ ลักษณะโครงสร้างแบบแตกชั้นของออร์แกโนเคลย์ถูกพบเมื่อพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยป่านศรนารายณ์ถูกเติมด้วยออร์กาโนเคลย์ชนิดคลอไรต์ 30 ปีที่ปริมาณ 1 3 และ 5 ส่วนใน 100 ส่วนของพอลิโพรพิลีน แต่การเติมออร์กาโนเคลย์ชนิดคลอไรต์ 30 ปีในปริมาณ 7 ส่วนใน 100 ส่วนของพอลิโพรพิลีนในพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยป่านศรนารายณ์แสดงการเกาะกลุ่มของออร์กาโนเคลย์

นอกจากนี้ การเพิ่มปริมาณของพอลิโพรพิลีนกราฟท์ด้วยมาเลอิกแอนไฮไดรด์ไม่ส่งผลกระทบต่ออย่างมีนัยสำคัญต่อดัชนีการไหลและความเสถียรทางความร้อนของพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยป่านศรนารายณ์กับออร์กาโนเคลย์ชนิดคลอไรต์ 30 ปี แต่ปรับปรุงสมบัติทางกลและสมบัติการต้านการตีไฟ รูปแบบจากเทคนิคการเลี้ยวเบนของรังสีเอ็กซ์ แสดงลักษณะโครงสร้างแบบการแตกชั้นของออร์กาโนเคลย์ในพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยป่านศรนารายณ์กับออร์กาโนเคลย์ชนิดคลอไรต์ 30 ปีเมื่อเติมพอลิโพรพิลีนกราฟท์ด้วยมาเลอิกแอนไฮไดรด์ในปริมาณ 5 7 และ 10 ส่วนใน 100 ส่วนของพอลิโพรพิลีน แต่แสดงเคลย์เกาะกลุ่มในพอลิเมอร์เชิงประกอบระหว่างพอลิโพรพิลีนกับเส้นใยป่านศรนารายณ์และออร์กาโนเคลย์ชนิดคลอไรต์ 30 ปีที่มีพอลิโพรพิลีนกราฟท์ด้วยมาเลอิกแอนไฮไดรด์ในปริมาณ 3 ส่วนใน 100 ส่วนของพอลิโพรพิลีน

สาขาวิชา วิศวกรรมพอลิเมอร์

ปีการศึกษา 2554

ลายมือชื่อนักศึกษา _____

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ลายมือชื่ออาจารย์ที่ปรึกษาร่วม _____

WICHUDA CHANPRAPANON : EFFECT OF ORGANOCCLAYS ON
PHYSICAL PROPERTIES OF POLYPROPYLENE/SISAL FIBER
COMPOSITES. THESIS ADVISOR : ASST. PROF. KASAMA
JARUKUMJORN, Ph.D., 116 PP.

NATURAL FIBER/POLYPROPYLENE/COMPOSITE/ORGANOCCLAY/
MALEIC ANHYDRIDE GRAFTED POLYPROPYLENE

This thesis aimed to study effect of organoclay (OMMT) on organoclay structures, mechanical properties, rheological properties, thermal properties, and flame retardant properties of polypropylene (PP)/sisal fiber (SF) composites. Sisal fiber content was 30 phr. The composites were prepared using an internal mixer and the test specimens were molded by an injection molding machine. In addition, maleic anhydride grafted polypropylene (MAPP) was used to enhance the interfacial adhesion between PP and SF and also to improve the dispersion of OMMT in PP.

Three commercial OMMTs; Cloisite[®] 15A (C15A), Cloisite[®] 20A (C20A), and Cloisite[®] 30B (C30B) were incorporated into PP and PP/SF composites. With the addition of OMMT, tensile and flexural strength of PP were increased. In addition, the presence of OMMT also enhanced thermal stability of PP. PP/C30B composite exhibited the highest thermal stability and flame retardancy. XRD patterns showed that PP/C15A composite and PP/C20A composite achieved an intercalated structure of the OMMT whereas PP/C30B composite revealed an exfoliated structure of the OMMT.

The addition of OMMT into PP/SF composites reduced tensile and flexural strength but retained impact strength and MFI of the composites. PP/SF/C30B

composite presented the highest mechanical, thermal, and flame retardant properties. XRD patterns showed an exfoliated structure of the OMMT for PP/SF/C30B composite whereas they presented an intercalated structure of the OMMT for the composites containing C15A and C20A.

Increasing C30B content exhibited insignificant effect on mechanical properties and MFI of PP/SF composites but enhanced thermal stability and flame retardancy of PP/SF composites. An exfoliated structure of the OMMT was achieved when PP/SF composite was incorporated with C30B at 1, 3, and 5 phr. However, adding C30B at 7 phr into PP/SF composite presented the OMMT agglomeration.

In addition, an increase in MAPP content insignificantly influenced MFI and thermal stability of PP/SF/C30B composite but enhanced mechanical and flame retarding properties. XRD patterns presented an exfoliated structure of the OMMT in PP/SF/C30B composites with incorporating MAPP from 5, 7 and 10 phr but revealed agglomerated clay in PP/SF/C30B composite containing MAPP at 3 phr.

School of Polymer Engineering

Academic Year 2011

Student's Signature _____

Advisor's Signature _____

Co-advisor's Signature _____

ACKNOWLEDGEMENTS

First, I would like to thank Suranaree University of Technology and Center of Excellence on Petrochemical and Materials Technology for financial supports.

I would like to express my deepest appreciation to my thesis advisor, Asst. Prof. Dr. Kasama Jarukumjorn, for all her continual guidance, support, and encouragement throughout my master degree's study. I would also like to offer thanks to my thesis co-advisor, Asst. Prof. Dr. Nitinat Suppakarn.

Many thanks go to Asst. Prof. Dr. Wimonlak Sutapan, Asst. Prof. Dr. Pranee Chumsamrong, and Asst. Prof. Dr. Yupaporn Ruksakulpiwat for being my committee members. I wish to thank all the faculty and staff members in School of Polymer Engineering for the unending support during my three years study here.

Further, I would like to acknowledge SCG Chemicals Co., Ltd. for supplying polypropylene (P700J), Southern Clay Products Inc., USA for providing organoclays (Cloisite[®] 15A, Cloisite[®] 20A, and Cloisite[®] 30B), and Chemical Innovation Co., Ltd. for supplying maleic anhydride grafted polypropylene (Fusabond P[®] MZ 109D).

Thank you to my good friends especially Ratchasit Jeencham for their help and friendship. My thanks also go to Kevin Rose for his assistance and inspiration.

Lastly, I would like to thank the most important people in my life, my family for their endless love, understandings, patience, encouragement and support always.

Wichuda Chanprapanon

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SYMBOLS AND ABBREVIATIONS

2M2HT	=	Dimethyl, dihydrogenated tallow, quaternary ammonium
APP	=	Ammonium polyphosphate
ASTM	=	American society of testing and material
CEC	=	Cation exchange capacity
FR	=	Flame retardant
D ₁₀	=	10 vol% less than or equal to a given diameter
D ₅₀	=	50 vol% less than or equal to a given diameter
D ₉₀	=	90 vol% less than or equal to a given diameter
HDPE	=	High density polyethylene
HRR	=	Heat release rate
HT	=	Hydrogenated tallow
LOI	=	Limiting oxygen index
MA	=	Maleic anhydride
MAPE	=	Maleic anhydride grafted polyethylene
MAPP	=	Maleic anhydride grafted polypropylene
meq	=	Milliequivalents
MFI	=	Melt flow index
MLR	=	Mass loss rate
MMT	=	Montmorillonite clay

SYMBOLS AND ABBREVIATIONS (Continued)

MT2EtOH	=	Methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium
MWNT	=	Multi-wall carbon nanotube
PALF	=	Pineapple leaf-fiber
PE	=	Polyethylene
phc	=	Parts per hundred of compound
OMMT	=	Organoclay
phr	=	Parts per hundred of resin
PHRR	=	Peak heat release rate
POSS	=	Polyhedral oligomeric silsesquioxane
PNC	=	Polymer nanocomposite
PP	=	Polypropylene
rpm	=	Revolutions per minute
SF	=	Sisal fiber
SWNT	=	Single-wall carbon nanotube
T	=	Tallow
T _{5%}	=	Thermal decomposition at 5% weight loss
T _{50%}	=	Thermal decomposition at 50% weight loss
T _{90%}	=	Thermal decomposition at 90% weight loss
TEM	=	Transmission electron microscopy
TGA	=	Thermogravimetric analysis
TTI	=	Time to ignition

SYMBOLS AND ABBREVIATIONS (Continued)

wt%	=	Percent by weight
vol%	=	Percent by volume
WAXD	=	Wide-angle X-ray diffractometer
XRD	=	X-ray diffractometer



CHAPTER I

INTRODUCTION

1.1 General introduction

In the last decade, natural fiber reinforced polymer composites have received considerable attention, particularly in construction, automotive, and aerospace industries, because of their eco-friendliness and cost-effectiveness. Natural fibers, such as wood fiber, banana, jute, sisal, flax, pineapple leaf, and bamboo, have numerous advantages, including light weight, low cost, biodegradability, renewable resources, ease of processing, absence of toxic by-products, and acceptable specific strength and modulus. Among natural fibers, sisal fiber is an interesting fiber because it is produced in a wide range of areas in Thailand. The exceptional mechanical characteristics of sisal fiber make its applications possible in the automotive industry and the civil construction (Fávaro, Ganzerli, De Carvalho Neto, Silva, and Radovanovic, 2010).

Up to now most of studies in the field of natural fiber composites have been focused on the use of polypropylene (PP) as a matrix due to its low price, low density, and good mechanical properties. However, the incompatibility between hydrophobic polymer and hydrophilic natural fiber results in poor interfacial adhesion between natural fiber and polymer, hence deteriorating the mechanical properties of the composites. In order to improve the adhesion between fiber and polymer, maleic anhydride grafted polypropylene (MAPP) is generally introduced as a compatibilizer

to improve the stress transfer between polymer matrix and fiber at low concentrations (Lee and Kim, 2009).

Another critical drawback of PP/natural fiber composites is their high flammability due to component materials and chemical structures of natural fiber and PP matrix. Thus, improving their flame retardancy is very important and can expand the range of their applications. Traditionally, the incorporation of flame retardants (FRs), such as halogenated compounds, phosphates, inorganic hydrated compounds, and intumescent flame retardants is widely used for enhancing the flame retardancy of PP composites (Laoutid, Bonnaud, Alexandre, Lopez-Cuesta, and Dubois, 2009). However, such FRs demonstrate significant disadvantages. Aluminium trihydrate and magnesium hydroxide require a very high loading to be effective, resulting in high density and low mechanical properties of the PP composites (Abu Bakar, Mohd Ishak, Mat Taib, Rozman, and Mohamad Jani, 2010; Sain, Park, Suhara, and Law, 2004). In addition, the halogenated flame retardants produce toxic gases and soot levels during combustion. Moreover, the intumescent flame retardant systems are relatively expensive.

In recent years, natural fiber reinforced polymer composites containing nanosized fillers have been extensively investigated to enhance the composite properties (Biswal, Mohanty, and Nayak, 2009; Deka and Maji, 2010; Ghasemi and Kord, 2009; Han, Lei, Wu, Kojima, and Suzuki, 2008; Hetzer and De Kee, 2008; Kord, 2011). Among the different nanoparticles, montmorillonite clay (MMT) is the main nanofiller presently used because it is relatively inexpensive and commercially available. It also exhibits a layered morphology with high aspect ratio and large specific surface areas. A small addition of the clay (≤ 5 wt%) into polymer composites

results a remarkable improvement in the material properties e.g. mechanical properties, thermal and dimensional stability, flame retardancy, barrier properties, and biodegradability (Biswal et al., 2009; Deka and Maji, 2010; Kord, 2011; Lee, Kang, Doh, Kim, Kim, Yoon, and Wu, 2008; Sinha Ray and Okamoto, 2003). An important key to achieve these enhanced properties is a good dispersion of the clay in polymer matrix to form an intercalated or exfoliated nanostructure. (Sinha Ray and Okamoto, 2003). However, clay is naturally hydrophilic whereas PP is hydrophobic; these lead to a low level dispersion of the clay layer in PP matrix and a poor interfacial adhesion between clay surface and PP matrix. Accordingly, the clay surface is generally modified via cation exchange with organic surfactants (Chiu, Lai, Chen, and Chu, 2004). Clay treated with any organic surfactants is called organoclay (OMMT). Several types of commercial OMMTs are currently available. In general, the main difference among of them concerns the type and the amount of organic modifiers used in the modification, which influence the final properties of the polymer nanocomposites (Santos, Liberman, Oviedo, and Mauler, 2008).

Nowadays, the main method to prepare PP nanocomposite is melt blending due to its cost effectiveness in using the conventional polymer compounding technique. This method is also compatible with the continuous nature of the industrial process, such as extrusion and injection molding (Hetzer and De Kee, 2008; Sinha Ray and Okamoto, 2003). Generally, MAPP acts as a dispersant and a compatibilizer to enhance the melt intercalation of PP molecule into the galleries of clay platelets (Lee and Kim, 2009; Yeh and Gupta, 2010).

1.2 Research objectives

The main objectives of this thesis are as follows:

(i) To study effect of OMMT type, commercially available, on OMMT structures, mechanical properties, rheological properties, thermal properties, and flame retardant properties of PP and PP/sisal fiber composites.

(ii) To study effect of commercial OMMT content on OMMT structures, mechanical properties, rheological properties, thermal properties, and flame retardant properties of PP/sisal fiber composites.

(iii) To study effect of compatibilizer content on OMMT structures, mechanical properties, rheological properties, thermal properties, and flame retardant properties of PP/sisal fiber composites filled with OMMT.

1.3 Scope and limitation of the study

In this study, effect of OMMT type, commercially available, on OMMT structures, mechanical properties, rheological properties, thermal properties, and flame retardant properties of PP and PP/sisal fiber composites was studied. Sisal fiber was used to reinforce PP. Three commercial OMMT types: Cloisite[®]15A, Cloisite[®]20A, and Cloisite[®]30B, which have different types and amounts of the modifiers were incorporated as a nanofiller to PP and PP/sisal fiber composites. In addition, MAPP was added as a compatibilizer to increase the compatibility between PP matrix and sisal fiber and also to assist the dispersion of OMMT in PP matrix. PP composites were prepared by melt blending in an internal mixer followed by an injection molding machine. Also, effect of OMMT content on OMMT structures, mechanical properties, rheological properties, thermal properties, and flame retardant

properties of PP/sisal fiber composites was investigated. OMMT contents were varied as 1, 3, 5, and 7 phr. Additionally, effect of compatibilizer content on OMMT structures, mechanical properties, rheological properties, thermal properties, and flame retardant properties of PP/sisal fiber/OMMT composites was studied. MAPP contents were varied as 3, 5, 7, and 10 phr.



CHAPTER II

LITERATURE REVIEW

2.1 Polypropylene/natural fiber composites

Over the last decade, the use of natural fibers as a reinforcing filler in polymer composites has received considerable interest both in terms of their industrial application and fundamental research. Unlike the synthetic fibers e.g. glass and carbon, the natural fibers have the advantages, such as low density, low cost, biodegradability, renewability, non-hazardous, and acceptable specific strength properties (Mohanty, Misra, Drzal, Selke, Harte, and Hinrichsen, 2005).

Natural fibers are renewable materials that can be derived from a vast range of plant. The three major components of natural fibers include cellulose, hemicelluloses, and lignin. The variations in composition of these components are derived from age, type, source of the fibers, and extraction condition used to obtain the fibers. Properties of the fibers, such as density, strength, and stiffness depend on the structure and the composition of the fibers. Cellulose is the main structural component that provides strength and stability of the plant cell wall. Hemicelluloses are plant cell wall polysaccharides closely associated to cellulose. They are also mainly responsible for moisture sorption and biodegradability. Lignin is a highly crosslinked molecular complex with amorphous structure and acts as glue between individual cells. The lignin content of the fibers is believed to influence on structure, properties, morphology, flexibility, and rate of hydrolysis (Methacanon, Weerawatsophon, Sumransin, Prahsarn, and Bergado, 2010). Properties of natural fibers, such as fiber

variability, crystallinity, and mechanical properties should be considered in selecting suitable the fibers for use in composites. Mechanical properties are the most important factor in selecting a natural fiber to give the best reinforcement in a composite material (Beckermann, 2007; Li, 2009). Table 2.1 and 2.2 show the chemical composition and mechanical properties of some common natural fibers, respectively.

Table 2.1 Chemical compositions of some common natural fibers (Bismarch, Mirshra, and Lampke, 2005).

Fiber	Cellulose (wt%)	Hemicellulose (wt%)	Lignin (wt%)	Pectin (wt%)	Waxes (wt%)
Flax	71	18.6-20.6	2.2	2.3	1.7
Hemp	70-74	17.9-22.4	3.7-5.7	0.9	0.8
Jute	61-71.5	13.6-20.4	12-13	0.2	0.5
Ramie	68.6-76.2	13.1-16.7	0.6-0.7	1.9	0.3
Coir	32-43	0.15-0.25	40-45	3-4	-
Sisal	66-78	10-14	10-14	10	2
Cotton	89-90	5.7	-	0-1	0.6

Table 2.2 Mechanical properties of some common natural fibers (Kozłowski and Władyka-Przybylak. 2008).

Fiber	Density (g/cm³)	Tensile strength (MPa)	Young's modulus (GPa)	Elongation to break (%)
Flax	1.40	800-1500	60-80	1.2-1.6
Hemp	1.48	550-900	70	1.6
Jute	1.46	400-800	10-30	1.8
Ramie	1.50	500	44	2
Coir	1.25	220	6	15-25
Sisal	1.33	600-700	38	2-3
Cotton	1.51	400	12	3-10

Polypropylene (PP) is one of the most popular thermoplastics used in short fiber reinforced composites because of its low processing temperature, good processability, and relatively low cost. However, hydrophobic polymers and hydrophilic fibers are naturally incompatible leading to poor dispersion of the fibers and weak interfacial interaction between the fibers and the polymer matrix, which then result in a composite material with poor mechanical properties. To improve the adhesion between the natural fibers and PP, maleic anhydride grafted polypropylene (MAPP) is generally introduced as a compatibilizer. It consists of long polymer chains with a MA (maleic anhydride) functional group grafted onto one end. MAPP acts as a bridge between the nonpolar polypropylene matrix and the polar fibers by chemical bonding and hydrogen bonding with the cellulose fibers through the MA groups and bonding to the matrix by means of polymer chain entanglement (Pandey, Ahn, Lee, Mohanty, and Misra, 2010). Many works have been shown that the

mechanical properties of PP/natural fiber composites are improved significantly when MAPP is used in the composites (Arzondo, Pérez, and Carella, 2005; Feng, Caulfield, and Sanadi, 2001; Gu and Kokta, 2009; Pickering, Beckermann, Alam, and Foreman, 2007; Rana, Mandal, Mitra, Jacobson, Rowell, and Banerjee, 1998). The mechanism of MAPP reacting with the fiber surface is showed in Figure 2.1.

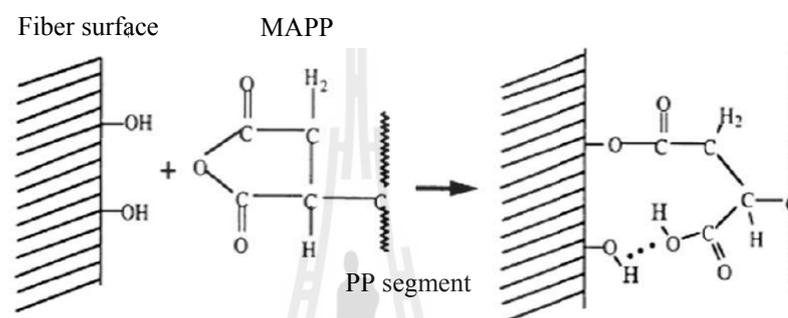


Figure 2.1 Mechanism of MAPP reacting with the cellulose fiber surface (Beckermann, 2007).

Besides the main mechanical properties of PP/natural fiber composites, fire behavior is required for many applications. PP/natural fiber composites are very sensitive to flame due to their structure and chemical composition. Both of natural fiber and PP behave differently in fire depending on their thermal stabilities, thus the flammability of the composite is influenced by them and any synergistic or antagonistic between them. Many works have been reported that the addition of natural fiber increased flammability of PP. Sain et al. (2004) reported the increase in burning rate of PP composite when either sawdust or rice husk was incorporated at 50 wt%. Moreover, the oxygen index of PP/sawdust composite and PP/rice husk composite was lower than that of pure PP. This implied the PP composites required

lower concentration of oxygen to burn. It indicated the incorporation of sawdust or rice husk increased flammability of PP. Similar observation was reported by Suppakarn and Jarukumjorn (2009). The incorporation of sisal fiber at 30 phr in PP showed higher burning rate than pure PP. It suggested that PP/sisal fiber composite exhibited high flammability. However, some studies have found that flammability of PP was decreased in the presence of natural fiber. Helwig and Paukzta (2000) reported that the introduction of flax fiber at 12.5 wt% into PP resulted in an increase in fire retardancy compared to pure PP observed by a reduction in peak heat release rate (PHRR) about 35% using a cone calorimeter test. Similarly, Borysiak, Paukzta, and Helwig (2006) also found the reduction of PHRR, time to ignition (TTI), and mass loss rates (MLR) in the PP composite with 50 wt% of pine wood. Recently, Stark, White, and Osswald (2010) reported the oxygen index of polyethylene (PE)/wood flour composites was higher than that of PE. The PHRR of PE/wood flour composites was lower than that of PE. This combination of results suggested that PE/wood flour composites exhibited improved fire performance.

Many works have been done in studying and developing the flame retardancy of PP/natural fibers composites by adding FRs, such as halogenated compounds, phosphates, inorganic hydrated compounds, intumescent flame retardants, and nanocomposites (Zhang and Horrocks, 2003). Unfortunately, the halogenated flame retardants increased undesirable productions of carbon monoxide and soot levels during combustion (Guo, Park, Lee, Kim, and Sain, 2007). In addition, these additives required a very high loading, usually more than 50 wt%, and also caused depression of mechanical properties of the PP composites (Jang and Lee, 2001; Sain et al., 2004).

Among various kind of flame retardant additives, ammonium polyphosphate (APP) is a very common and popular flame retardant for polymers (Chen and Wang, 2010). In addition, Abu bakar et al. (2010) suggested that APP was also an effective FR for materials with high oxygen contents, such as cellulose and some oxygen containing polymers. APP acts as a flame and smoke retardant by promoting the development of a char on material's surface to prevent volatile, combustible gases, and decomposition of the material.

Jeencham, Suppakarn, and Jarukumjorn (2009) reported that the addition of APP slowed down burning rate of PP/sisal fiber composites. Increasing APP contents from 10 to 40 phr decreased the burning rate of PP/sisal fiber composites. It indicated the improvement of flame retardancy of PP/sisal fiber composites with the presence of APP. On the other hand, the incorporation of APP decreased tensile, flexural, and impact properties of PP/sisal fiber composites.

Abu bakar et al. (2010) also investigated flammability and mechanical properties of PP/wood flour composites containing APP. Adding 30 wt% APP into PP/wood flour composite improved flame retardancy by increasing the oxygen index. The incorporation of APP into PP/wood flour composite reduced tensile, flexural, and impact strength.

According to environmental concerns and deteriorated mechanical properties, the focus has been shifting away from the use of conventional flame retardant additives. A new and promising approach to enhance the flame retardancy of polymer composite concerns the use of nanoscale materials and technologies accompanying with superior physical properties to offer significant advantages over conventional formulations.

2.2 Polymer/clay nanocomposites

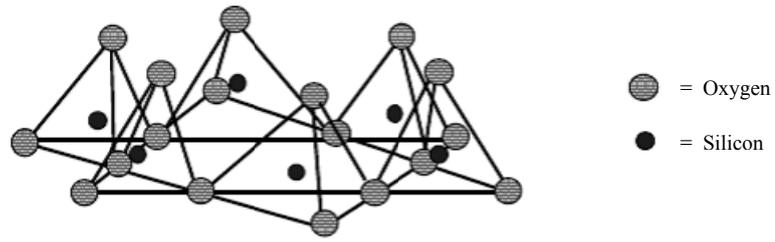
In the past decade, nanocomposites have gained a great deal of attention due to their remarkable improvement in properties. Polymer nanocomposites (PNCs) consist of a polymeric material and a reinforcing nanoscale material (nanoparticles), such as nanoclays, carbon nanotubes, nanofibers, and nanotitanium dioxide (Koo, 2005). The incorporation of nanosized filler to produce composite materials shows greater enhancement in material properties when compared with those of the microsized fillers. The main nanosized fillers used today are carbon nanotubes (synthetics) and clay (natural product). When compared with carbon nanotubes, clay is more interesting because it is relatively inexpensive and commercially available. Table 2.3 lists the economics of several common nanoparticles used to manufacture polymer nanocomposites. In addition, it exhibits a layered morphology with high aspect ratio and large specific surface areas (Nourbakhsh and Ashori, 2009). Incorporation of clay at very low loading (≤ 5 wt%) into polymeric material can improve mechanical, thermal, and processing properties as well as enhance flammability resistance and barrier properties.

Table 2.3 Economics of different types of nanoparticles (Koo, 2005).

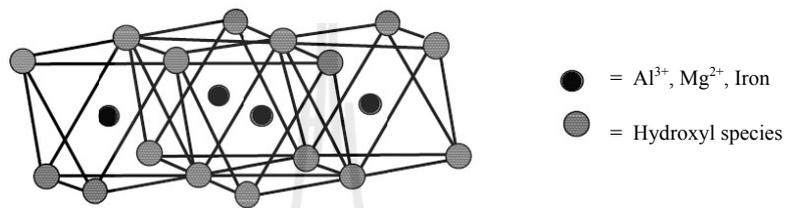
Type of nanoparticles	Cost
Montmorillonite organoclays (OMMT)	\$3.50/lb
Nanosilica	\$8.50/lb
Carbon nanofibers	\$85/lb
Polyhedral oligomeric silsesquioxane (POSS)	\$500/lb
Multi-wall carbon nanotubes (MWNTs)	\$3,000/lb
Single-wall carbon nanotubes (SWNTs)	\$227,000/lb
Nanoaluminium oxide	\$11.80/lb
Nanotitanium dioxide	\$11.80/lb

2.2.1 Clay

The most commonly used clay (layered silicates) for preparation polymer nanocomposite is smectite group, such as montmorillonite clay (MMT), which belong to the family of 2:1 layered or phyllosilicates. MMT exhibits high strength, stiffness, cation exchange capacity (CEC), aspect ratio, surface area, surface reactivity, and absorption properties. In addition, it is naturally abundant and inexpensive (Barick and Tripathy, 2010; Sardashti, 2009). The crystal structure consists of nanometer thick layers of aluminium octahedral sheet sandwiched in between two silicon tetrahedral sheets as called 2:1 type. Figure 2.2 presents the structure of MMT as 2:1 layered silicate.



Tetrahedral silicate sheet structure of clay.



Octahedral silicate sheet structure of clay.

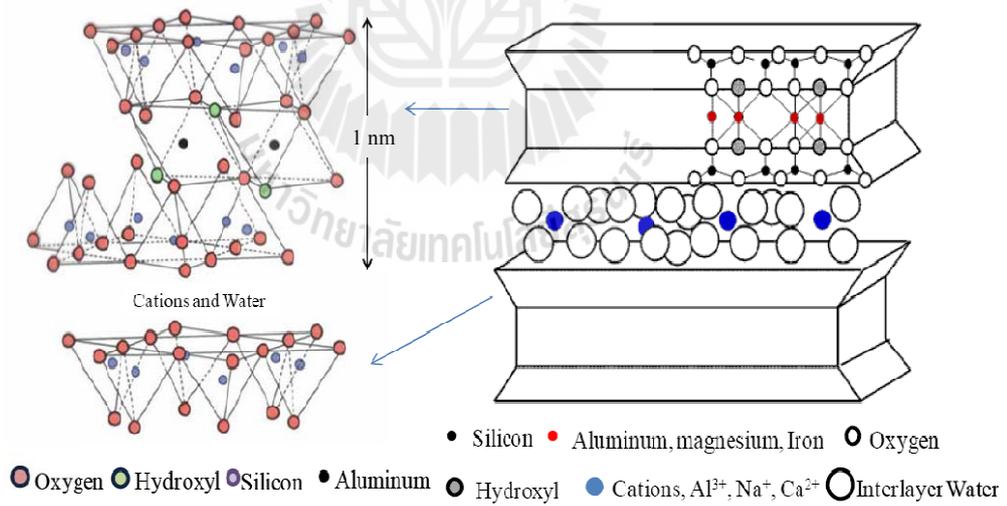


Figure 2.2 The structure of MMT, 2:1 layered silicate (Sardashti, 2009).

2.2.2 Organically modified clay (Organoclay)

By considering the surface of natural clay as hydrophilic, thus clay has a better interaction with hydrophilic polymers than with hydrophobic polymers. The incompatibility between the hydrophobic polymers and the clay particles causes agglomeration of clay in the polymer leading to the undesired composite properties. Therefore, it is necessary to modify the clay with organic surfactants.

Clay treated with any organic compound is usually called organoclay (OMMT). There are different ways to modify clays, including, adsorption, ion exchange with inorganic cations and organic cations, binding of inorganic and organic anions (mainly at the edges), grafting of organic compounds, reaction with acids, pillaring by different types of poly(hydroxo metal) cations, intraparticle and interparticle polymerization, dehydroxylation and calcination, delamination and reaggregation of smectites, and lyophilisation, ultrasound, and plasma (Bergaya and Lagaly, 2001).

Generally, the organophilic clay is typically derived from purified MMT by cation exchange with some organic surfactants, usually using ammonium cations with long alkyl tails including primary, secondary, tertiary, and quaternary alkylammonium or alkylphosphonium cations, which replace the hydrated metal cation from the interlayers in the pristine layered silicates and typically result in a larger interlayer spacing (Charu, 2008; He, Ma, Zhu, Yuan, and Qing, 2010; Santos et al., 2008). These organic modifiers mostly exchange the positively charged inorganic gallery cations with bulky ions, such as ammonium cations (polar head) connected to short hydrocarbons (non-polar tails) as shown in Figure 2.3

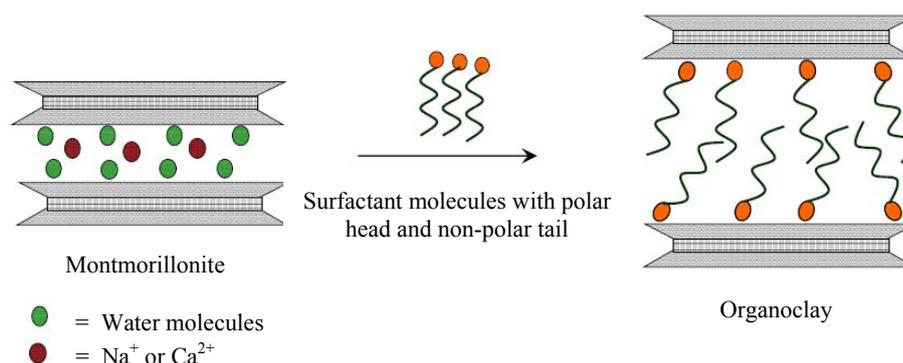


Figure 2.3 Surface modification of MMT clay with organic modifiers (Sardashti, 2009).

Nowadays, there are several worldwide suppliers for OMMTs. Southern Clay Products and Nanocor are two major suppliers in the United States. Others are Rheox Source Clay Mineral and Kunimine in Japan, Sud-Chemie in Germany, Laviosa Chimica Mineraria in Italy, and several companies in China.

The most commonly used types of ammonium ions surfactants in commercially available OMMTs are presented in Figure 2.4. The ammonium ions (N^+) can contain one aliphatic chain as shown in Figure 2.4(a) and Figure 2.4(c), or have two aliphatic chains as shown in Figure 2.4(b). The other places can be occupied by methyl groups as shown in Figure 2.4(a) or by hydroxyethyl groups as presented in Figure 2.4(c). Moreover, the chains can be consisted of (hydrogenated) tallow (<http://www.scprod.com>), which has approximately 65% C-18, 30% C-16, and 5% C-14 or coconut oil, which has mainly chain sizes between C-12 and C-16 (Xie, Gao, Liu, Pan, Vaia, Hunter, and Singh, 2001).

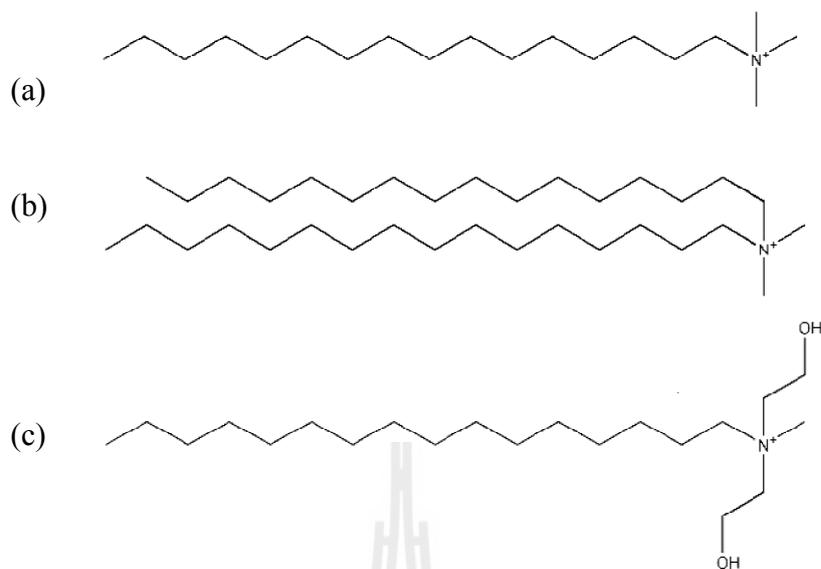


Figure 2.4 Types of ammonium ions surfactants used in commercially available OMMTs (Charu, 2008).

The structure of the organic cation on the organoclay is a key factor on physical properties of the polymer/clay nanocomposites. In general, a longer chain increases the interlayer distance and reduces the bonding strength between the clay layers, enabling the polymer chain to intercalate (Giannelis, Krishnamoorti, and Manias, 1999). Reichert, Nitz, Klinke, Brandsch, Thomann, and Mülhaupt (2000) investigated the influence of the chain length of the ammonium ion on morphology and mechanical properties of PP nanocomposites. The results showed a dramatic improvement in modulus of PP nanocomposites when the chain length reached C-12 and an optimum modulus was obtained with the chain length around C-16. Besides the chain length, Fornes, Yoon, Hunter, Keskkula, and Paul (2002) found that the number of chains (usually one or two), the presence of double bonds in the chains, and the other groups on the ammonium ion were important as well. The results

showed that without exception the OMMTs made from the surfactants with one long alkyl group led to better exfoliation and subsequently greater modulus than surfactants with two long alkyl groups. They also studied the effect of saturation level of tallow on the ammonium ion on mechanical properties and morphology of nylon 6 nanocomposites. The chain based on tallow contained a certain level of unsaturation (i.e. double bonds). It can be used in the natural and partially unsaturated state, or can be hydrolyzed to decrease the amount of double bonds, called as the hydrogenation. It was found that the hydrogenation of the tallow double bonds had no effect on morphology and mechanical properties of nylon 6 nanocomposite.

According to many commercial OMMTs modified with different types and concentrations of organic modifiers, a few studies have been attempted to compare the effect of different commercial OMMTs on physical properties of polymer nanocomposites.

Santos et al. (2008) reported the effect of OMMT type on flexural modulus of PP/OMMT nanocomposites. MAPP was used at 5 wt%. Two commercial OMMTs were Cloisite[®]15A and Cloisite[®]20A. OMMT content was fixed at 5 wt%. Both OMMTs were modified with quaternarium ammonium salt with the two long alkyl groups with 65% C-18, 30% C-16, 5% C-14, derived from hydrogenated tallow. However, the amount of ammonium salt of Cloisite[®]15A was higher than Cloisite[®]20A. XRD patterns showed increasing interlayer space from 2.68 to 3.39 nm for Cloisite[®]20A and Cloisite[®]15A, respectively. It indicated that the OMMT treated with higher amount of ammonium salt exhibited the larger interlayer space. With the incorporation of MAPP, PP/Cloisite[®]20A nanocomposite had higher flexural modulus than PP/Cloisite[®]15A nanocomposite. It was because Cloisite[®]20A was treated with a

smaller amount of organic modifier than Cloisite[®] 15A, resulting in a less organophilic clay. Thus PP/Cloisite[®] 20A nanocomposite had larger interaction capacity with the polar groups of MAPP than PP/Cloisite[®] 15A nanocomposite. When MAPP interacted with the hydroxyl group of the clay surface, the clay layers were delaminated in individual platelates, resulting in a reduction of the agglomeration. TEM micrographs of PP nanocomposites showed intercalated and partially exfoliated morphology for PP/Cloisite[®] 20A nanocomposite and presented agglomerated and intercalated morphology for PP/Cloisite[®] 15A nanocomposite.

2.2.3 Preparation methods of polymer/clay nanocomposites

In general, there are three methods used in the preparation of polymer/clay nanocomposites, including in situ polymerization, solution blending, and melt intercalation. Recently, the melt intercalation has become the standard for the preparation of polymer/clay nanocomposites, especially in industries. This method has advantages over the in situ polymerization and the solution blending. In the melt intercalation process, the layered silicate surface is mixed with the polymer matrix in the molten state. If the layer surfaces are sufficiently compatible with the chosen polymer, the polymer enters into the interlayer space and forms either an intercalated or an exfoliated nanocomposite. No solvent is required in this technique leading to an environmentally sound (Koo, 2005; Pannirselvam, 2008; Sinha Ray and Okamoto, 2003). In addition, this method is cost effectiveness in using the conventional polymer compounding technique and the compatible with the continuous nature of the industrial process, such as extrusion and injection molding (Dong and Bhattacharyya, 2008; Hetzer and De Kee, 2008; Sinha Ray and Okamoto, 2003).

2.2.4 Types of polymer/clay nanocomposites

The association of clays with polymers gives materials with different structures depending on the strength of interfacial interactions between the layered silicate and the polymer matrix. Different types of the clay dispersion in polymer/clay nanocomposite are shown in Figure 2.5.

The most desirable structure for polymer/clay nanocomposite is exfoliation, followed by intercalation (Koo, 2005). In the intercalated nanocomposite, the polymer chains are inserted in between the clay layers, increasing the long period of the stacks of the original clay structure but not destroying them. Exfoliated nanocomposite shows better homogeneity than the intercalated nanocomposite because the clay layers are uniformly dispersed in the polymer matrix and the individual clay layers are lost. In addition, the morphology of a polymer nanocomposite can be a mixture of these two extreme types.

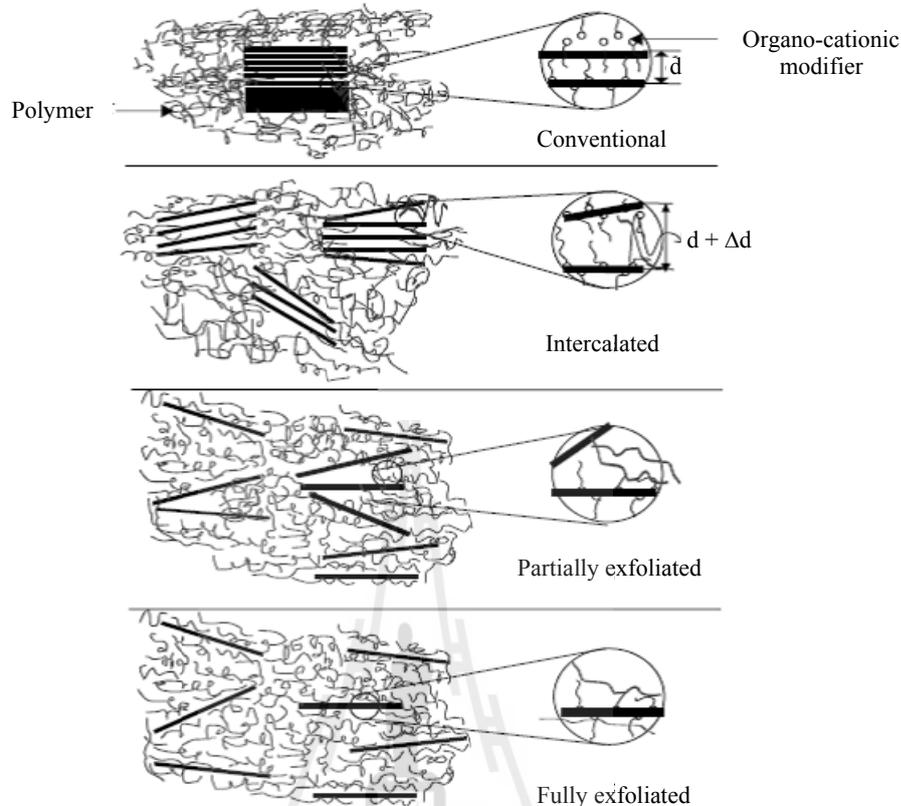


Figure 2.5 Schematic of types of the clay dispersion in polymer/clay nanocomposite (Lee, 2008).

2.2.5 Effect of compatibilizer on physical properties of polymer/clay nanocomposites

To prepare polymer/clay nanocomposites by melt processing technique, the use of compatibilizer is generally applied to resolve the different polarity between hydrophobic polymers and clay surface which even is modified with organic surfactant but it is not enough to render the compatibility between the polymer matrix and the organoclay. Chiu et al. (2004) reported the effect of MAPP on physical properties of PP/OMMT composites. X-ray diffraction (XRD) analysis and Transmission electron microscopy (TEM) results showed that PP/Cloisite[®]20A

composite achieved an intercalated structure of OMMT whereas PP/Cloisite[®]20A composite filled with MAPP exhibited a better dispersion of OMMT in PP matrix due to an adequate compatibilizer role, achieving an exfoliated structure of OMMT. In addition, adding MAPP enhanced the dynamic mechanical properties and the thermal stability of PP/Cloisite[®]20A composite. Hasegawa, Okamoto, Kawasumi, Kato, Tsukigase, and Usuki (2000) compared the clay dispersion level between PP/OMMT composite and MAPP/OMMT nanocomposite. Wide-angle X-ray diffraction (WAXD) patterns showed that the diffraction peak of PP/OMMT composite was at the same position of the OMMT. On the other hand, there was no peak in WAXD patterns of MAPP/OMMT nanocomposite, indicating an exfoliated structure of OMMT. TEM micrographs also showed that the OMMT exfoliated and uniformly dispersed in MAPP matrix. Figure 2.6 illustrated the clay dispersion process in MAPP/OMMT nanocomposite. The driving force of the intercalation originated from the strong hydrogen bonding between the MA groups and the polar clay surface. During melt blending, MAPP was first intercalated into the OMMT, resulting in an increase in the interlayer spacing of the clay. Then the layered structures of the intercalation compound were disordered by shear force. Finally, the silicate layers were exfoliated into MAPP matrix.

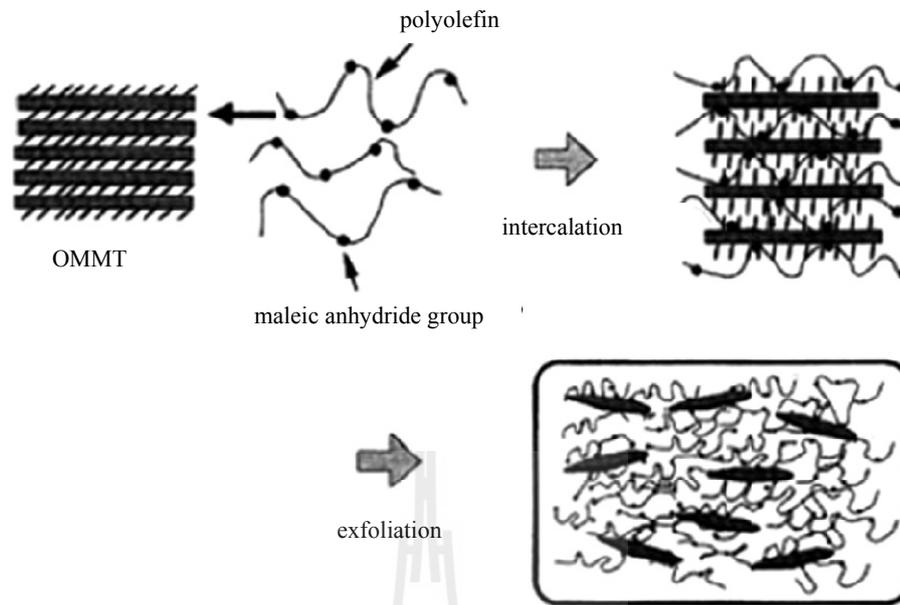


Figure 2.6 Schematic representation of the clay dispersion process (Hasegawa et al., 2000).

2.3 Polymer/natural fiber/organoclay composites

In the past, both of polymer/natural fiber composites and polymer/clay nanocomposites have been experienced extensively, but have been done separately. In recent years, few studies have attempted to combine polymer, natural fiber, and organoclay to produce the composites with improved properties. However, it can be hypothesized that the introduction of clay at a small amount into polymer/natural fiber composite can be satisfied for enhancing mechanical properties, thermal stability, barrier, and flame retarding properties. It seems that the key for these improved properties is strong interfacial adhesion between polymer matrix and the fillers and rests in exfoliating and dispersing completely individual platelets with high aspect ratios in the polymer matrix (Pannirselvam, 2008; Sinha Ray and Okamoto, 2003). Since polyolefins as polypropylene (PP) and polyethylene (PE) are hydrophobic and

have poor miscibility with hydrophilic natural fiber. In general, a compatibilizer is used to improve the adhesion between the polymer and the fiber. According to the case of organoclay and polyolefins, the introduction of a compatibilizer enhances the interaction between the polymer and the organoclay and assists the dispersion and the exfoliation of the organoclays in the polymers as well (Han et al., 2008; Hetzer and Dee Kee, 2008, Lee and Kim, 2008, and Lei, Wu, Clemons, Yao, and Xu, 2007).

2.3.1 Mechanical properties

In the case of polymer nanocomposites, most studies report the mechanical properties as a function of clay content, especially when well dispersed nanocomposites are formed. In addition, the enhancement of mechanical properties in the nanocomposite could be achieved when the interaction between polymer and nanofiller is strong (Pannirselvam, 2008; Sinha Ray and Okamoto, 2003).

Recently, the effects of clay content and compatibilizer content on mechanical properties of polymer/natural fiber composites have been investigated by many researchers. Lee and Kim (2009) found a slight improvement in tensile and flexural properties of PP/wood flour composites when OMMT was incorporated. Impact strength of PP/wood flour composite with 1 phr of OMMT was slightly higher than that without OMMT. It was because the PP/wood flour composite with OMMT had relatively higher absorption energy than the PP composite without OMMT.

Lei et al. (2007) reported that flexural and tensile strength of high density polyethylene (HDPE)/wood flour composites increased with the addition of OMMT at 1 wt%, but slightly decreased with the addition of OMMT at 3 wt%. Flexural and tensile modulus increased with increasing OMMT content as well.

Impact strength was lowered at 7.5% by the addition of 1 wt% OMMT while it had no change when OMMT content increased from 1 to 3 wt%.

Nourbakhsh and Ashori (2008) found that tensile modulus and yield of PP/bagasse flour composites increased drastically with addition 1-3 wt% OMMT, but then decreased slightly at 4 wt% OMMT. Impact strength of the composites was lowered with the addition of OMMT. Additionally, the mechanical properties of the composites were improved with the incorporating MAPP.

Biswal et al. (2009) studied the effect of OMMT content on mechanical properties of PP/pineapple leaf fiber (PALF) composites. The incorporation of OMMT at 1-3 wt% increased tensile and flexural strength of PP/PALF composites to 20% and 20.43%, respectively. Impact strength of PP/PALF composites decreased about 7.5% with the addition of OMMT. Moreover, adding OMMT at 5-7 wt% did not show any significant increase in the mechanical properties of the composites.

Kord, Hemmasi, and Ghasemi (2010) studied the properties of PP/wood flour/OMMT nanocomposites. OMMT contents were 0, 3, and 6 per hundred compounds (phc). MAPP was at 2 phc. Flexural and tensile modulus of the composite increased with the addition of OMMT at 3 phc. When 6 phc of OMMT was added into PP/wood flour composite, flexural and tensile modulus decreased due to the agglomeration of nanoparticles. However, impact strength of the composites was lower than that of PP.

Reddy, Sardashti, and Simon (2010) prepared PP/wheat straw fiber/OMMT composites. Contents of wheat straw fiber, OMMT, and MAPP were varied. Increasing wheat straw fiber content up to 50% increased flexural modulus of

PP/wheat straw fiber/OMMT composites. The presence of OMMT increased the flexural modulus of PP/wheat straw fiber composites. Furthermore, adding MAPP from 2-4 wt% improved the flexural properties of PP/wheat straw fiber composites.

On the other hand, Han et al. (2008) reported that the addition of OMMT at 2-12 wt% led to the negative effect on mechanical properties of HDPE/bamboo fiber composites. It was probably due to the migration of clay to the interface between fiber and HDPE. However, adding maleic anhydride grafted polyethylene (MAPE) as a compatibilizer into HDPE/bamboo fiber/OMMT composites increased the tensile strength and the impact strength.

In addition, the effect of the different compounding procedures on mechanical properties of polymer/natural fiber/OMMT composites was investigated. Yeh and Gupta (2010) attempted to develop a proper compounding procedure for PP/wood flour/OMMT composite. PP, wood flour, and OMMT were compounded in a counter-rotating twin screw extruder in two different ways. In one-step compounding, wood flour, OMMT, PP, and additives were introduced together at once. In two-step compounding, instead of feeding all of material at once, wood flour, PP, MAPP, and antioxidant were pre-compounded in the first step. Then, OMMT was introduced in the PP/wood flour composites in the second step. It was found that PP/wood flour/OMMT composites made with two-step compounding showed better tensile strength and impact strength than those with one-step compounding. This was because in two-step compounding, PP, wood flour, and MAPP were compounded first to have the fiber-matrix adhesion resulting in the chemical reaction between wood flour and MAPP. However, the different compounding procedures did not affect modulus of PP/wood flour/OMMT composites. Since all composites had the equal

MAPP content. Thus, the dispersion of OMMT in polymer matrix was in the same level.

Lee, Kuboki, Park, Sain, and Kontopoulou (2010) also examined the effect of mixing procedures on mechanical properties of HDPE/wood fiber/OMMT nanocomposites. Two different mixing procedures were used: direct melt blending and two-step melt-blending. In the direct mixing process, HDPE, wood fiber, MAPE, and OMMT were added to a kinetic batch mixer at the same time. Then the compounds were melt-blended in a counter-rotating twin screw extruder. In the two-step melt-blending process, a masterbatch was prepared by melt blending the MAPE and OMMT using the high shear kinetic mixer first. Then the masterbatch granules, HDPE, and wood fiber were compounded in a counter-rotating twin screw extruder. It was found that the HDPE/wood fiber/OMMT nanocomposites prepared using a two-step melt-blending process showed greater improvements in tensile and flexural properties than those with the direct melt-blending process.

2.3.2 Morphological properties

Morphology of polymer nanocomposites can be observed by monitoring the position, shape, and intensity of the basal spacing from the distributed silicate layers and also the order dispersion of clay layer in polymer. XRD and TEM are generally used to study the morphology of nanocomposites (Koo, 2005; Sinha Ray and Okamoto, 2003). XRD offers a convenient method to determine the interlayer spacing of the silicate layers in the clay and in the nanocomposites. On the other hand, TEM allows an understanding the internal structure, spatial distribution of the various phases, and views of the defective structure through direct visualization. However, to

achieve the enhancement properties of polymer composite, a good exfoliation and a well dispersion of clay layers in polymer matrix are required.

Lei et al. (2007) studied the effect of compatibilizer on the morphology of HDPE/wood flour/OMMT composites. XRD patterns showed the peak of HDPE/wood flour/OMMT at 2 wt% composite shifted to a lower angle compared with that of clay. This implied that the interlayer distance of clay increased, indicating intercalated structure of OMMT. With the addition of 2 wt% MAPE, the peak of HDPE/wood flour/OMMT composite was disappeared. This indicated that the clay was exfoliated. Additionally, Han et al. (2008) also reported that MAPE was necessary for HDPE/bamboo fiber/OMMT nanocomposite to achieve clay exfoliation. The higher clay contents, the higher the MAPE needed to exfoliate the added clay.

Zhong, Poloso, Hetzer, and De Kee (2007) investigated the effects of wood flour and OMMT on the clay structure of HDPE/wood flour/OMMT composites. Wood flour was added at 50 wt%. OMMT contents were varied as 1-5 wt%. MAPE was used at 5 wt%. The results showed that the clay in HDPE/wood flour/OMMT composites had larger d-spacing than those without adding wood flour, indicating the further separation of clay platelets during melt compounding. In addition, increasing OMMT content from 1 to 5 wt% decreased the d-spacing of HDPE/wood flour composites.

Biswal et al. (2009) reported the effect of adding pineapple leaf-fiber (PALF) on morphology of PP/OMMT nanocomposite. MAPP was used at 3 wt%. XRD pattern of OMMT showed a peak at $2\theta = 4^\circ$ which corresponded to a d-spacing of 2.42 nm. In case of PP/OMMT nanocomposite, this peak shifted to lower angle at $2\theta = 3.5^\circ$ with a d-spacing of 2.80 nm. This indicated the intercalated structure of

OMMT. Additionally, XRD pattern of PP/PALF/OMMT nanocomposite showed a disappearance of the peak, indicating the exfoliation of clay layers.

Ghasemi and Kord (2009) studied the effects of OMMT and MAPP content on morphology of PP/wood flour/OMMT nanocomposites. MAPP was at 2 phc. XRD pattern of OMMT showed a peak at $2\theta = 4.76^\circ$ with a d-spacing of 1.85 nm. XRD pattern of PP/wood flour/OMMT nanocomposite at 3 phc of OMMT, the peak shifted to lower angle at $2\theta = 4.48^\circ$ with a d-spacing of 1.97 nm. This implied the intercalated morphology. When 6 phc of OMMT was added, the peak appeared at $2\theta = 4.54^\circ$ corresponding to a d-spacing of 1.94 nm. These results showed that the nanocomposite with 3 phc of OMMT presented higher order of intercalation than the nanocomposite with 6 phc. This was probably because of the limited content of MAPP. In addition, increasing MAPP content to 4 phc resulted in an increase in d-spacing of PP/wood flour/OMMT nanocomposites. TEM micrograph of PP/wood flour/OMMT at 3 phc nanocomposite showed the better dispersion of the clay layers in the polymer matrix than that with 6 phc OMMT as confirmed by increased d-spacing from XRD. TEM micrograph of the nanocomposite with 6 phc of OMMT showed the larger size or even aggregated of dispersed clay. With increasing MAPP content, the better clay dispersion in polymer was observed.

Lee et al. (2010) examined the morphology of HDPE/wood fiber/OMMT nanocomposites prepared by two different mixing procedures. In a direct mixing process, HDPE, wood fiber, OMMT, and MAPE were added into a kinetic batch mixer at the same time. The compounds were subsequently melt-blended in a counter-rotating twin screw extruder. In the two-step melt-blending process, a masterbatch was prepared by melt blending the MAPE and OMMT using a high shear

kinetic mixer first. Then the masterbatch granules, HDPE and wood fiber were compounded in a counter-rotating twin screw extruder. XRD patterns of the nanocomposite prepared by the direct process showed a shifted peak toward lower angle than that of pure OMMT. It indicated the intercalated structure. On the other hand, the peak of nanocomposites made with the two-step melt-blending process disappeared, indicating the exfoliated structure. In addition, TEM micrographs of nanocomposites prepared by two different methods were also investigated. The nanocomposites made by the direct blending showed some clay stacks, indicating an intercalated structure. However, for the nanocomposites made by the two-step melt-blending, the silicate layers were well dispersed in the HDPE matrix, indicating an exfoliated structure.

Reddy et al. (2010) studied the morphology of PP/wheat straw fiber/OMMT composites by XRD. The PP/OMMT composite exhibited a peak shifted to lower angle than that of pure OMMT, indicating the intercalated structure. When OMMT was added into PP/wheat straw composites, the peak was shifted to lower angle than PP/OMMT composites. This results indicated that PP/wheat straw fiber/OMMT composite exhibited higher degree of intercalation than PP/OMMT composites.

2.3.3 Rheological properties

In order to understand the processability of any polymeric materials, one must understand the detailed rheological behavior of these materials in the molten state. The rheological properties of polymeric materials are greatly affected by the concentration of the particles in mixture. It has been reported that adding nanosized clay particles into pure polymers changes the rheological properties of the polymer

matrix (Lei, Hoa, and Ton-That, 2006; Sinha Ray and Okamoto, 2003; Wang, Liang, Zhao, Qu, Tan, Du, Qin, and Qiang, 2007). Understanding the rheological properties of nanocomposite melts is not only important in gaining a fundamental knowledge of the processability, but also helpful in understanding the structure-property relationships in these materials.

Zhong et al. (2007) studied the effect of OMMT on viscosity of PE/wood flour composites using a capillary rheometer. The results indicated that shear viscosity of PE/wood flour composites did not remarkably change when OMMT was added up to 5 wt%. It suggested that the addition of OMMT to 5 wt% exhibited no effect on the processability of the composites.

Sardashti (2009) studied the melt flow index (MFI) of PP/wheat straw fiber/OMMT composites with different wheat straw contents, OMMT contents, and MAPP contents. Increasing amount of wheat straw reduced the MFI of PP/wheat straw fiber/OMMT composite. The incorporation of MAPP increased the MFI of the composite due to low molecular weight of the anhydride grafted polymer. Adding OMMT reduced the MFI of the composites. Furthermore, MFI of the composites was slightly decreased with increasing OMMT to 5 wt%.

Lee et al. (2010) investigated the effects of clay dispersion and clay content on rheological properties of HDPE/wood fiber/OMMT nanocomposites by dynamic oscillatory shear measurements. HDPE/wood fiber composite showed the shear thinning behavior with the absence of Newtonian plateau. The addition of OMMT increased the complex viscosity and improved the shear-thinning behaviors of the composites.

2.3.4 Thermal properties

The thermal stability of polymeric materials is usually studied by thermogravimetric analysis (TGA). The weight loss due to the formation of volatile products after degradation at high temperature is monitored as a function of temperature. The thermal stability of nanocomposites is improved because the clay acts as a superior insulator and a mass transport barrier to the volatile products and assists in the formation of char during thermal decomposition. In the early stages of thermal decomposition, the clay normally shifts the decomposition to higher temperature. After that, this heat barrier effect results in a reverse thermal stability. In other words, the stacked silicate layers could hold accumulated heat that could be used as a heat source to accelerate the decomposition process, in conjunction with the heat flow supplied by the outside heat source (Pannirselvam, 2008; Sinha Ray and Okamoto, 2003).

Lei et al. (2007) studied the effect of OMMT on thermal properties of HDPE/wood flour composites. In case of HDPE/wood flour composite, there were two degradation peaks. The first peak was due to the wood degradation which appeared at about 351-352°C and started at 263-268°C. The second peak was the HDPE decomposition which appeared at about 470°C. The addition of 2% OMMT slightly decreased the initial degradation temperature and the first decomposition peak of HDPE/wood flour composite. It was due to the release of the low molecular weight compounds from the surfactant which was used to treat the clay to become an organoclay. Adding OMMT into HDPE/wood flour composite increased the residue weight because the inorganic compounds in clay which covered on the material

surface delayed the volatile products. It indicated that thermal stability of HDPE/wood flour composite was enhanced with the addition of OMMT.

Lee et al. (2008) studied the thermal properties of PP/wood flour/OMMT nanocomposites. The addition of OMMT (1-5 phr) increased the decomposition temperature at 50% weight loss ($T_{50\%}$) of PP because of the hindered diffusion of volatile decomposition products caused by the silicate layers in PP. Incorporation of MAPP into PP/OMMT composite also increased the $T_{50\%}$ because the dispersion of clay was improved. This resulted in an improvement in physico-chemical adsorption of the volatile products on the clay. In addition, adding wood flour at 10 and 20 phr increased the $T_{50\%}$ of PP/OMMT composites. But the $T_{50\%}$ of PP/OMMT composite decreased with the presence of wood flour at content of 30 phr.

Lee and Kim (2009) found that the addition of OMMT at 1 phr increased the initial decomposition temperature at 5% weight loss ($T_{5\%}$) of PP/wood flour composite because OMMT decreased permeability of oxygen and acted as a heat insulator.

Biswal et al. (2009) reported the effect of OMMT on thermal properties of PP/pineapple leaf-fiber (PALF) composites. The addition of PALF improved the thermal stability of PP by increasing the initial decomposition temperature and the final decomposition temperature. PP/PALF composite exhibited two decomposition peaks. The first peak was between 249 and 342.3°C due to dehydration from cellulose unit and thermal cleavage of glycosidic linkage by transglycosylation and scission of C–O and C–C bonds. The second peak was noticed around 361 and 432°C which attributed to the PP degradation. PP/PALF composite left char residue at 2.1% because the PALF as lignocellulosic fillers had a component

called lignin, which formed char during thermal degradation. Char reduced the combustion rate of polymeric materials by acting as a protective layer to not allowing the oxygen to reach the combustion zone easily resulting in the reduction in thermal degradation in the material (Abu bakar et al., 2010). In addition, the presence of OMMT in PP/PALF composite increased the initial decomposition peak and the final decomposition peak. PP/PALF/OMMT composite left more char residue at 7.8%. It was a sign of an improvement in thermal stability of PP/PALF composite.

2.3.5 Flame retardant properties

The flame retardancy is one of the most promising properties of the nanocomposites. By comparing with the composite containing conventional FRs, polymer/clay nanocomposites offer significant advantages in the area of flame retardancy. In fact, only a small amount of clay is necessary in the nanocomposites, resulting in low density, low cost, and ease of processing. In addition, clay is an environmentally friendly alternative to conventional FRs.

The clearest evidence for the flammability of nanocomposite is characterized through the cone calorimetry (Kiliaris and Papaspyrides, 2010; Pavlidou and Papaspyrides, 2008). Zhao, Qin, Gong, Feng, Zhang, and Yang (2005) found that time to ignition (TTI) of PE/OMMT nanocomposites was slightly reduced and the initial mass loss rate (MLR) and heat release rate (HRR) were higher than those of pure PE. Increasing OMMT content up to 15 phr further decreased TTI but increased initial MLR and HRR. It was caused by the decomposition of the alkyl ammonium salt used for the modification of clay (Pavlidou and Papaspyrides, 2008). However, the peak heat release rate (PHRR) and HRR of nanocomposites were significantly reduced as compared with pure PE during the combustion. With increasing OMMT

content, PHRR and HRR of PE/OMMT nanocomposites further decreased. It was because the PE/OMMT nanocomposites allowed the residue formed to act as a protective barrier on the outer surface by reducing heat and mass transfer between flame and polymer. This also acted as an insulator for the underlying materials (Laoutid et al., 2009). At the end of combustion, pure PE left no residue, while the PE/OMMT nanocomposites left a solid char-like residue.

The important key to accomplish the remarkable improvement of flame retardancy of nanocomposite is the nanodispersed clay in polymer matrix to achieve intercalated or exfoliated structures. In general, the main mechanism on flame retardancy of polymer/clay nanocomposite is the development of a formation of a high-performance carbonaceous-silicate char on the surface of nanocomposite during the burning. The carbonaceous char layers act as a barrier that protects the substrate from heat and oxygen and slows down the escape of flammable volatiles generated during polymer degradation, resulting in the improvement of flammability properties (Kiliaris and Papaspyrides, 2010; Laoutid et al., 2009; Pannirselvam, 2008; Sinha Ray and Okamoto, 2003).

Lee et al. (2010) prepared HDPE/wood fiber/OMMT nanocomposites with different OMMT contents and degree of clay dispersion. Two different mixing procedures were used to compare the clay dispersion in the composites. There were a direct melt blending and a melt blending masterbatch process. It was observed that the samples prepared by a melt blending masterbatch process had better clay dispersion than those prepared by a direct melt blending. The nanocomposites prepared by a melt blending masterbatch process achieved an exfoliated structure, while those prepared by a direct melt blending process showed an intercalated structure. The burning rate

of the nanocomposites with exfoliated structure was lowered than that of the nanocomposites with intercalated structure due to the higher degree of clay dispersion forming an insulator on the surface. In addition, increasing OMMT content up to 5 wt% decreased the burning rate of the nanocomposites.

Similarly, Kord (2011) investigated the effect of OMMT content on flammability of HDPE/rice husk flour/OMMT nanocomposites by using a burning rate test and a cone calorimetry test. The char residue of HDPE/rice husk flour/OMMT nanocomposites increased with increasing in OMMT content due to the formation of a carbonaceous silicate on the surface, which acted as an insulating barrier. No char was left in pure HDPE. The burning rate and the heat release rate (HRR) of nanocomposites decreased with increasing OMMT content. The presence of OMMT also reduced the total smoke production. It was because the inorganic nanodispersed layered silicate produced an insulator like a ceramic skin, which acted as a smoke suppressor.

CHAPTER III

EXPERIMENTAL

3.1 Materials

Isotactic polypropylene (PP; P700J) was supplied from SCG Chemicals Co.,Ltd. Sisal fiber (SF; *Agave sisalana*) was purchased from the Sisal-Handicraft OTOP group in Tambon Ban Kao, Amphur Dan Khun Thod, Nakhon Ratchasima, Thailand. The sisal fiber was cut into an approximate length of 2 mm. The average diameter of the fiber, the average length of the fiber, and the average ratio of fiber length to fiber diameter were $317.23 \pm 91.77 \mu\text{m}$, $2.13 \pm 0.46 \text{ mm}$, and 7.2 ± 2.4 , respectively. Tensile strength, Young's modulus, and elongation at break of the fiber were $329.54 \pm 90.46 \text{ MPa}$, $21.36 \pm 6.20 \text{ GPa}$, and $3.18 \pm 0.98 \%$, respectively (Kaewkuk, 2010). Three organoclays (OMMTs; Cloisite[®] 15A, Cloisite[®] 20A, and Cloisite[®] 30B) were supplied from Southern Clay Products Inc., USA. The physical properties of OMMTs used in this study are shown in Table 3.1. The chemical structures of organic modifiers of OMMTs are presented in Figure 3.1. Maleic anhydride grafted polypropylene with 0.55 wt% of maleic anhydride (MAPP; Fusabond[®] P MZ 109D, DuPont) was supplied from Chemical Innovation Co., Ltd.

Table 3.1 Physical properties of OMMTs (<http://www.scprod.com>).

OMMTs	Organic modifier	Modifier concentration (meq/100 g clay)	%Weight loss on ignition	Gallery distance (Å)
Cloisite [®] 15A	2M2HT ^a	125	43	31.5
Cloisite [®] 20A	2M2HT ^a	95	38	24.2
Cloisite [®] 30B	MT2EtOH ^b	90	30	18.5

Typical dry particle sizes of OMMTs: D₁₀ = 2 μm, D₅₀ = 6 μm, and D₉₀ = 13 μm

^a 2M2HT: dimethyl, dihydrogenated tallow, quaternary ammonium

^b MT2EtOH: methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium



Figure 3.1 Chemical structures of the organic modifiers of OMMTs: (a) Cloisite[®] 15A and Cloisite[®] 20A where HT is hydrogenated tallow (approximately 65% C-18, 30% C-16, 5% C-14) and (b) Cloisite[®] 30B where T is tallow (approximately 65% C-18, 30% C-16, 5% C-14) (<http://www.scprod.com>).

3.2 Experimental

3.2.1 Composite preparation

Prior the preparation of samples, sisal fiber and OMMTs were dried in an oven at 70°C overnight. Composites were prepared using an internal mixer (Haake Rheomix, 3000p). Sisal fiber content was fixed at 30 phr (Jeencham, 2010). MAPP was added into all PP composites. MAPP content was fixed at 5 phr (Jeencham, 2010). First, PP and MAPP were fed to the mixing chamber for 3 min and then the

sisal fiber and/or OMMT were added. The total mixing time was 15 min. The mixing temperature was 170°C and the rotation speed was 60 rpm. The test specimens were injection molded at 180°C by an injection molding machine (Chuan Lih Fa, CLF 80T).

Designation and composition of PP and PP composites containing 5 phr of MAPP with three OMMT types are shown in Table 3.2. According to the mechanical and flame retarding properties, PP/SF/3-C30B/5MAPP composite giving the optimum properties was chosen to study the effect of OMMT content on physical properties of the PP/SF composites containing 5 phr of MAPP. OMMT contents were varied as 1, 3, 5, and 7 phr. Their designation and composition are listed in Table 3.3. Furthermore, the PP/SF/3-C30B/5MAPP composite was selected to study the effect of MAPP content on physical properties of the PP/SF/3-C30B composites. MAPP contents were varied as 3, 5, 7, and 10 phr. Their designation and composition are shown in Table 3.4.



Table 3.2 Designation and composition of PP, PP/SF composite, PP/OMMT composites, and PP/SF/OMMT composites.

Designation	PP (phr)	SF (phr)	OMMTs (phr)			MAPP (phr)
			Cloisite®15A	Cloisite®20A	Cloisite®30B	
PP	100	-	-	-	-	-
PP/SF/5MAPP	100	30	-	-	-	5
PP/3-C15A/5MAPP	100	-	3	-	-	5
PP/3-C20A/5MAPP	100	-	-	3	-	5
PP/3-C30B/5MAPP	100	-	-	-	3	5
PP/SF/3-C15A/5MAPP	100	30	3	-	-	5
PP/SF/3-C20A/5MAPP	100	30	-	3	-	5
PP/SF/3-C30B/5MAPP	100	30	-	-	3	5

Cloisite®30B was selected to study the effect of organoclay content on physical properties of PP/SF composites containing 5 phr of MAPP.

Table 3.3 Designation and composition of PP/SF composites at various OMMT contents.

Designation	PP (phr)	SF (phr)	OMMT (phr)	MAPP (phr)
PP/SF/1-C30B/5MAPP	100	30	1	5
PP/SF/3-C30B/5MAPP	100	30	3	5
PP/SF/5-C30B/5MAPP	100	30	5	5
PP/SF/7-C30B/5MAPP	100	30	7	5

PP/SF/3-C30B composite was selected to study the effect of compatibilizer content on physical properties of the composites.

Table 3.4 Designation and composition of PP/SF/OMMT composites at various MAPP contents.

Designation	PP (phr)	SF (phr)	OMMT (phr)	MAPP (phr)
PP/SF/3-C30B/3MAPP	100	30	3	3
PP/SF/3-C30B/5MAPP	100	30	3	5
PP/SF/3-C30B/7MAPP	100	30	3	7
PP/SF/3-C30B/10MAPP	100	30	3	10

3.2.2 Composite characterization

3.2.2.1 Organoclay structures

Structure of OMMTs and OMMTs in the composites was characterized by an X-ray diffractometer (XRD; Bruker, D5005) operating at 40 kV and 40 mA with a Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$). XRD patterns were recorded between 2° to 10° , with a step size of 0.02° and a scan speed of $1.0^\circ/\text{min}$. The test samples were prepared by hot pressing the composite pellets from compounding process on a compression molding machine (Labtech, L1320) and were mounted to the XRD sample holders for analysis. In cases of organoclays, the powder was placed inside the XRD sample holders for the measurement. The XRD patterns were used to calculate the basal spacing or d-spacing from Bragg's law:

$$\lambda = 2d\sin\theta \quad (3.1)$$

Where λ is the wavelength of X-rays, d is the interlayer spacing of clays, and θ is the diffraction angle.

3.2.2.2 Mechanical properties

Tensile properties of PP and PP composites were examined according to ASTM D 638 using a universal testing machine (UTM; Instron, 5565) with a load cell of 5 kN, a crosshead speed of 5 mm/min, and a gauge length of 80 mm.

Flexural properties of PP and PP composites were measured following to ASTM D 790 using a three point bending mode of a universal testing machine (UTM; Instron, 5565) with a load cell of 5 kN, a crosshead speed of 15 mm/min, and a span length of 56 mm.

Unnotched Izod impact strength of PP and PP composites was evaluated according to ASTM D 256 using an impact testing machine (Atlas, BPI).

In all cases, the average values of five specimens at least were taken for each sample.

3.2.2.3 Rheological properties

Melt flow index (MFI) of PP and PP composites was measured according to ASTM D 1238 using a melt flow indexer (Kayeness, 4004) with a load of 2.16 kg at 180°C.

3.2.2.4 Thermal properties

Thermal stability of PP, OMMTs, and PP composites was examined using a thermogravimetric analyzer (TA Instruments, SDT2960) at a heating rate of 20°C/min under an air flowing rate of 100 ml/min. The temperature

ranged from room temperature to 700°C. The weight of each sample was kept within 10-15 mg. The weight change was recorded as a function of temperature.

3.2.2.5 Flame retarding properties

Flammability of PP and PP composites was studied by a horizontal burning test according to ASTM D 635, which gives a quantitative measurement of the burning rate of the material, using a horizontal vertical flame chamber instrument (Atlas, HVUL). The dimensions of the specimens used were 127 mm×12.7 mm×3.0 mm. Test specimens were placed horizontally in the flammability apparatus shown in Figure 3.2. The burning rate was calculated according to the formula:

$$V = 60L/t \quad (3.2)$$

where V is the linear burning rate in mm/min, L is the length the flame travels (75 mm), and t is the time in s for the flame to travel the distance L.

Five measurements per sample were taken in order to confirm the repeatability of the data.

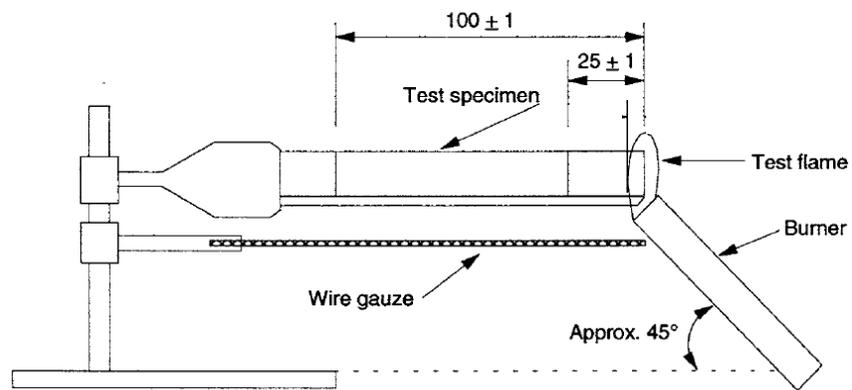
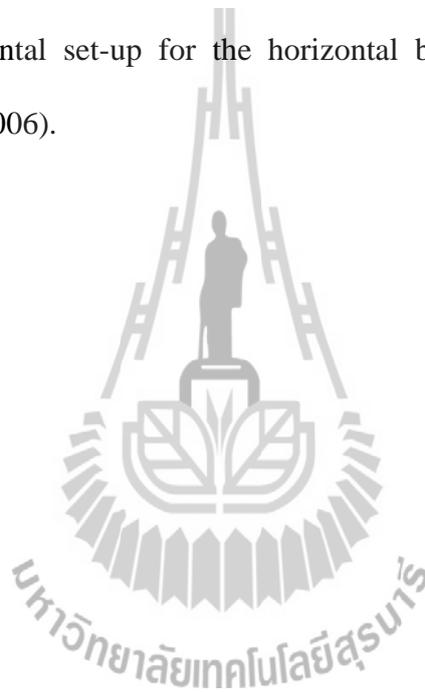


Figure 3.2 Experimental set-up for the horizontal burning test (ASTM Standard D 635, 2006).



CHAPTER IV

RESULTS AND DISCUSSION

4.1 Characterization of organoclays

4.1.1 Organoclay structures

XRD is used to identify the dispersion status of layered clays in the polymeric matrix. XRD helps to investigate intercalation and/or exfoliation levels by monitoring the diffraction peak and then calculating the d-spacing according to Bragg's equation (Chiu et al., 2004; Sardashti, 2009).

Figure 4.1 displays XRD patterns of three OMMT types; C15A, C20A, and C30B. The characteristic diffraction peaks and the interlayer distances of the platelets of three OMMT types are listed in Table 4.1. C15A and C20A were modified with the same organic modifier, a quaternary ammonium salt with the two long alkyl tails. C15A showed a diffraction peak at $2\theta = 2.87^\circ$ with a d-spacing of 3.08 nm. C20A showed a diffraction peak at $2\theta = 3.31^\circ$ with a d-spacing of 2.67 nm. The slightly higher d-spacing of C15A compared to C20A could be attributed to the higher loading of the organic modifier (Santos et al., 2008). For C30B, substitution of one long alkyl group and one methyl group with two hydroxyethyl groups in the C15A and the C20A resulted in lower d-spacing as evidenced by XRD pattern which showed a diffraction peak at $2\theta = 4.81^\circ$ with a d-spacing of 1.84 nm.

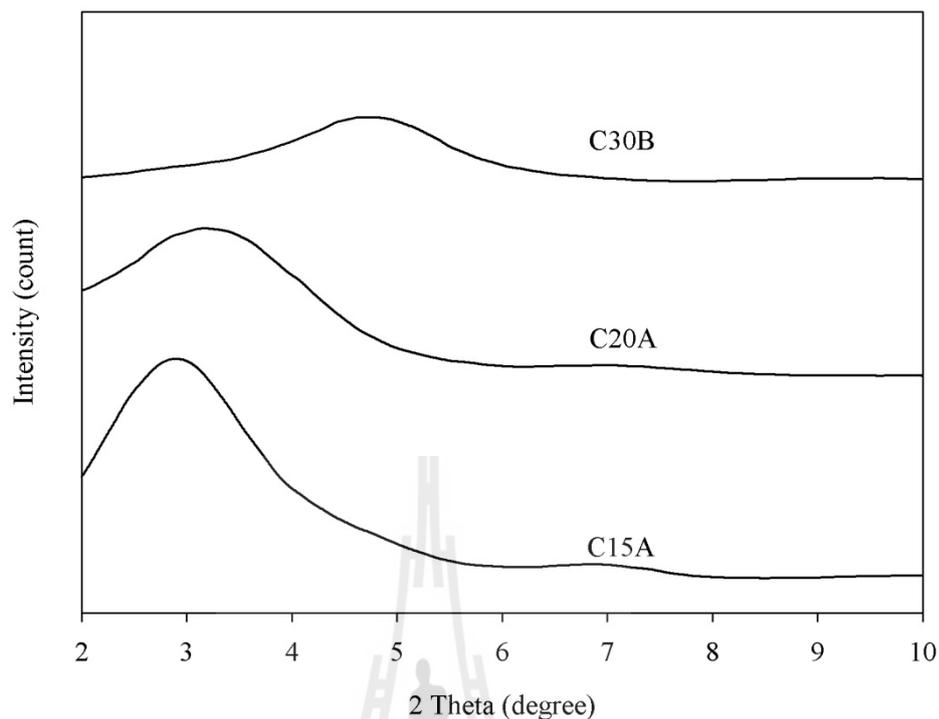


Figure 4.1 XRD patterns of three OMMT types; C15A, C20A, and C30B.

Table 4.1 2 Theta and interlayer spacing of three OMMT types; C15A, C20A, and C30B.

Designation	2 Theta (degree)	Interlayer spacing (nm)
C15A	2.87	3.08
C20A	3.31	2.67
C30B	4.81	1.84

4.1.2 Thermal properties

TGA is employed to evaluate the thermal stability of polymeric materials. Figure 4.2 and 4.3 show TGA and DTG curves of three OMMT types, respectively. TGA data of three OMMT types are presented in Table 4.2. Three

OMMT types displayed the decomposition process in three stages. The first transition was at the temperature below 200°C. It was associated with the elimination of free water and physically adsorbed water in the internal layer of clay. The second transition occurred in the temperature range from 200 to 500°C due to the thermal degradation of the organic surfactants. The third transition occurred in the temperature range from 500 to 700°C, corresponded to the removal of the structural water region in clay. This similar decomposition process of OMMT was also stated by Marras, Tsimpliaraki, Zuburtikudis, and Panayiotou (2007) and Xie et al. (2001).

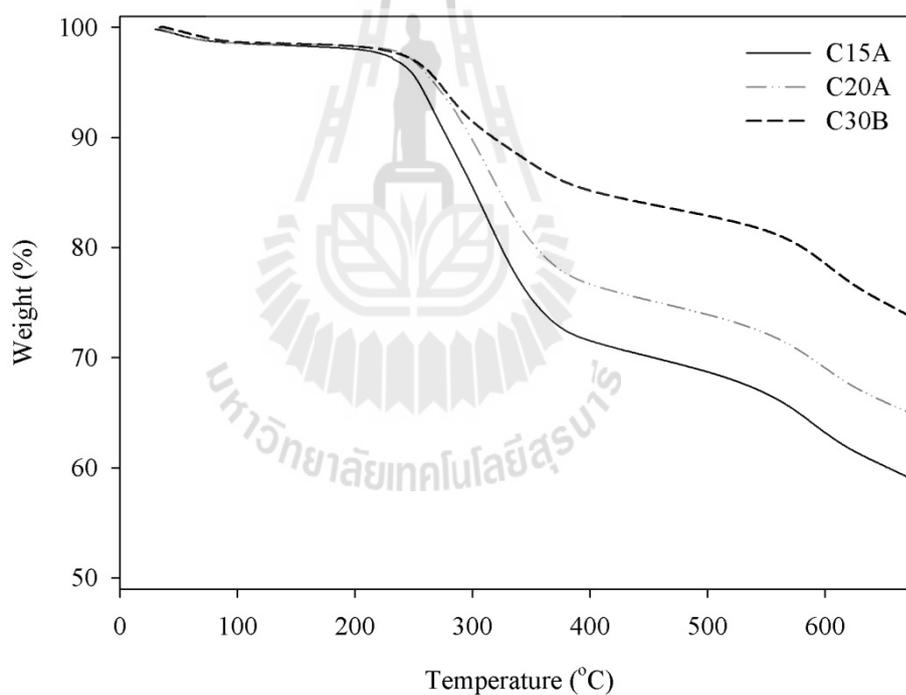


Figure 4.2 TGA curves of three OMMT types; C15A, C20A, and C30B.

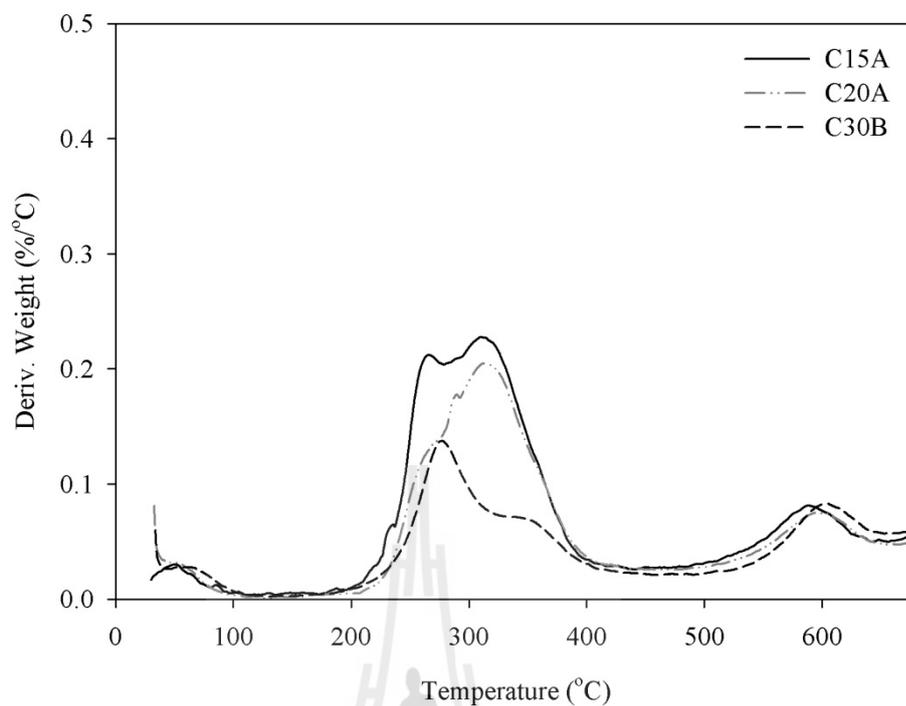


Figure 4.3 DTG curves of three OMMT types; C15A, C20A, and C30B.

Table 4.2 TGA data of three OMMT types; C15A, C20A, and C30B.

Designation	T _d (°C)		
	1 st transition	2 nd transition	3 rd transition
C15A	51	305	588
C20A	50	308	595
C30B	53	273	602

4.2 The effect of organoclay type on properties of PP and PP/sisal fiber composites

4.2.1 Organoclay structures

XRD patterns of C15A and C15A based composites are shown in Figure 4.4. C15A showed a diffraction peak at $2\theta = 2.87^\circ$ with a d-spacing of 3.08 nm. Both PP/3-C15A/5MAPP and PP/SF/3-C15A/5MAPP composites had a shift of diffraction peak to lower angle at $2\theta = 2.54^\circ$ with a d-spacing of 3.48 nm. This observation clearly indicated that these composites achieved the intercalated structure of the OMMT (Kord et al., 2010; Sinha Ray and Okamoto, 2003).

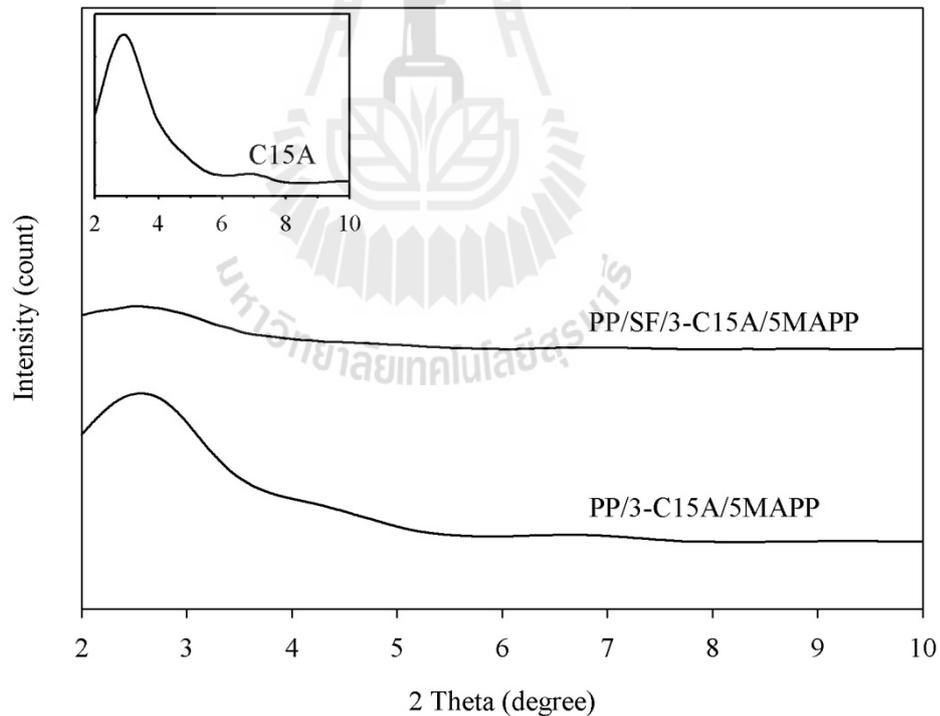


Figure 4.4 XRD patterns of C15A and C15A based composites.

XRD patterns of C20A and C20A based composites are presented in Figure 4.5. As seen, the diffraction peak of C20A was at $2\theta = 3.31^\circ$ with a d-spacing of 2.67 nm. Similar to the C15A, the peaks of PP/3-C20A/5MAPP composite and PP/SF/3-C20A/5MAPP composite were shifted to $2\theta = 2.65^\circ$ with a d-spacing of 3.33 nm and at $2\theta = 2.54^\circ$ with a d-spacing of 3.48 nm, respectively. This suggested that these composites showed intercalated structure of the OMMT.

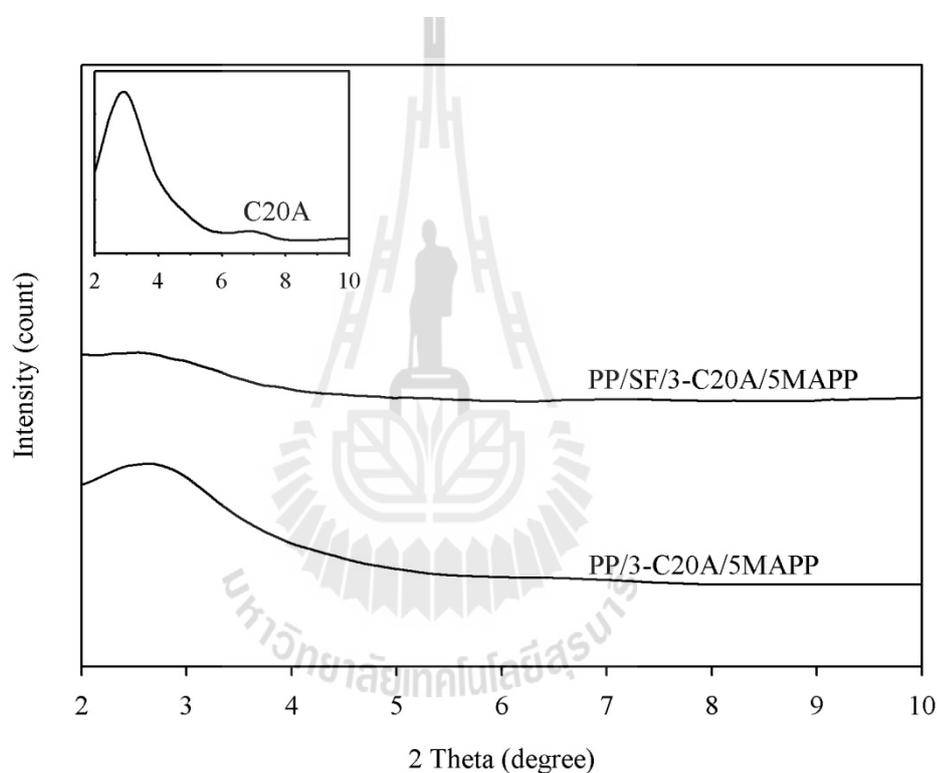


Figure 4.5 XRD patterns of C20A and C20A based composites.

XRD patterns of C30B and C30B-based composites are represented in Figure 4.6. C30B exhibited the diffraction peak at $2\theta = 4.81^\circ$ with a d-spacing of 1.84 nm. For PP/3-C30B/5MAPP composite and PP/SF/3-C30B/5MAPP composite, the diffraction peaks disappeared, indicating that the OMMT could be achieved an exfoliated structure (Barick and Tripathy, 2010; Sinha Ray and Okamoto, 2003).

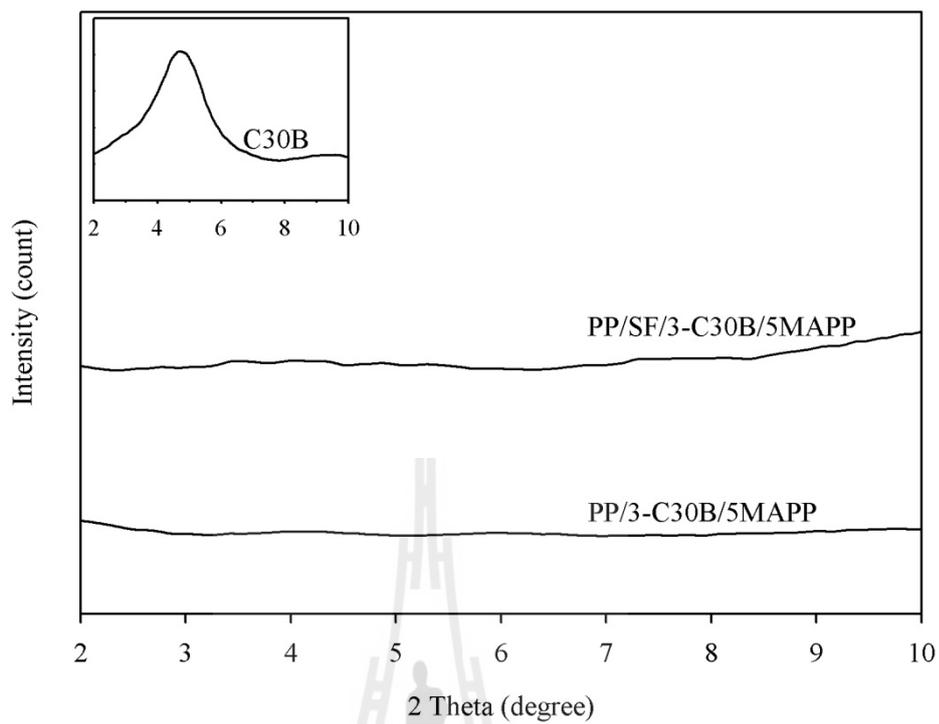


Figure 4.6 XRD patterns of C30B and C30B based composites.

The characteristic diffraction peaks and the interlayer distances of OMMTs and PP composites are listed in Table 4.3.

Table 4.3 2 Theta and interlayer spacing of three OMMT types, PP/OMMT composites, and PP/SF/OMMT composites.

Designation	2 Theta (degree)	Interlayer spacing (nm)
C15A	2.87	3.08
C20A	3.31	2.67
C30B	4.81	1.84
PP/3-C15A/5MAPP	2.54	3.48
PP/3-C20A/5MAPP	2.65	3.33
PP/3-C30B/5MAPP	-	-
PP/SF/3-C15A/5MAPP	2.54	3.48
PP/SF/3-C20A/5MAPP	2.54	3.48
PP/SF/3-C30B/5MAPP	-	-

4.2.2 Mechanical properties

Mechanical properties of PP and PP composites are summarized in Table 4.4. Figure 4.7 and 4.8 show tensile strength and modulus of PP and PP composites, respectively. MAPP was as a compatibilizer to improve the compatibility between PP and SF and also assisted the clay dispersion in PP matrix. Many researchers reported an improvement in mechanical properties of PP/natural fiber composites and PP/OMMT/natural fiber composite with the addition of MAPP as mentioned in Chapter II. In this study, all PP composites exhibited higher tensile strength and modulus than PP due to the reinforcing effect from sisal fiber and/or OMMTs. The addition of three OMMT types into PP drastically enhanced the tensile strength. It was because OMMT well dispersed in PP matrix. PP/3-C15A/5MAPP composite and PP/3-C20A/5MAPP composite achieved an intercalated structure of

OMMT while PP/3-C30B/5MAPP composite revealed an exfoliated structure of OMMT. However, there was no significant difference in tensile strength of PP filled with different OMMT types.

Adding sisal fiber into PP extremely increased tensile strength and tensile modulus shown in Figure 4.7 and 4.8. However, the tensile strength of PP/SF composites were reduced when OMMTs were added. It was probably because of the lack of MAPP or the compounding process that resulted in poor interaction between the polymer matrix and the fiber. Lee et. al (2009) found that tensile strength of PE/wood fiber composite was decreased with incorporating OMMT at 5 wt% in the direct mixing process whereas tensile strength of the composite was increased when OMMT was added in the masterbatch mixing process. Among PP/SF/OMMT composites, PP/SF/3-C30B/5MAPP composite exhibited the highest tensile strength. This could be explained by the interaction between OMMT and maleic anhydride (MA) group from MAPP as shown in Figure 4.9. C30B was treated with the organic modifier that had hydroxyethyl groups. The OH groups in the organic modifier treated C30B and unmodified side of clay might be able to react with MA group and formed hydrogen bonding as well as covalent bonding. Therefore, PP/SF/3-C30B/5MAPP composite had stronger interaction between OMMT and PP than PP/SF/3-C15A/5MAPP and PP/SF/3-C20A/5MAPP composites, resulting in higher tensile strength. There was no remarkable effect of OMMT types on tensile modulus of PP/SF composites.

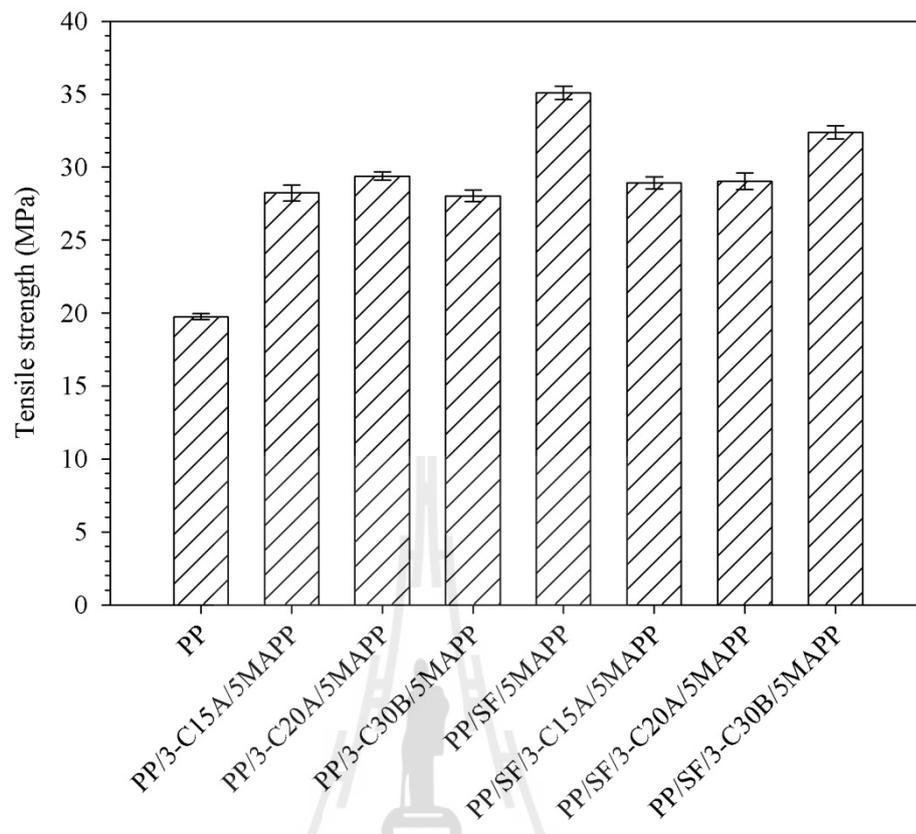


Figure 4.7 Tensile strength of PP, PP/SF composite, PP/OMMT composites, and PP/SF/OMMT composites.

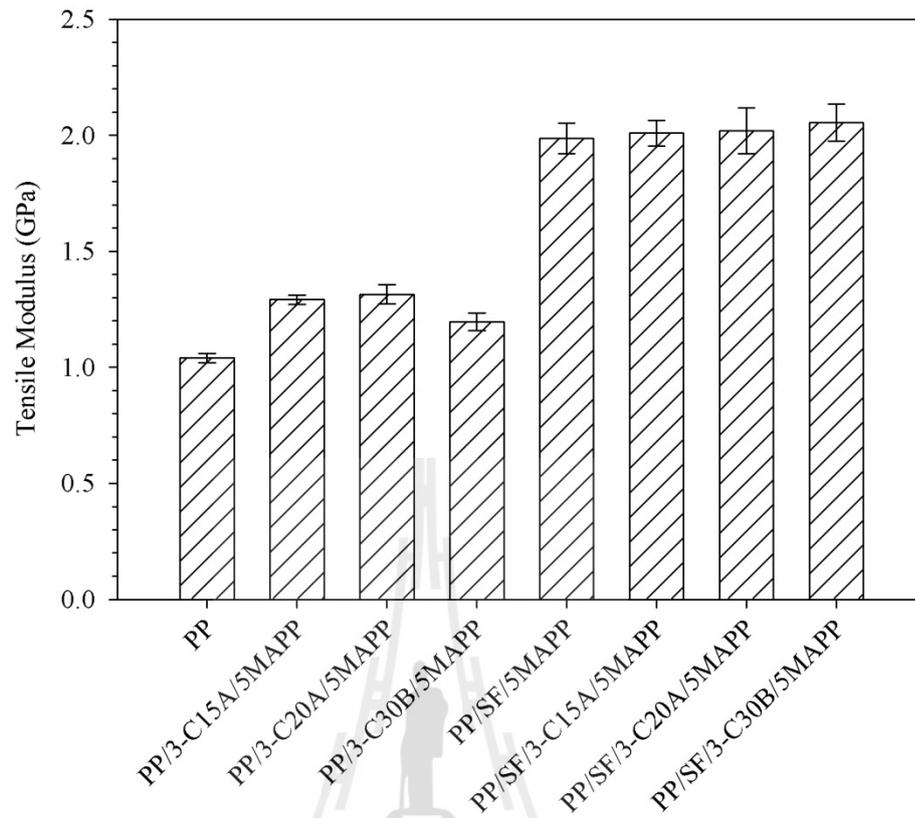


Figure 4.8 Tensile modulus of PP, PP/SF composite, PP/OMMT composites, and PP/SF/OMMT composites.

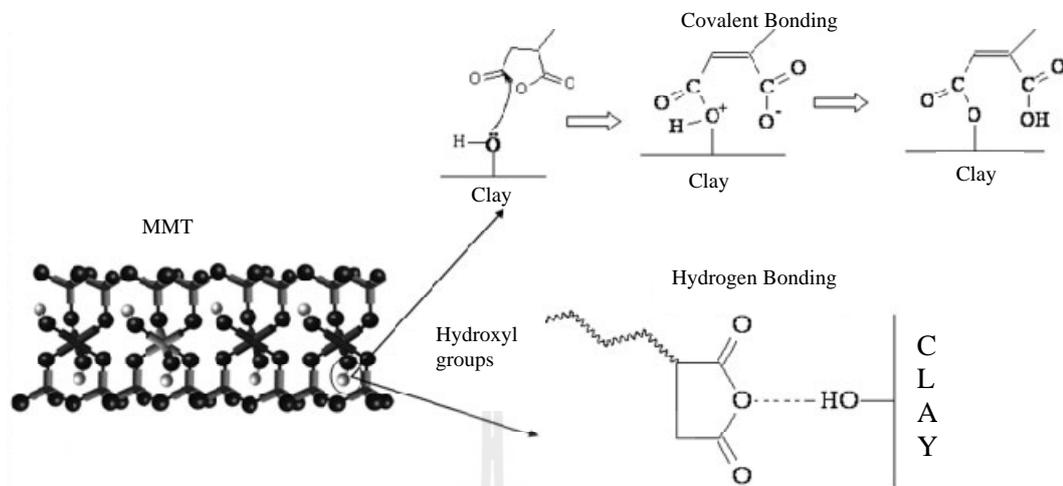


Figure 4.9 The interactions between OMMT and MA group from MAPP (Santos et al., 2008).

Flexural strength and modulus of PP and PP composites are illustrated in Figure 4.10 and 4.11, respectively. Incorporation of OMMTs significantly improved the flexural properties of PP. It was because PP/OMMT composites achieved the intercalated or the exfoliated structures of OMMT as shown in XRD patterns.

Flexural properties of PP were improved with adding sisal fiber. However, the addition of OMMTs decreased flexural strength of PP/SF composite. Sardashti (2009) also found the similar result that the incorporation of OMMT into PP/wheat straw composites decreased flexural strength because MAPP used to help the clay dispersion in PP was not enough. Among PP/SF composites containing OMMTs, PP/SF/3-C30B/5MAPP composite had the highest flexural strength. This observation could be discussed in the same way as the result of tensile strength in the

previous paragraph. In addition, it was found that adding OMMTs into PP/SF composites exhibited insignificant effect on flexural modulus.

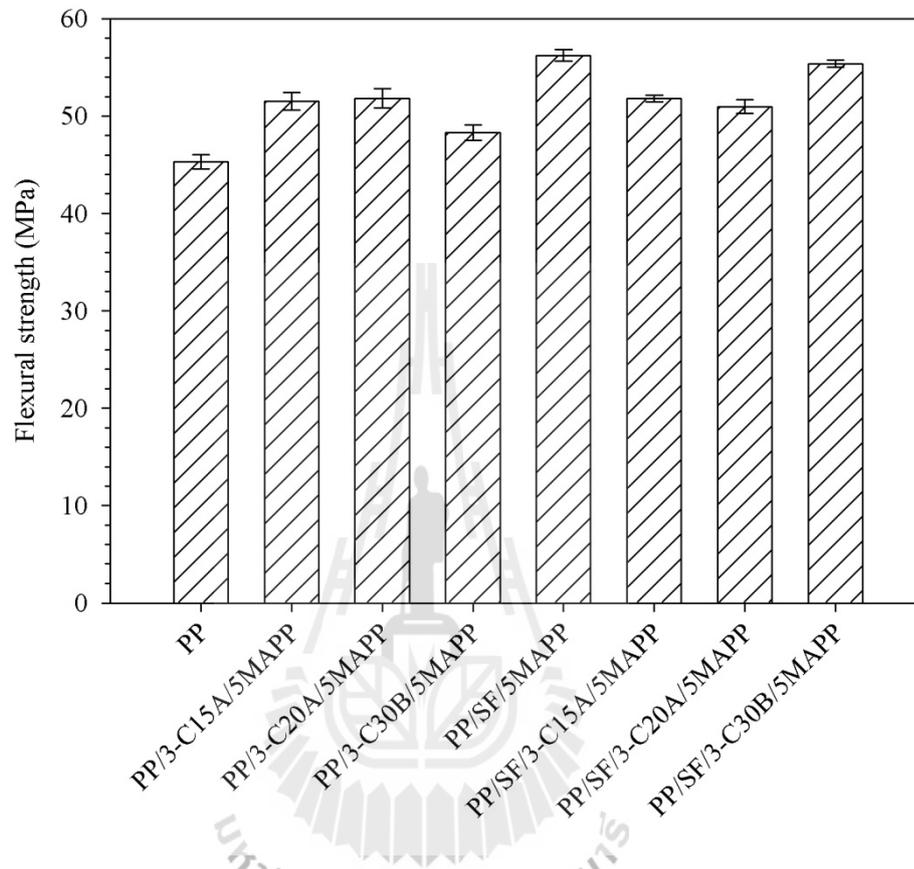


Figure 4.10 Flexural strength of PP, PP/SF composite, PP/OMMT composites, and PP/SF/OMMT composites.

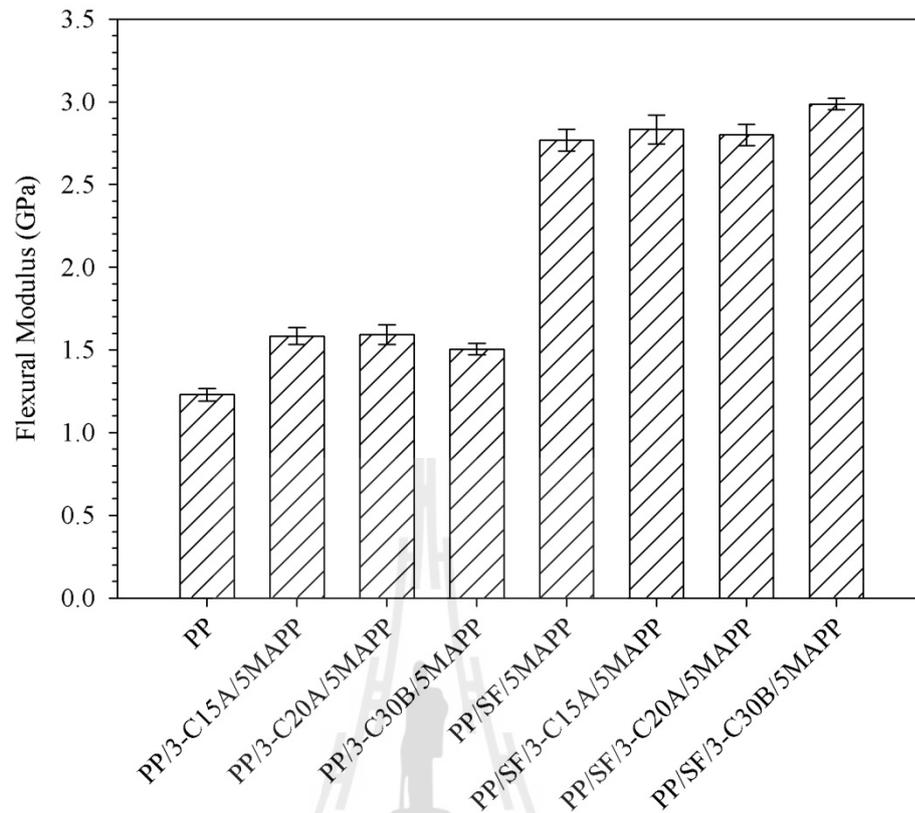


Figure 4.11 Flexural modulus of PP, PP/SF composite, PP/OMMT composites, and PP/SF/OMMT composites.

Impact strength of PP and PP composites is presented in Figure 4.12.

The result showed that the incorporation of sisal fiber and/or OMMT decreased impact strength of PP. Addition of fillers in polymer matrix reduced the impact strength because the filler particles provided sites in polymer matrix for crack initiation (Nourbakhsh and Ashori, 2009). The impact strength of PP was reduced about 29-41% with the presence of three OMMT types. The impact strength of PP/SF composite also was lowered than that of PP about 86%. However, it was observed that adding OMMTs retained the impact strength of PP/SF composites. Lee and Kim (2009) found that adding 1 phr of OMMT insignificantly increased the impact

strength of PP/wood flour composite, indicating a positive effect of the OMMT inclusion. It was because the silicate layer in composite with OMMT had higher absorption energy than the composite without OMMT during the fracture processes.

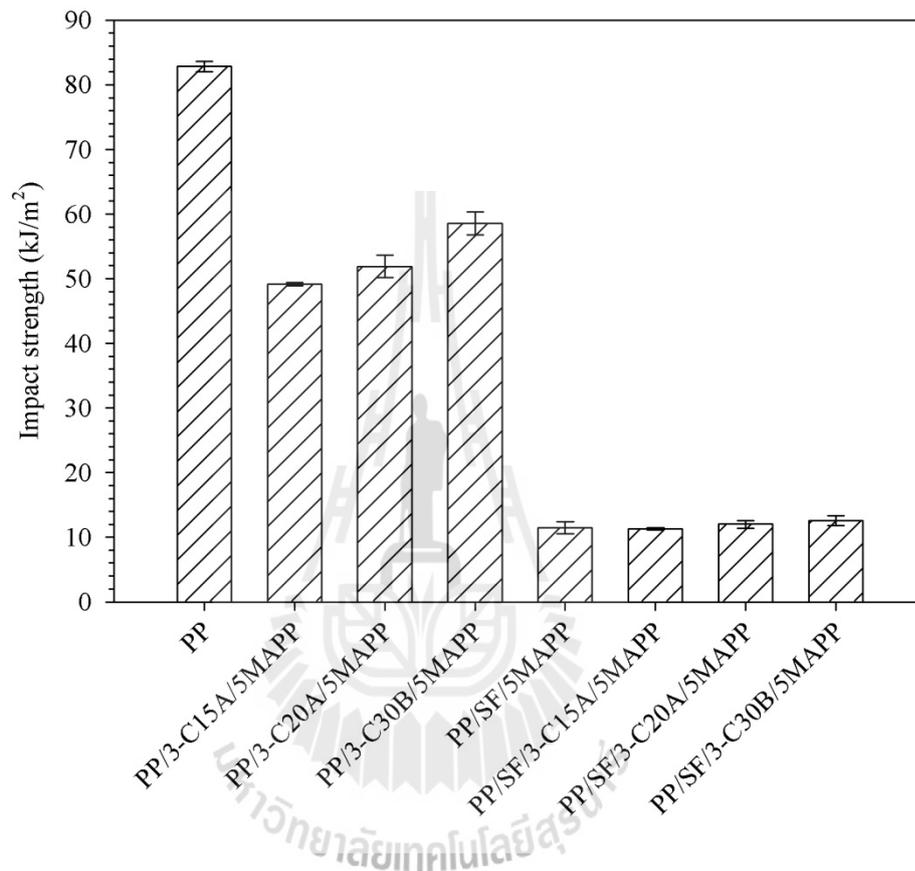


Figure 4.12 Impact strength PP, PP/SF composite, PP/OMMT composites, and PP/SF/OMMT composites.

Table 4.4 Mechanical properties of PP, PP/SF composite, PP/OMMT composites, and PP/SF/OMMT composites.

Designation	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength (kJ/m²)
PP	19.75±0.21	1.040±0.021	45.33±0.74	1.229±0.037	82.85±0.82
PP/3-C15A/5MAPP	28.23±0.55	1.292±0.020	51.52±0.89	1.583±0.051	49.18±0.25
PP/3-C20A/5MAPP	29.39±0.29	1.315±0.040	51.83±0.98	1.592±0.058	51.91±1.72
PP/3-C30B/5MAPP	28.04±0.38	1.196±0.038	48.31±0.79	1.505±0.035	58.57±1.80
PP/SF/5MAPP	35.10±0.44	1.986±0.066	56.23±0.60	2.768±0.066	11.48±0.94
PP/SF/3-C15A/5MAPP	28.92±0.42	2.010±0.055	51.78±0.33	2.833±0.087	11.30±0.19
PP/SF/3-C20A/5MAPP	29.04±0.58	2.019±0.099	50.97±0.70	2.800±0.063	12.02±0.60
PP/SF/3-C30B/5MAPP	32.39±0.47	2.055±0.079	55.38±0.38	2.987±0.034	12.57±0.78



4.2.3 Rheological properties

Table 4.5 lists MFI values of PP and PP composites. Adding C30B modified with a quarternary ammonium salt with the one long alkyl tail and two hydroxyethyl groups decreased MFI of PP. Lee et al., (2010) reported that adding OMMT increased the viscosity of HDPE/wood fiber composites because of the good clay dispersion in HDPE, achieving an exfoliated structure of OMMT. The high aspect ratio and large surface area caused a higher fraction of polymer chains to be confined by nanoplatelets; in turn, the mobility of the polymer chains was restricted. On the other hand, incorporating C15A and C20A that had the same organic modifier, a quarternary ammonium salt with the two long alkyl tails, slightly increased MFI of PP. Legon'kova and Bokarev (2005) also reported that MFI of copolyamide prepared by copolycondensation of adipic and sebacic acids with hexamethylenediamine was increased with incorporating OMMT due to the plasticizing effect of OMMT in the system.

The incorporation of SF significantly decreased the MFI of PP. It was because SF perturbed the flow of polymer and hindered the mobility of chain segments in melt flow. Adding C15A and C20A slightly increased MFI of PP/SF composites, whereas incorporating C30B exhibited no effect in MFI of PP/SF composite. Zhong et. al (2007) found that the shear viscosity of HDPE/wood flour composites did not change with adding OMMT upto 5 wt% compared with that of the composite without OMMT.

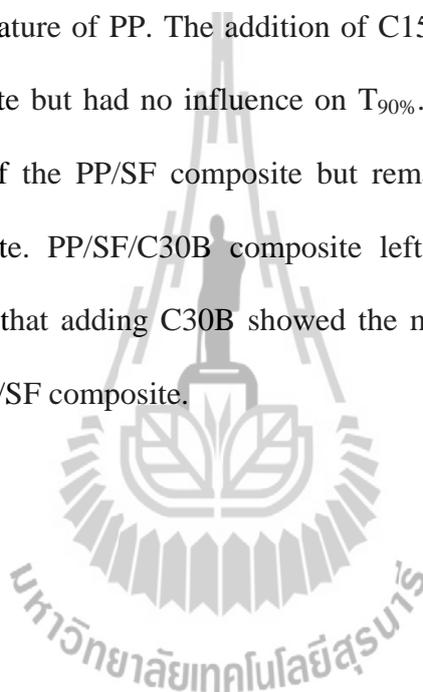
Table 4.5 Melt flow index of PP, PP/SF composite, PP/OMMT composites, and PP/SF/OMMT composites.

Designation	MFI (g/10 min)
PP	6.19±0.12
PP/3-C15A/5MAPP	7.10±0.12
PP/3-C20A/5MAPP	9.65±0.17
PP/3-C30B/5MAPP	3.97±0.07
PP/SF/5MAPP	2.06±0.14
PP/SF/3-C15A/5MAPP	5.70±0.25
PP/SF/3-C20A/5MAPP	6.17±0.22
PP/SF/3-C30B/5MAPP	1.73±0.10

4.2.4 Thermal properties

Temperature at 5% weight loss ($T_{5\%}$), temperature at 90% weight loss ($T_{90\%}$), and %weight residue at 600°C of PP and PP composites are listed in Table 4.6. As shown in Figure 4.13, TGA curves of PP and PP/OMMT composites displayed single-step degradation process. Once mass loss began, the sample weight percentages decreased continuously until reaching the residual level. PP showed $T_{5\%}$ and $T_{90\%}$ at 291°C and 406°C, respectively and left no char residue. The incorporation of OMMTs delayed the $T_{5\%}$ and the $T_{90\%}$ of PP. PP/OMMT composites left char residue at 600°C. It indicated that adding OMMT enhanced the thermal stability of PP. This similar result was reported by Chiu et al., (2004), Qin et al., (2004), and Zhao et al., (2005). It was because the clay acted as a superior insulator and a mass transport barrier to the volatile products and assisted in the formation of char during thermal decomposition, resulting in the enhancement of thermal stability of PP.

Figure 4.14 presents TGA curves of PP, PP/SF composite, and PP/SF/OMMT composites. When compared to PP, PP/SF composite exhibited two main stages of weight loss. The stage was at 250 to 400°C due to the decomposition of PP. The second stage was at 400 to 500°C due to lignin and cellulose degradation. Moreover, PP/SF composite left char residue at 1.94%. This may be because lignin, a composition of SF, acted as a char residue, resulting in an increase in thermal decomposition temperature of PP. The addition of C15A and C20A reduced the $T_{5\%}$ of the PP/SF composite but had no influence on $T_{90\%}$. In contrast, adding C30B did not change the $T_{5\%}$ of the PP/SF composite but remarkably increased the $T_{90\%}$ of PP/SF/C30B composite. PP/SF/C30B composite left the highest amount of char residue. This implied that adding C30B showed the most effective enhancement in thermal stability of PP/SF composite.



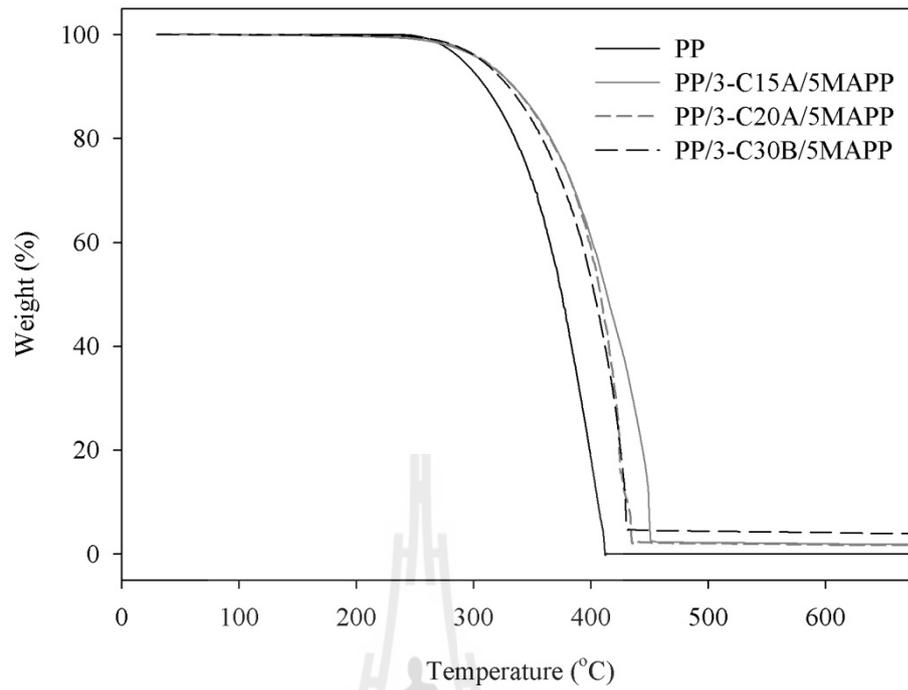


Figure 4.13 TGA curves of PP and PP/OMMT composites.

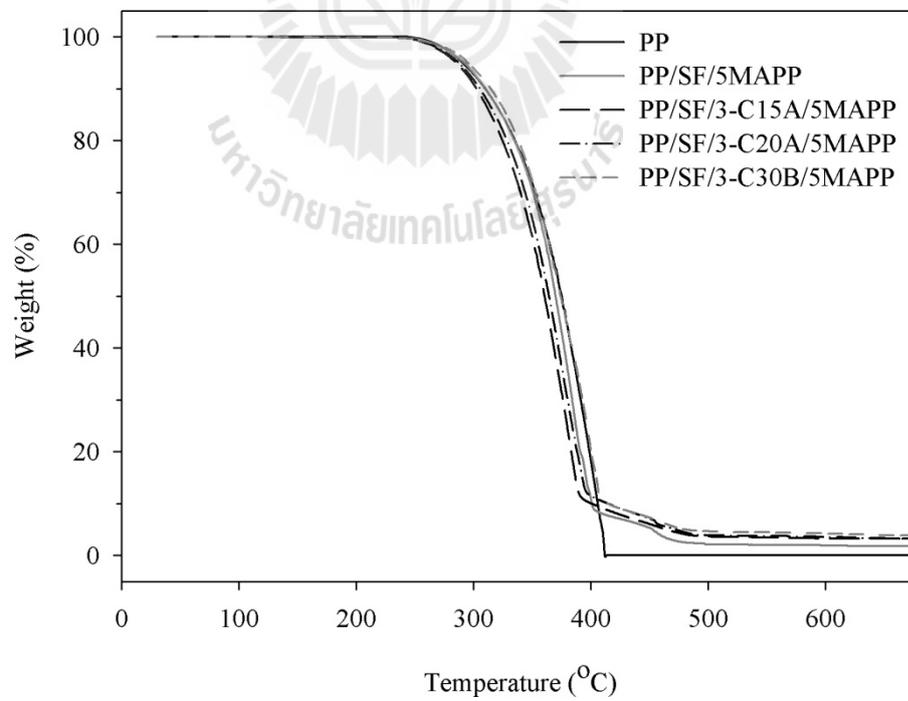


Figure 4.14 TGA curves of PP, PP/SF composite, and PP/SF/OMMT composites.

Table 4.6 Thermal properties of PP, PP/SF composite, PP/OMMT composites, and PP/SF/OMMT composites.

Designation	T _{5%} (°C)	T _{90%} (°C)	Residue at 600°C (%)
PP	291	406	0.00
PP/3-C15A/5MAPP	308	449	1.97
PP/3-C20A/5MAPP	308	431	1.75
PP/3-C30B/5MAPP	307	429	4.15
PP/SF/5MAPP	292	401	1.94
PP/SF/3-C15A/5MAPP	285	401	3.28
PP/SF/3-C20A/5MAPP	287	406	3.59
PP/SF/3-C30B/5MAPP	295	415	4.24

4.2.5 Flame retardant properties

Burning rates of PP, PP/SF composite, PP/OMMT composites, and PP/SF/OMMT composites measured by a horizontal burning test are presented in Figure 4.15 and Table 4.7. Generally, early ignition of polymer/clay nanocomposite was caused by the decomposition of the modifier used for OMMT which can accelerate the decomposition of the polymer (Pannirselvam, 2008). As the result, the burning rate of PP was not decreased with incorporating C15A and C20A. However, PP/3-C30B/5MAPP composite exhibited the lowest burning rate. This was because PP/3-C30B/5MAPP composite achieved an exfoliated structure of OMMT and also had the highest amount of char residue which acted as a barrier. Zhang, Horrocks, Hull, and Kandola (2006) reported that adding OMMT at 5 phr did not affect the limiting oxygen index (LOI) value of PP. PP/OMMT composite left char residue observed by TGA in air at 600°C due to the addition of OMMT. Wang, Hu,

Zhongkai, Wang, Chen, and Fan (2003) prepared PE/MMT composite by adding hexadecyl trimethyl ammonium bromide as a reactive compatibilizer. The peak heat release rate (PHRR) of the composite, achieving an exfoliated structure of MMT, was lowered than that of pure HDPE at 32%.

The addition of SF into PP increased the burning rate from 27.34 to 29.51 mm/min because SF, a natural fiber, was highly flammable. It indicated that adding SF enhanced the flammability of PP. Many studies also reported that adding natural fibers would increase the burning rate of PP (Abu bakar et al., 2010; Sain et al., 2004; Suppakarn and Jarukumjorn, 2009). When three OMMT types were added into PP/SF composites, the burning rates of PP/SF/3-C15A/5MAPP composite and PP/SF/3-C20A/5MAPP composite insignificantly changed whereas the burning rate of PP/SF/3-C30B/5MAPP composite considerably reduced to 24.15 mm/min due to the highest char residue left from TGA results and the good dispersion of OMMT in PP. The flame mechanism of OMMTs involved the formation of a high-performance carbonaceous-silicate char that built up and covered on the surface during burning (Lee et al., 2010; Sinha Ray and Okamoto, 2003). Lee et al. (2010) also suggested that when a small amount of clay was used, a higher degree of exfoliation of clay played an important role to enhance the flame retardant properties of PE/wood fiber composites.

According to mechanical properties, thermal properties, and flammability of PP/OMMT composites and PP/SF/OMMT composites, C30B was selected to study effect of OMMT content on the physical properties of PP/SF composites.

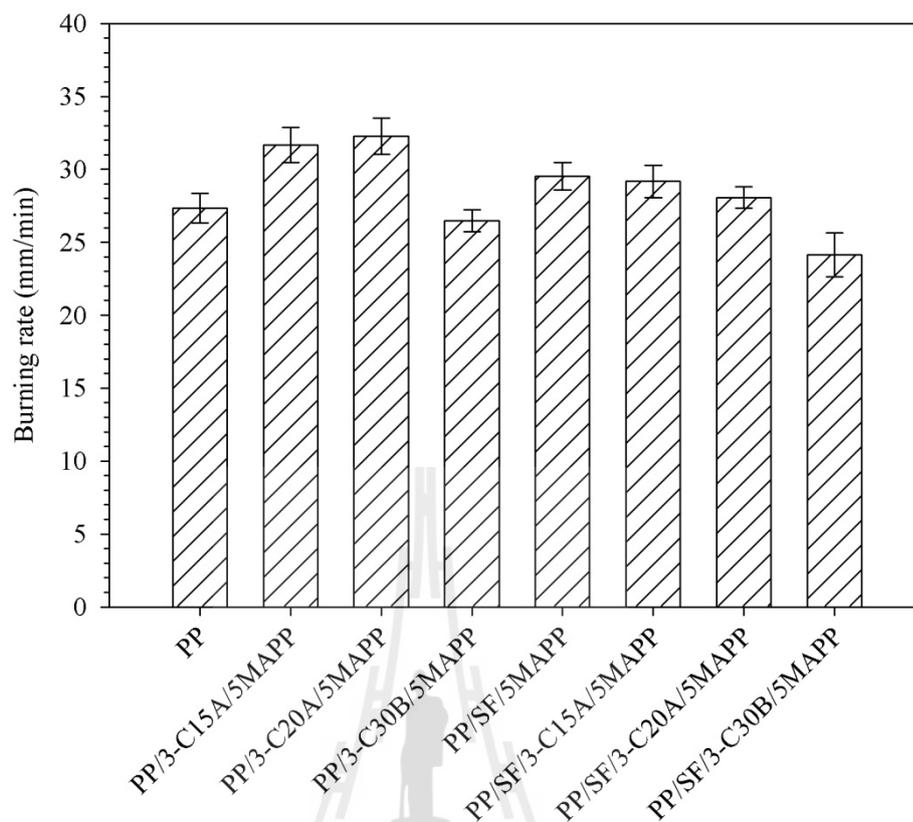


Figure 4.15 Burning rate of PP, PP/SF composite, PP/OMMT composites, and PP/SF/OMMT composites.

Table 4.7 Burning rate of PP, PP/SF composite, PP/OMMT composites, and PP/SF/OMMT composites.

Designation	Burning rate (mm/min)
PP	27.34±1.02
PP/3-C15A/5MAPP	31.68±1.20
PP/3-C20A/5MAPP	32.27±1.23
PP/3-C30B/5MAPP	26.49±0.75
PP/SF/5MAPP	29.51±0.94
PP/SF/3-C15A/5MAPP	29.18±1.12
PP/SF/3-C20A/5MAPP	28.07±0.75
PP/SF/3-30B/5MAPP	24.15±1.50

4.3 The effect of organoclay content on properties of PP/sisal fiber composites

4.3.1 Organoclay structure

XRD patterns of C30B and PP/SF composites at various OMMT contents are presented in Figure 4.16 and their diffraction peaks and interlayer distances are listed in Table 4.8. The diffraction peak of C30B was at $2\theta = 4.81^\circ$ with a d-spacing of 1.84 nm. The diffraction peaks of PP/SF composites containing 1, 3, and 5 phr of OMMT were disappeared, indicating an exfoliated structure of the OMMT (Biswal et al., 2009). However, PP/SF composite with 7 phr of OMMT exhibited a shift of diffraction peak at $2\theta = 5.48^\circ$ with a d-spacing of 1.61 nm, indicating the poor dispersion of OMMT or agglomerated OMMT in PP matrix (Chiu et al, 2004).

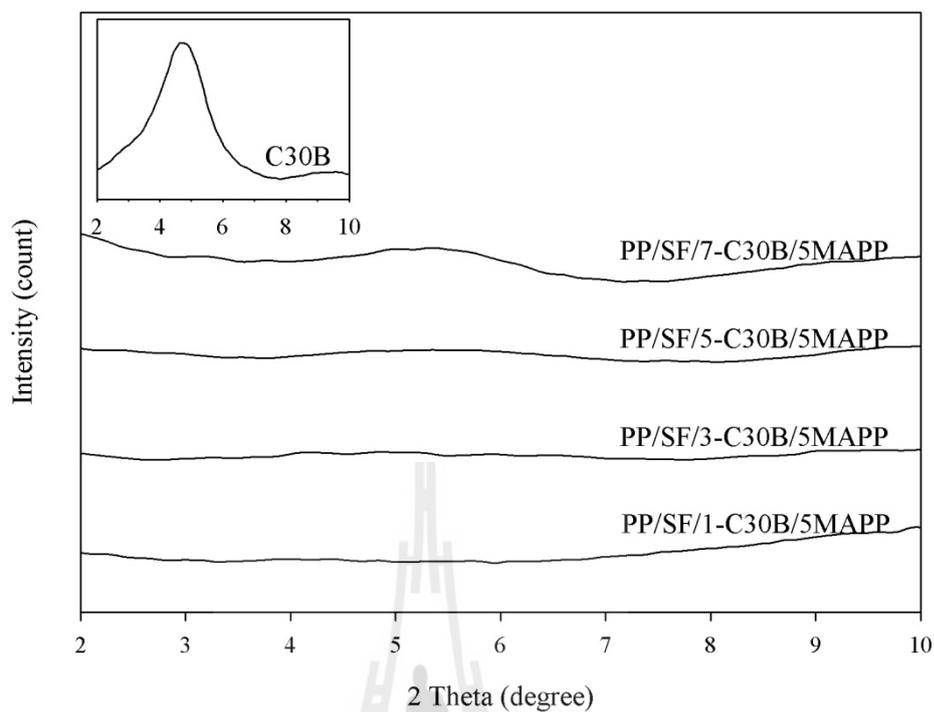


Figure 4.16 XRD patterns of PP/SF composites at various OMMT contents.

Table 4.8 2 Theta and interlayer spacing of PP/SF composites at various OMMT contents.

Designation	2 Theta (degree)	Interlayer spacing (nm)
C30B	4.81	1.84
PP/SF/1-C30B/5MAPP	-	-
PP/SF/3-C30B/5MAPP	-	-
PP/SF/5-C30B/5MAPP	-	-
PP/SF/7-C30B/5MAPP	5.48	1.61

4.3.2 Mechanical properties

Mechanical properties of PP/SF composites at various OMMT contents are listed in Table 4.9. Figure 4.17 shows tensile strength and modulus of PP/SF

composites with various OMMT contents. The PP/SF composite without OMMT showed the highest tensile strength. Incorporation of OMMT slightly reduced the tensile strength of PP/SF composites. In addition, the tensile strength of PP/SF composites was retained with increasing OMMT contents. Yeh and Gupta (2009) found the reduction in tensile strength of PP/wood flour composite with increasing OMMT content. However, adding OMMT did not affect the tensile modulus of PP/SF composites. Similar observation was investigated by Lei et al. (2007). The Young's modulus of HDPE/wood flour/OMMT composites with 2% MAPE was insignificantly changed when OMMT was varied from 1 to 3%. It may be because adding OMMT into polymer composite increased the interfacial area between PP and OMMT. Therefore that higher MAPE contents probably were required to enhance the adhesion between PP and OMMT.



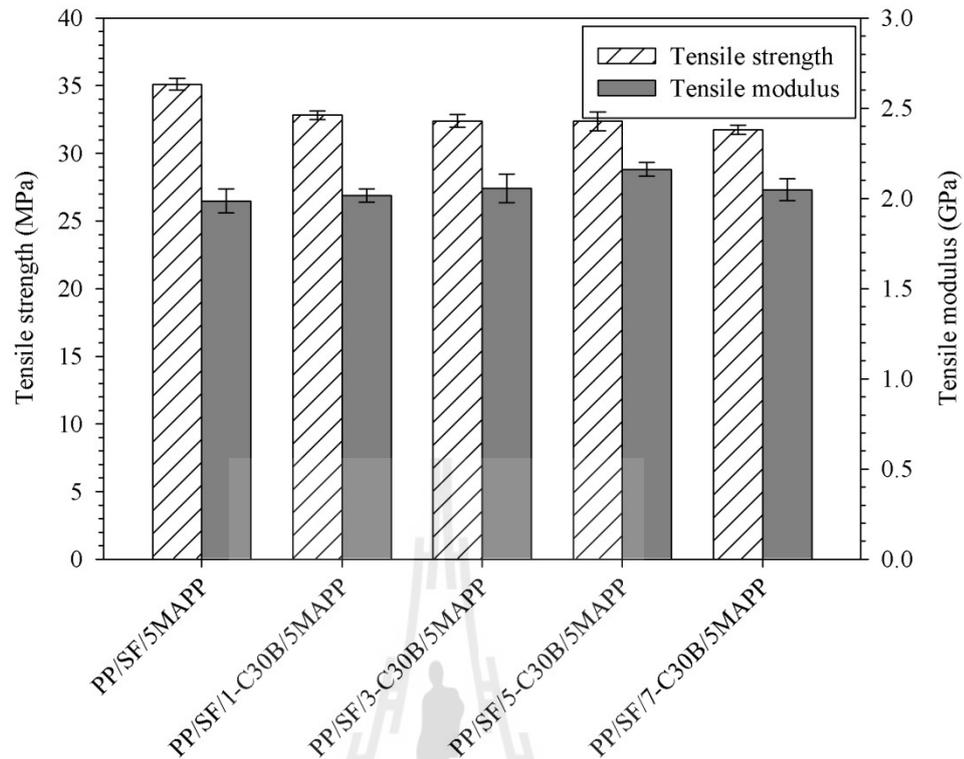


Figure 4.17 Tensile properties of PP/SF composites at various OMMT contents.

Figure 4.18 presents flexural properties of PP/SF composites at various OMMT contents. The flexural properties of PP/SF composites with adding OMMT showed the same trend as the tensile properties. PP/SF composite without OMMT showed the highest flexural strength. Addition of OMMT reduced the flexural strength of PP/SF composites. In addition, increasing OMMT contents exhibited insignificant change on the flexural strength of PP/SF composites. In addition, Sardashti (2009) found that flexural strength of PP/wheat straw fiber composite with 2% MAPP was reduced with an increase in OMMT content from 2 to 5%. This was probably due to the poor interaction between the polymer matrix and the filler. However, flexural modulus of PP/SF composites was insignificantly changed with the presence of OMMT.

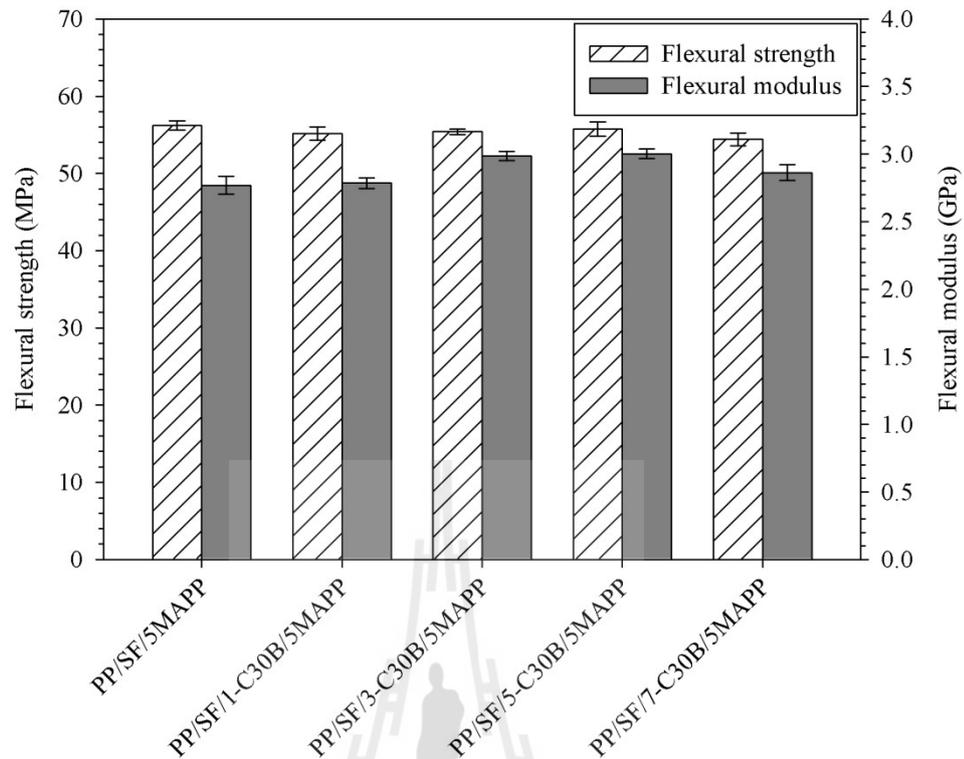


Figure 4.18 Flexural properties of PP/SF composites at various OMMT contents.

Impact strength of PP/SF composites with different OMMT contents is shown in Figure 4.19. Impact strength of PP/SF composite insignificantly change with adding OMMT. Han et al. (2008) reported that the impact strength of HDPE/bamboo fiber composites had a small change with adding 1 wt% OMMT. However, Nourbakhsh and Ashori (2009) found that increasing OMMT content decreased the impact strength of PP/bagasse flour composite. They suggested that the OMMT particles in PP matrix provided sites for crack initiation and may be due to the stiffening of polymer chains. Kord et al. (2010) also investigated a decrease in impact strength of PP/wood flour composite with increasing OMMT content. It was due to the formation of agglomeration and the presence of un-exfoliated aggregates and voids.

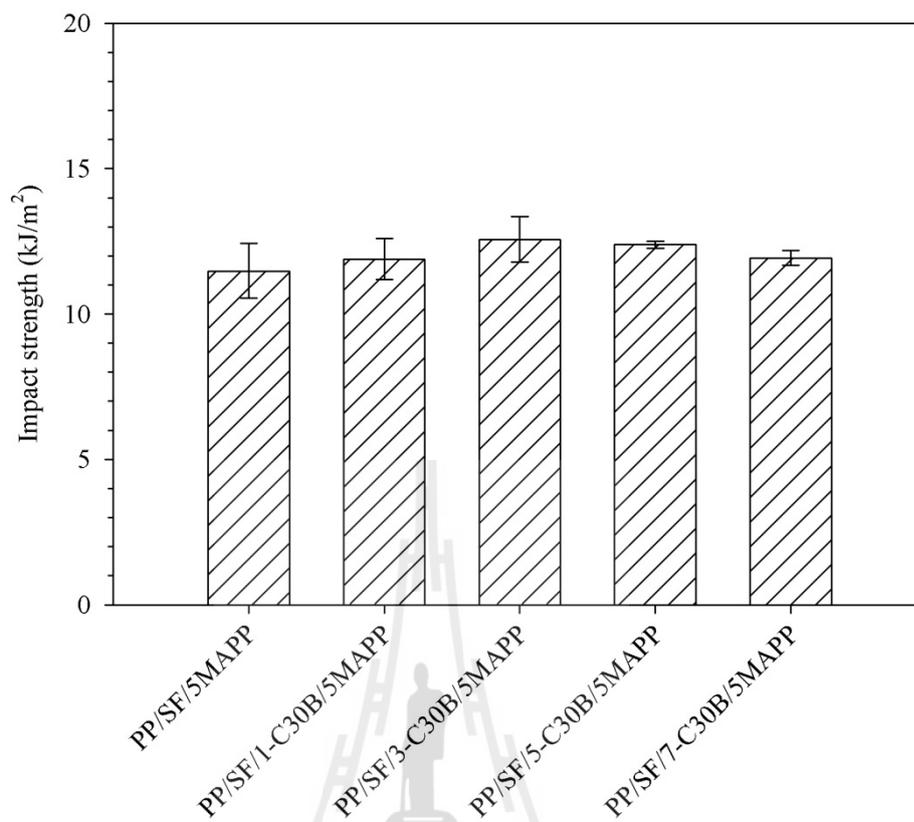


Figure 4.19 Impact strength of PP/SF composites at various OMMT contents.



Table 4.9 Mechanical properties of PP/SF composites at various OMMT contents.

Designation	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength (kJ/m²)
PP/SF/5MAPP	35.10±0.44	1.986±0.066	56.23±0.60	2.768±0.066	11.48±0.94
PP/SF/1-C30B/5MAPP	32.83±0.32	2.016±0.038	55.15±0.88	2.785±0.040	11.89±0.71
PP/SF/3-C30B/5MAPP	32.39±0.47	2.055±0.079	55.38±0.38	2.987±0.034	12.57±0.78
PP/SF/5-C30B/5MAPP	32.28±0.69	2.161±0.039	55.77±0.93	3.003±0.035	12.39±0.12
PP/SF/7-C30B/5MAPP	31.74±0.34	2.049±0.060	54.41±0.81	2.863±0.057	11.93±0.26



4.3.3 Rheological properties

MFI of PP/SF composites at various OMMT contents is listed in Table 4.10. OMMT exhibited insignificant effect on MFI of PP/SF composites. It suggested that the processability of PP/SF composites was not influenced by the addition of OMMT.

Table 4.10 Melt flow index of PP/SF composites at various OMMT contents.

Designation	MFI (g/10 min)
PP/SF/5MAPP	2.06±0.14
PP/SF/1-C30B/5MAPP	1.90±0.15
PP/SF/3-C30B/5MAPP	1.73±0.10
PP/SF/5-C30B/5MAPP	1.60±0.17
PP/SF/7-C30B/5MAPP	1.45±0.09

4.3.4 Thermal properties

TGA curves and thermal properties of PP/SF composites at various OMMT contents are shown in Figure 4.20 and Table 4.10, respectively. Increasing OMMT content showed insignificant change on the $T_{5\%}$ but remarkably affected the $T_{90\%}$ and the char residue of PP/SF composites. The PP/SF composite with 7 phr of OMMT had the highest $T_{90\%}$ at 436°C and also left the highest amount of char residue at 5.19% whereas the composite without OMMT exhibited the $T_{90\%}$ at 401°C and had the char residue only 1.94%. It indicated the thermal stability of the PP/SF composite was improved with increasing OMMT content. Sardashti (2009) reported that adding OMMT 2-4% into PP/wheat straw fiber composites slightly improved the onset of the

degradation of the composites and also increased the char residue, indicating that the presence of OMMT enhanced the thermal stability of PP/wheat straw fiber composite.

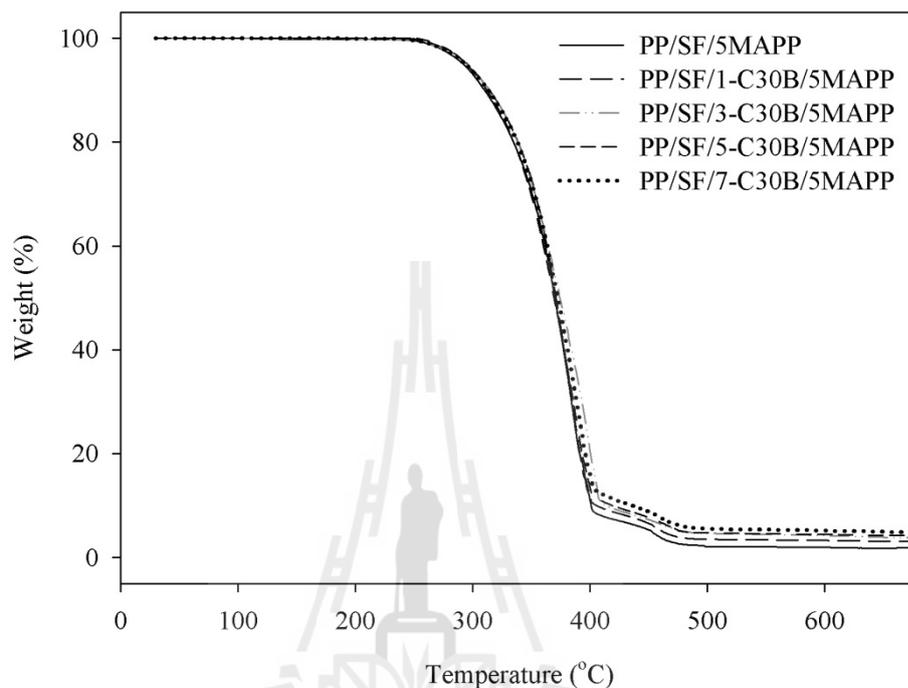


Figure 4.20 TGA curves of PP/SF composites at various OMMT contents.

Table 4.11 Thermal properties of PP/SF composites at various OMMT contents.

Designation	T _{5%} (°C)	T _{90%} (°C)	Residue at 600°C (%)
PP/SF/5MAPP	292	401	1.94
PP/SF/1-C30B/5MAPP	296	406	3.30
PP/SF/3-C30B/5MAPP	295	415	4.24
PP/SF/5-C30B/5MAPP	295	419	4.45
PP/SF/7-C30B/5MAPP	296	436	5.19

4.3.5 Flame retardant properties

Burning rate of PP/SF composites at various OMMT contents are presented in Figure 4.21. The composite without OMMT had the highest burning rate at 29.51 mm/min as listed in Table 4.12. Interestingly, adding just a small amount of OMMT at 1 phr into PP/SF composite reduced the burning rate by 8.91%. Moreover, increasing OMMT content further decreased the burning rate of the PP/SF composite. The addition of OMMT at 7 phr into the PP/SF composite exhibited the dramatic reduction of burning rate about 28.2%. It indicated that incorporating OMMT enhanced the flame resistance of the PP/SF composite. This was due to the formation of char that covered on the surface during the burning and then slowed down the mass loss rate of the materials decomposition. Lee et al. (2010) reported that the burning rate of HDPE/wood fiber composite was decreased with the addition of OMMT. Increasing OMMT from 1 to 5 wt% also reduced the burning rate of HDPE/wood fiber composites, indicating a significant improvement in flame retardancy. Adding OMMT at 5 wt% exhibited the reduction of burning rate of HDPE/wood fiber composite by 27%. Kord (2011) also found the reduction of burning rate of HDPE/rice husk flour composite in the presence of OMMT. Adding OMMT at 2 to 6 phr further decreased the burning rate of the composite.

According to mechanical properties, thermal properties, and flammability of PP/SF/OMMT composites, PP/SF composites containing 3 phr of OMMT was selected to study the effect of MAPP content on the physical properties of PP/SF/OMMT composites.

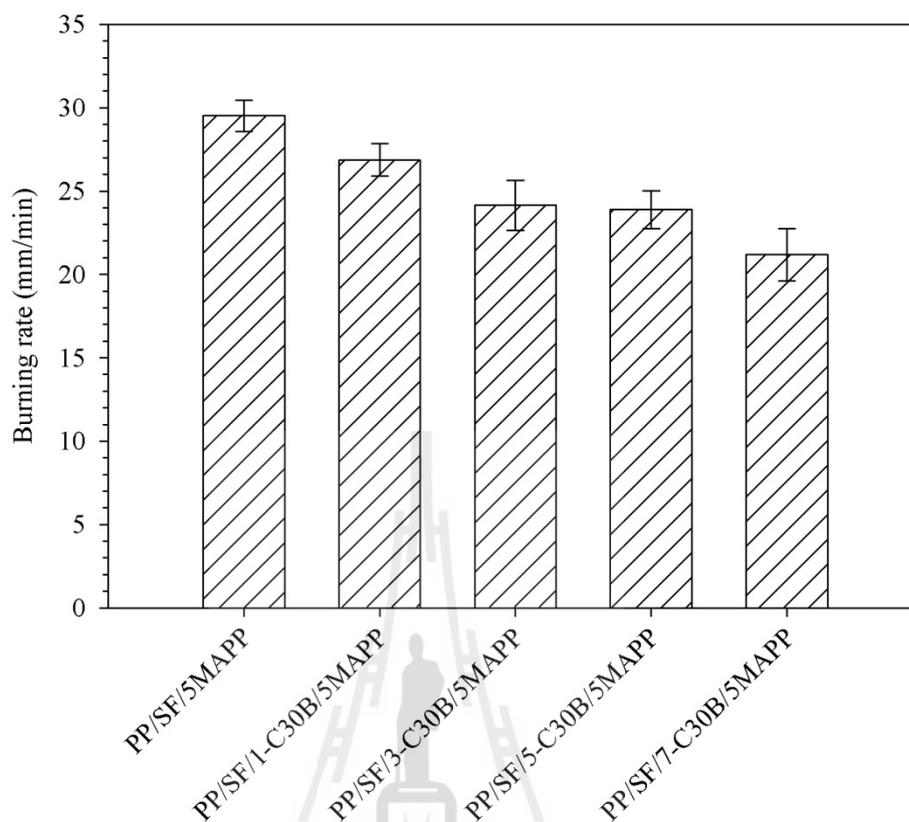


Figure 4.21 Burning rate of PP/SF composites at various OMMT contents.

Table 4.12 Burning rate of PP/SF composites at various OMMT contents.

Designation	Burning rate (mm/min)
PP/SF/5MAPP	29.51±0.94
PP/SF/1-C30B/5MAPP	26.88±0.97
PP/SF/3-C30B/5MAPP	24.15±1.50
PP/SF/5-C30B/5MAPP	23.88±1.13
PP/SF/7-C30B/5MAPP	21.18±1.58

4.4 The effect of MAPP content on properties of PP/sisal fiber/organoclay composites

4.4.1 Organoclay structures

XRD patterns of C30B and PP/SF/OMMT composites at various MAPP contents are shown in Figure 4.22. Their characteristic diffraction peaks and interlayer distances are presented in Table 4.13. C30B showed a diffraction peak at $2\theta = 4.81^\circ$ with a d-spacing of 1.84 nm. PP/SF/3-C30B/3MAPP composite exhibited a shift of diffraction peak to higher angle at $2\theta = 5.76^\circ$ with a d-spacing of 1.53 nm. It could be attributed to poor dispersion of OMMT in PP (Chiu et al, 2004). The peaks of PP/SF/OMMT composites containing MAPP at 5 to 10 phr were disappeared, indicating an exfoliated structure of the OMMT (Lee et al., 2010).

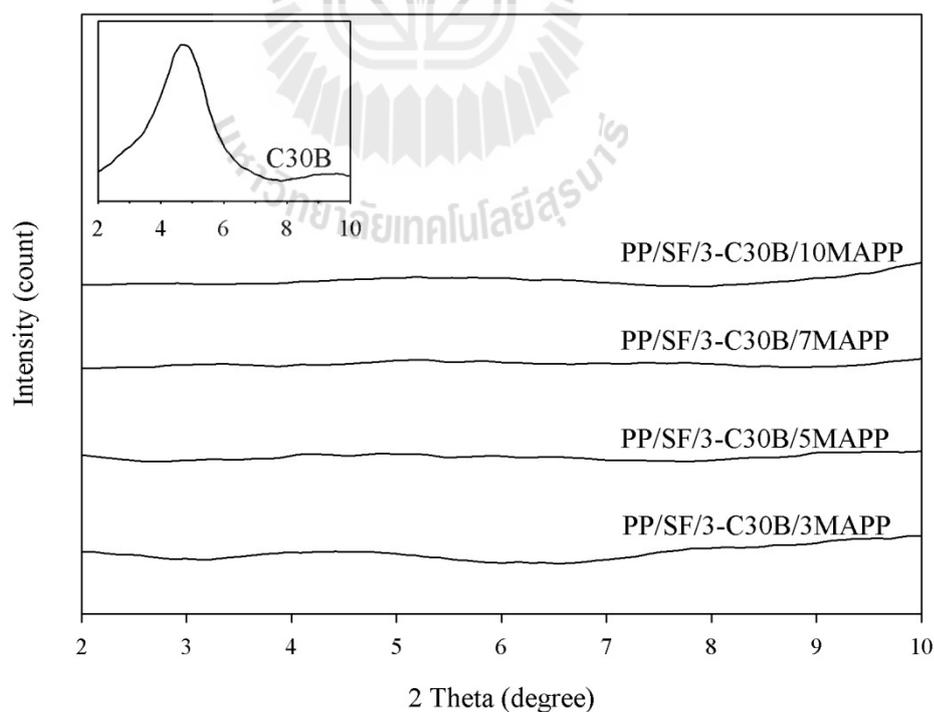


Figure 4.22 XRD patterns of PP/SF/OMMT composites at various MAPP contents.

Table 4.13 2 Theta and interlayer spacing of PP/SF/OMMT composites at various MAPP contents.

Designation	2 Theta (degree)	Interlayer spacing (nm)
C30B	4.81	1.84
PP/SF/3-C30B/3MAPP	5.76	1.53
PP/SF/3-C30B/5MAPP	-	-
PP/SF/3-C30B/7MAPP	-	-
PP/SF/3-C30B/10MAPP	-	-

4.4.2 Mechanical properties

Mechanical properties of PP/SF/OMMT composites at various MAPP contents are listed in Table 4.14. Figure 4.23 presents tensile properties of PP/SF/OMMT composites at various MAPP contents. With increasing MAPP content from 3 to 10 phr, tensile strength and modulus of the PP/SF/OMMT composites significantly improved. This was because to the presence of MAPP enhanced interfacial adhesion between PP and SF. Some OH groups from SF reacted with MA from MAPP to form the linkages and improved the dispersion of SF in PP. Mechanism of MAPP reacting with the cellulose fiber surface is previously presented in Figure 2.1. In addition, MAPP improved a dispersion of OMMT in PP matrix and enhanced the interaction between OMMT and PP as shown in Figure 4.7. Nourbaskhsh and Ashori (2009) also reported that PP/bagasse/OMMT nanocomposites containing 4 wt% of MAPP exhibited higher tensile strength and Young's modulus than the nanocomposites containing 2% of MAPP due to improved adhesion between PP and SF and a better dispersion of OMMT in PP.

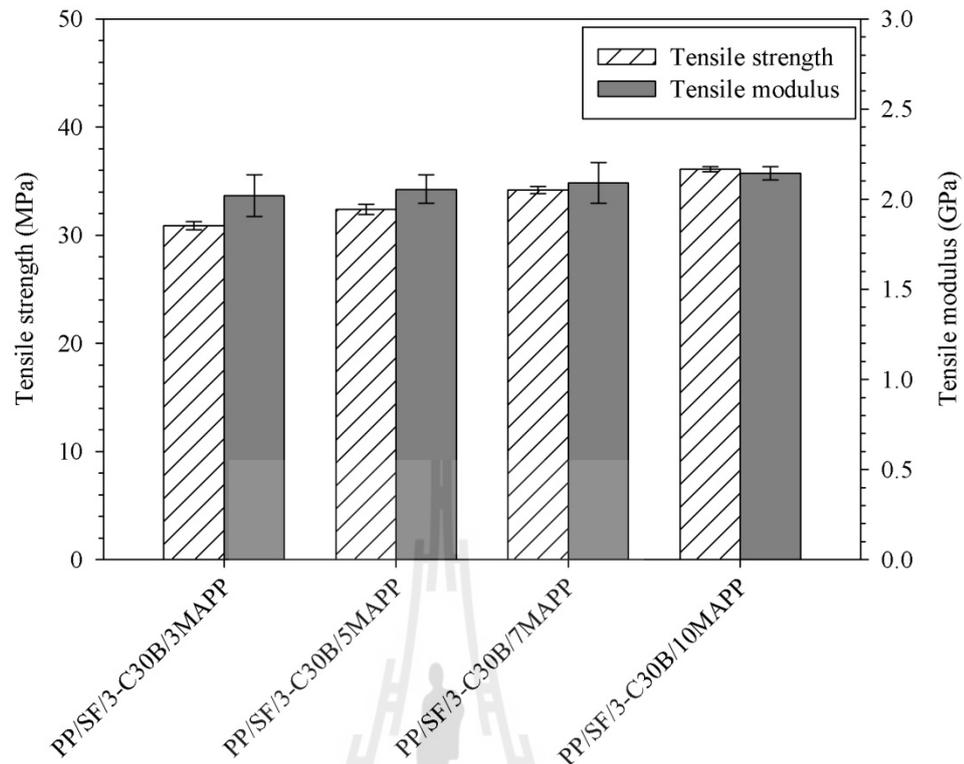


Figure 4.23 Tensile properties of PP/SF/OMMT composites at various MAPP contents.

Flexural properties of PP/SF/OMMT composites at various MAPP contents are represented in Figure 4.24. It was seen that increasing MAPP content generally improved the flexural strength of PP/SF/OMMT composites. This was consistent with the results reported by Sardashti (2009). PP/wheat straw/OMMT composite filled with 4 wt% of MAPP had higher flexural strength and flexural modulus than the composite filled with 2 wt% of MAPP. This was attributed to the improvement in the interfacial interaction between the PP matrix and the fiber

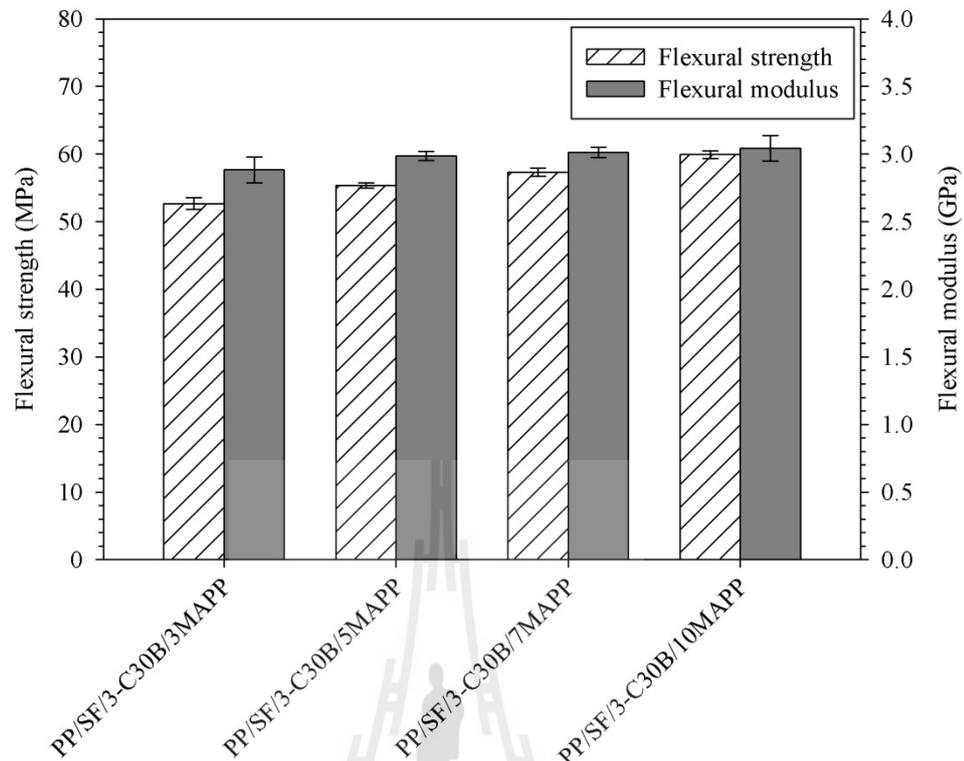


Figure 4.24 Flexural properties of PP/SF/OMMT composites at various MAPP contents.

Impact strength of PP/SF/OMMT composites with different MAPP contents is shown in Figure 4.25. It was observed that the impact strength of PP/SF/OMMT composite insignificantly changed with increasing MAPP content. Han et al. (2008) reported that the impact strength of HDPE/bamboo fiber composites was unimportantly affected when OMMT was added at 1 wt% at MAPE up to 2 wt%. However, at MAPE up to 6 wt%, the impact strength of HDPE bamboo fiber was decreased with the incorporation of OMMT at 3 and 5 wt%.

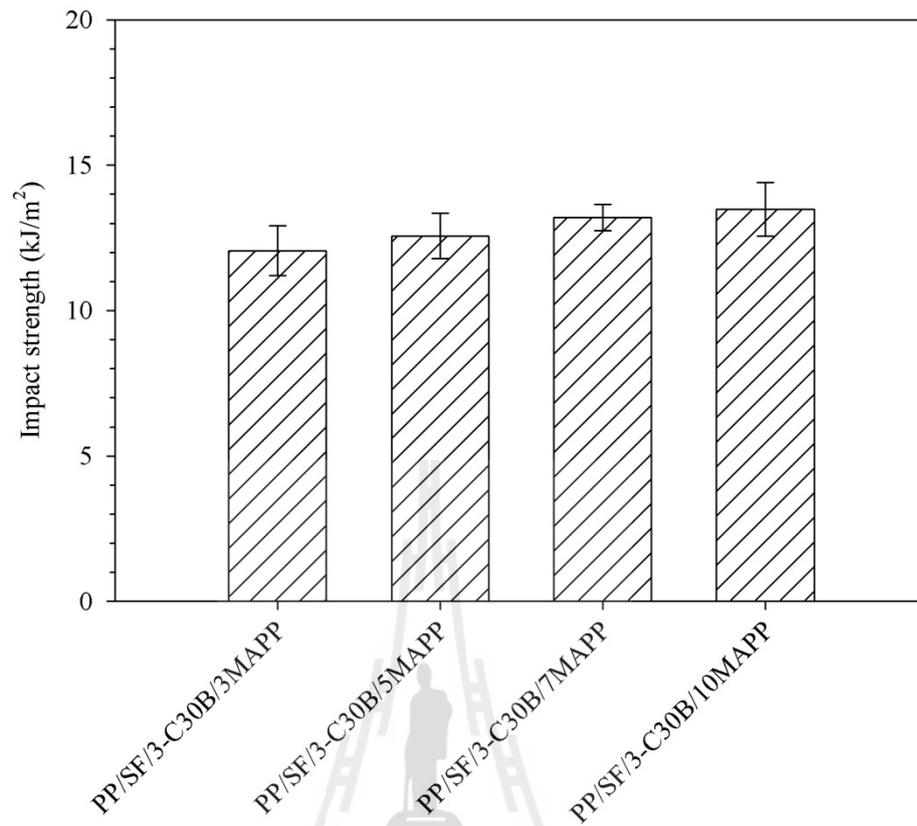


Figure 4.25 Impact strength of PP/SF/OMMT composites at various MAPP contents.

Table 4.14 Mechanical properties of PP/SF/OMMT composites at various MAPP contents.

Designation	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Impact strength (kJ/m²)
PP/SF/3-C30B/3MAPP	30.89±0.37	2.021±0.116	52.66±0.88	2.884±0.096	12.06±0.85
PP/SF/3-C30B/5MAPP	32.39±0.47	2.055±0.079	55.38±0.38	2.987±0.034	12.57±0.78
PP/SF/3-C30B/7MAPP	34.18±0.32	2.090±0.114	57.21±0.60	3.013±0.036	13.20±0.45
PP/SF/3-C30B/10MAPP	36.12±0.23	2.144±0.038	59.93±0.57	3.042±0.094	13.49±0.92



4.4.3 Rheological properties

Table 4.15 presents MFI of PP/SF/OMMT composites at various MAPP contents. No significant change of MFI of PP/SF/OMMT composites was observed when MAPP content was increased. It indicated that incorporating MAPP did not influence on the processability of PP/SF/OMMT composites. Sardashti (2009) also reported that MAPP content showed no effect on MFI of PP/wheat straw fiber/OMMT composites.

Table 4.15 Melt flow index of PP/SF/OMMT composites at various MAPP contents.

Designation	MFI (g/10 min)
PP/SF/3-C30B/3MAPP	1.55±0.21
PP/SF/3-C30B/5MAPP	1.73±0.10
PP/SF/3-C30B/7MAPP	1.81±0.20
PP/SF/3-C30B/10MAPP	2.26±0.31

4.4.4 Thermal properties

TGA curves and thermal properties of PP/SF/OMMT composites at various MAPP contents are presented in Figure 4.26 and Table 4.16, respectively. Increasing MAPP content insignificantly affected $T_{5\%}$, $T_{90\%}$, and %char residue of PP/SF/OMMT composites. Similar observation was reported by Sardashti (2009). He found that the decomposition temperatures and %char residue of PP/wheat straw fiber/OMMT composite insignificantly changed with increasing MAPP content.

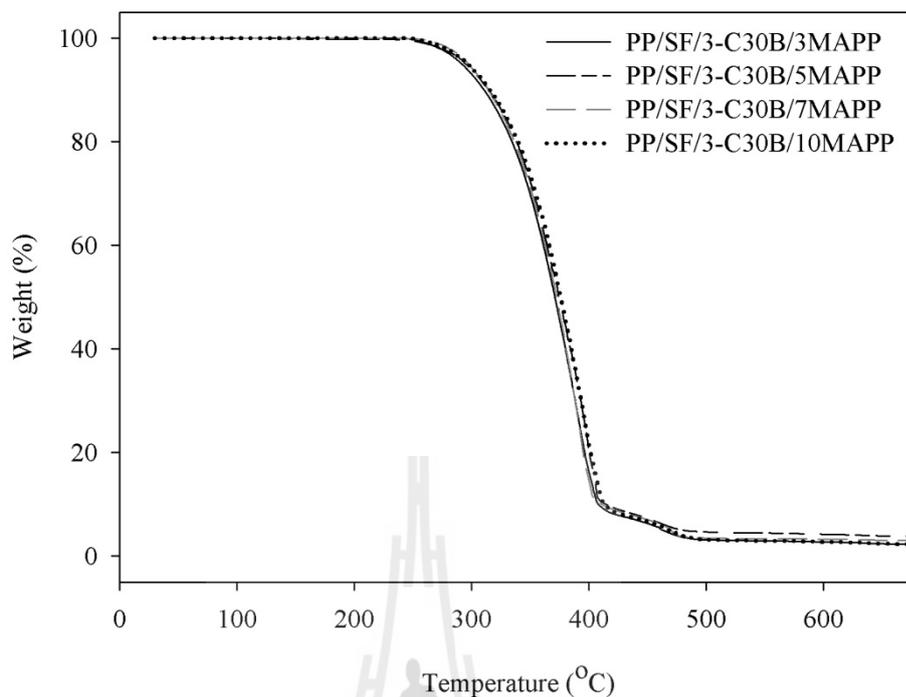


Figure 4.26 TGA curves of PP/SF/OMMT composites at various MAPP contents.

Table 4.16 Thermal properties of PP/SF/OMMT composites at various MAPP contents.

Designation	T _{5%} (°C)	T _{90%} (°C)	Residue at 600°C (%)
PP/SF/3-C30B/3MAPP	292	409	2.77
PP/SF/3-C30B/5MAPP	295	415	4.24
PP/SF/3-C30B/7MAPP	297	411	3.29
PP/SF/3-C30B/10MAPP	297	413	2.79

4.4.5 Flame retardant properties

Burning rate of PP/SF/OMMT composites is presented in Figure 4.27 and Table 4.17. It was observed that increasing MAPP content decreased the burning

rate of PP/SF/OMMT composites. The significant reduction of burning rate of PP/SF/OMMT composite was achieved when MAPP was added at 10 phr. It was attributed to an enhancement in the adhesion between PP and SF and also the good dispersion of OMMT in PP (Lee et al., 2010).

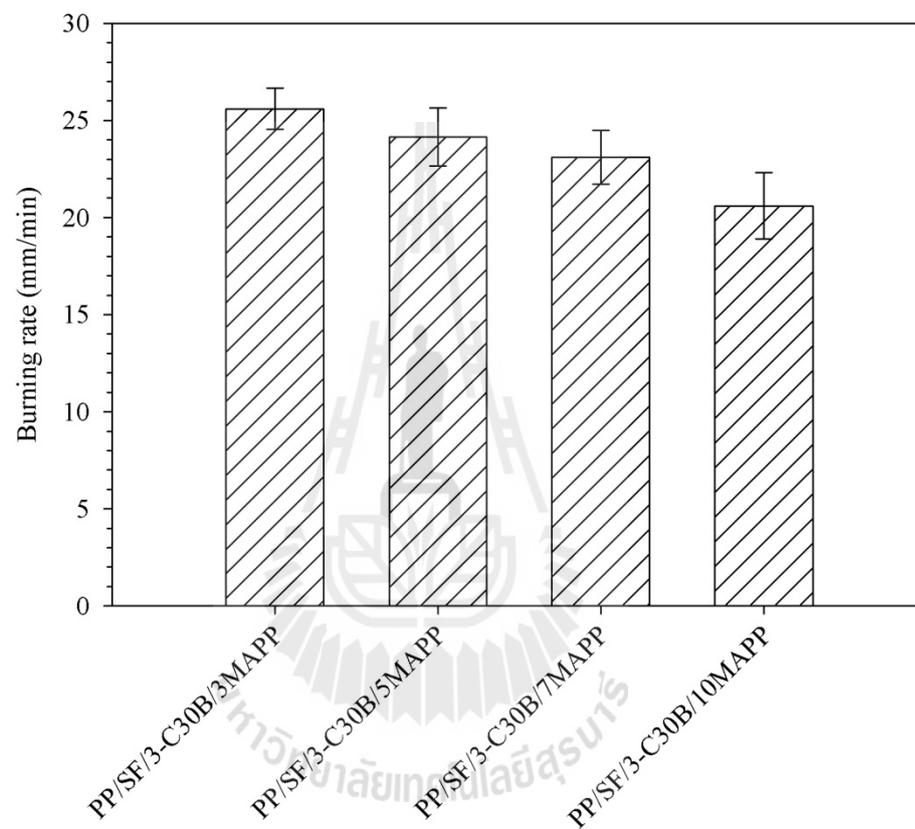


Figure 4.27 Burning rate of PP/SF/OMMT composites at various MAPP contents.

Table 4.17 Burning rate of PP/SF/OMMT composites at various MAPP contents.

Designation	Burning rate (mm/min)
PP/SF/3-C30B/3MAPP	25.60±1.05
PP/SF/3-C30B/5MAPP	24.15±1.50
PP/SF/3-C30B/7MAPP	23.11±1.38
PP/SF/3-C30B/10MAPP	20.60±1.71



CHAPTER V

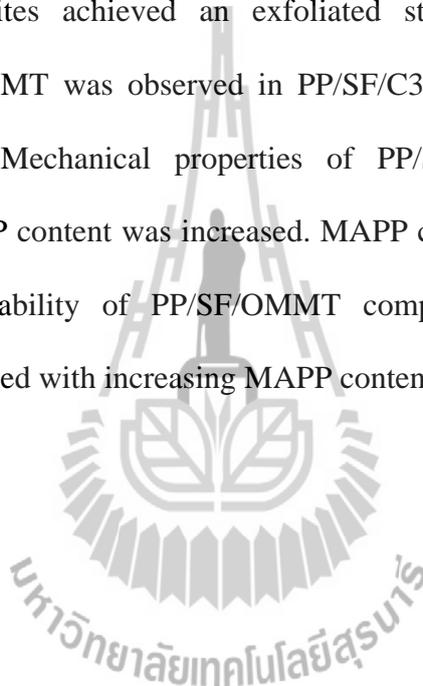
CONCLUSIONS

In this study, three OMMT types were added into PP and PP/SF composites. XRD patterns showed that shifting of diffraction peak towards lower angle than pure OMMT was found for PP/C15A composite and PP/C20A composite, indicating the presence of an intercalated structure of the OMMT. On the other hand, the diffraction peak of C30B disappeared for PP/C30B composite, suggesting an exfoliated structure of the OMMT. Incorporating OMMT increased tensile and flexural strength but reduced impact strength of PP. With the addition of OMMT, thermal stability of PP was improved. OMMT types had insignificant effect on mechanical properties of PP but improved its thermal stability. Among PP/OMMT composites, PP/C30B composite exhibited the highest thermal stability and flame retardancy.

Incorporating OMMTs into PP/SF composites deteriorated tensile and flexural strength but retained modulus and impact strength. OMMT did not influence MFI of PP/SF composites. Flame retardancy of PP/SF composites insignificantly changed with the addition of C15A and C20A but improved with adding C30B. PP/SF/C30B composite showed the highest mechanical, thermal, and flame retarding properties. From XRD patterns, the shift of diffraction peak to lower angle of C15A and C20A in PP was observed. It indicated the intercalated structure of the OMMT for PP/SF/C15A composite and PP/SF/C20A composite. In contrast, the diffraction peak of C30B was disappeared, resulting in the exfoliated structure of the OMMT.

PP/SF composite containing 1 to 5 phr of C30B presented an exfoliated structure of the OMMT. However, with increasing C30B content to 7 phr, the clay agglomeration was observed. C30B content had no considerable effect on mechanical properties and MFI of PP/SF composites. Thermal stability and flame retardancy of PP/SF composites were enhanced with an increase in C30B content.

With increasing MAPP content from 5 to 10 phr, XRD patterns of PP/SF/C30B composites achieved an exfoliated structure of the OMMT. An agglomeration of OMMT was observed in PP/SF/C30B composite when 3 phr of MAPP was added. Mechanical properties of PP/SF/OMMT composites were improved when MAPP content was increased. MAPP content insignificantly affected MFI and thermal stability of PP/SF/OMMT composites. However, the flame retardancy was enhanced with increasing MAPP content.



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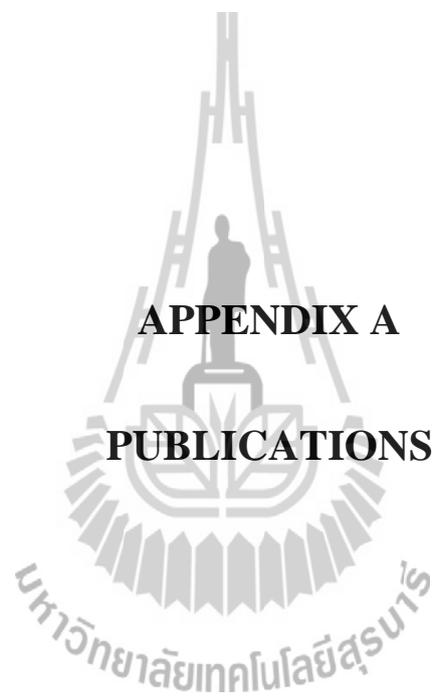
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APPENDIX A

PUBLICATIONS

List of publications

- Chanprapanon, W., Suppakarn, N., and Jarukumjorn, K. (2011). Effect of nanoclay on mechanical properties and flame retardancy of sisal fiber/polypropylene composites. In **Proceedings of the Pure and Applied Chemistry International Conference 2011**. (pp 495-498). Bangkok, Thailand.
- Chanprapanon, W., Suppakarn, N., and Jarukumjorn, K. (2011). Effect of organoclay types on mechanical properties and flammability of polypropylene/sisal fiber composites. In **Proceedings of the 18th International Conference on Composite Materials**. Jeju, Korea.
- Chanprapanon, W., Suppakarn, N., and Jarukumjorn, K. (2012). Flame retardancy, thermal stability, and mechanical properties of sisal fiber/organoclay/polypropylene composites. **Advanced Materials Research**. 410: 47-50.

EFFECT OF NANOCCLAY ON MECHANICAL PROPERTIES AND FLAME RETARDANCY OF SISAL FIBER/PP COMPOSITES

W. Chanprapanon^{1,2}, N. Suppakarn^{1,2} and K. Jarukumjorn^{1,2*}

¹ Suranaree University of Technology /Institute of Engineering /School of Polymer Engineering, Nakhon Ratchasima, Thailand

² Center for Petroleum, Petrochemicals, and Advanced Materials /Chulalongkorn University, Bangkok, Thailand

*kasama@sut.ac.th

Abstract: Natural fiber reinforced polypropylene (PP) has gained a lot of interests due to low cost, low density, acceptable strength and stiffness, and fiber biodegradability. However, shortcomings of this composite are relatively low modulus, low notched impact resistance, large thermal expansion, and substantial creep. Moreover, its high flammability is one of the critical drawbacks of the composite. In this study, to improve the mechanical properties and flame retardancy of sisal fiber (Si)/PP composites, an organoclay (OMMT) as a nanosize filler was added into the composites. PP composites containing 30 phr of sisal fiber were prepared using an internal mixer. The test specimens were molded using an injection molding machine. In addition, maleic anhydride grafted polypropylene (MAPP) was used to enhance the interfacial adhesion between PP matrix and sisal fiber and also to improve the dispersion of the organoclay in PP matrix. It was observed that the tensile properties of PP and PP/Si composite were further increased with the addition of 3 phr of OMMT. Moreover, the incorporation of OMMT into PP and PP/Si composite also improved their flame retarding properties and thermal stability. X-ray diffraction analysis revealed that PP/OMMT composite exhibited the intercalated nanostructure. However, PP/Si/OMMT composite formed the exfoliated nanostructure.

Introduction

Nowadays, the use of natural fibers to reinforce polymer has received considerable attention, particularly in structural and automotive industry due to cost effectiveness and eco-friendliness. By comparing with inorganic fillers, the main advantages of natural fibers are light weight, low cost, biodegradability, renewable nature, easiness of processing, the absence of toxic by-products, and high specific strength and modulus. The addition of natural fibers to polymers can cause a change in properties of the derived composites, which depends on properties of the natural materials and those of the polymers.

Polypropylene (PP) is particularly interesting thermoplastics used in composites because it has good and extensive properties, ease of processing, and low cost also. However, the incompatibility between hydrophobic polymers and hydrophilic natural fibers results in poor interfacial adhesion between the natural fibers and polymers. In order to solve it, maleic

anhydride grafted polypropylene (MAPP) is generally introduced as a compatibilizer to improve the stress transfer between the polymer matrix and natural fiber at low concentrations [1].

Another critical drawback of the use of natural fiber in PP composites is their high flammability due to their structure and chemical composition. Improving their flame retardancy will thus expand the range of their applications. In recent years, nanosized fillers have been good candidates for overcoming the aforementioned drawbacks of polymer composites. Incorporation of nanoclay at very low loading (less than 5 wt%) can improve properties e.g. high modulus, increased strength and heat resistance, decreased gas permeability and flammability, and increased biodegradability of biodegradable polymers [2]. In order to achieve the good property enhancement, clay particles should be homogeneously dispersed and exfoliated within the polymer matrix [3]. Melt blending is the main method for the preparation of nanocomposite due to its cost effectiveness in using the conventional polymer compounding technique and the compatible with the continuous nature of the industrial process, such as extrusion and injection molding [2-4].

The objective of this work was to study the effect of nanoclay on the mechanical, thermal and flame retarding properties of sisal fiber/PP composites.

Materials and Methods

Materials: Polypropylene (PP; P700J) was supplied by SCG Chemicals Co.,Ltd. Sisal fiber (Si) was purchased from the Sisal-Handicraft OTOP group, Nakhon Ratchasima, Thailand. The sisal fiber was cut into approximate length of 2 mm. Organoclay (OMMT; Cloisite®30B, an originally modified montmorillonite) was supplied from Southern Clay Products Inc., USA. Maleic anhydride grafted polypropylene (MAPP; Fusabond®P MZ 109D, Dupont) was supplied from Chemical Innovation Co., Ltd.

Preparation of composites: Prior the composite preparation, sisal fiber and OMMT were dried in an oven at 70°C over night. PP compounds were prepared by melt blending using an internal mixer (Haake Rheomix, 3000p). The total mixing time was 15 min.

The mixing temperature was 170°C and the rotation speed was 60 rpm. Test specimens were molded by an injection molding machine (Chuan Lih Fa, CLF 80T) to produce the specimens according ASTM standard. Composition of PP and PP composites and their designation used are shown in Table 1.

Structure characterization: The structure of OMMT and PP composites were performed by an X-ray diffractometer (XRD; Oxford, D5005) equipped with a Cu K α radiation source of wavelength 1.5406 Å operated at 40 kV and 40 mA at room temperature. The scanning rate and step size were 2.0°/min and 0.02° with 2 θ varying from 2° to 10°. The XRD patterns were used to calculate the basal spacing or *d*-spacing from Bragg's law.

Mechanical test: Tensile properties of PP and PP composites were measured according to ASTM D638 on a universal testing machine (UTM; Instron 5569). Impact test was performed on unnotched PP and PP composites followed ASTM D256 using an impact testing machine (Atlas, BPI). In all cases, the average values of five specimens at least were taken for each sample.

Flammability test: The flame retardancy of PP and PP composites was characterized by a horizontal burning test according to ASTM D635 on a horizontal vertical flame chamber instrument (Atlas, HVUL). The sample was held horizontally and a flame was applied to light one end of the sample. The burning rate of the sample was calculated according to the formula:

$$V = 60L/t \quad (1)$$

Where *V* is the burning rate in millimeters per minute; *L* is the length the flame travels from the first reference mark (25 mm from the end) to the second reference mark, which is at 100 mm from the end; and *t* is the time in seconds for the flame to travel. Five measurements per sample were taken.

Thermal analysis: Thermal behaviors of PP and PP composites were carried out on a thermogravimetric analyzer (TGA; TA Instrument, SDT2960) at a constant heating rate of 20°C/min under air flow. The temperature ranged from the room temperature to 700°C. The weight of each sample was kept within 10-15 mg.

Table 1: Formulation of PP and PP composites.

Designation	PP (phr)	Sisal (phr)	OMMT (phr)	MAPP (phr)
PP	100	-	-	-
PP/Si	100	30	-	5
PP/OMMT	100	-	3	5
PP/Si/OMMT	100	30	3	5

Results and Discussion

XRD patterns of PP, OMMT, PP/OMMT composite, and PP/Si/OMMT composite are shown in Figure 1. XRD pattern of OMMT showed a peak at 2 θ = 4.77° that corresponds to *d*-spacing of 1.85 nm.

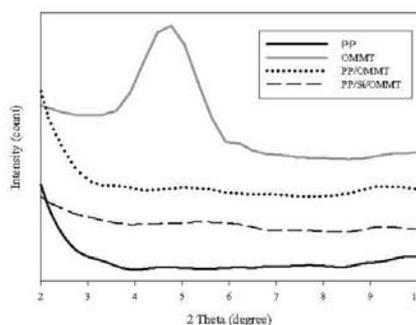


Figure 1. XRD patterns of PP, OMMT, PP/OMMT and PP/Si/OMMT composites.

PP/OMMT composite presented a shift of diffraction peak to a lower angle at 2 θ = 3.81° which corresponds to *d*-spacing of 2.32 nm, indicating the formation of an intercalated structure [2]. For PP/Si/OMMT composite, the peak was disappeared. This implied that the silicate layers could be exfoliated and dispersed in PP matrix forming a nanometer scale composite [5].

Table 2: Mechanical properties of PP and PP composites.

Designation	Tensile strength (MPa)	Young's modulus (GPa)	Impact strength (kJ/mm ²)
PP	14.06 ± 0.55	0.92 ± 0.03	78.67 ± 0.94
PP/Si	30.60 ± 0.37	2.32 ± 0.04	11.39 ± 0.25
PP/OMMT	26.53 ± 0.75	1.40 ± 0.05	60.34 ± 0.85
PP/Si/OMMT	31.82 ± 1.60	2.36 ± 0.03	12.79 ± 0.50

The mechanical properties of PP and PP composites are summarized in Table 2. Tensile properties of PP and PP composites are shown in Figure 2. It was observed that all PP composites exhibited higher tensile strength and Young's modulus than PP due to the reinforcing effect from sisal fiber and/or organoclay. In addition, adding 3 phr of OMMT into PP/Si composite slightly increased the tensile strength and Young's modulus due to the formation of exfoliated nanocomposite structures formed at this clay loading [6-8].

Figure 3 represents the unnotched Izod impact strength of PP and PP composites. The addition of fillers decreased the impact strength of PP. It was because the filler particles in PP matrix provided sites for crack initiation [6]. However, the impact strength of PP/OMMT composite was higher than that of PP/Si composite. Riley et al. (1990) reported that the impact strength depends on both the size and the shape of the filler and is also affected by the micromorphology. Impact strength is enhanced by small, low aspect ratio filler particles [7]. Furthermore, the incorporation of OMMT into PP/Si composite slightly increased the impact strength. Similarly, Lee and Kim (2008) found the impact strength of wood/PP composite filled 1 phr

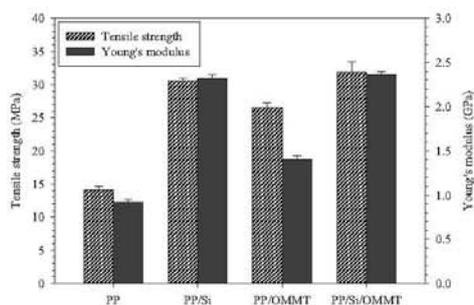


Figure 2. Tensile properties of PP and PP composites.

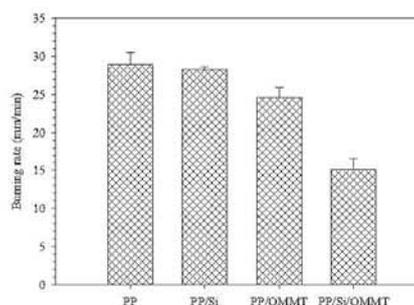


Figure 4. Burning rates of PP and PP composites.

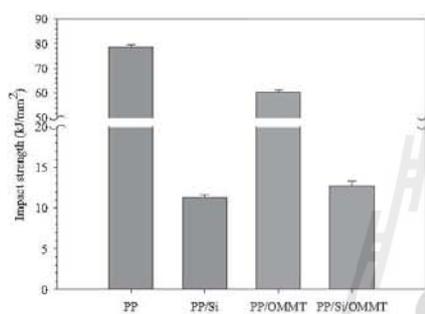


Figure 3. Impact strength of PP and PP composites.

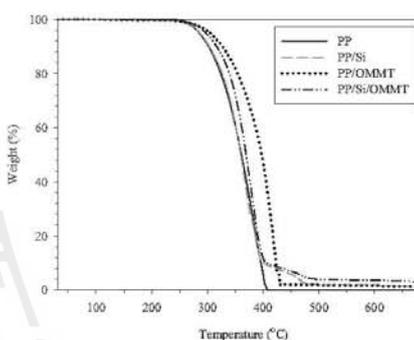


Figure 5. TGA curves of PP and PP composites.

of OMMT was slightly higher than that without OMMT, indicating a positive effect of the OMMT inclusion [1].

Burning rates of PP and PP composites measured by a horizontal burning test are shown in Figure 4. PP exhibited the highest burning rate at about 28.89 mm/min. The addition of sisal fiber into PP did not substantially affect the flammability. The incorporation of OMMT into PP showed 16% reduction of the burning rate of PP. The flame retardancy mechanism of OMMT involves a high-performance carbonaceous-silicate char, which builds up on the surface during burning [2]. Moreover, the dramatic reduction of burning rate about 37.5% was observed when OMMT was added into PP/Si composite. Similarly, Lee et. al. (2010) reported that the presence of clay at a small amount decreased the burning rate of wood fiber/HDPE composites and also suggested that achieving a higher degree of exfoliation of nanoclay is the key to enhance the flame retarding properties of natural fiber/polymer composites [8].

Generally, improvement in thermal stability is found for which the nanocomposite morphology plays an important role [9]. The incorporation of clay into the polymer matrix enhances thermal stability by acting as a superior insulator and mass transport barrier to the volatile products generated during decomposition [2]. Figure 5 shows TGA curves of PP and PP composites. The temperature at 5% weight loss ($T_{5\%}$) and weight residue at 600°C of PP and PP

composites are shown in Table 3. The $T_{5\%}$ of PP was at 285°C and no char residue left. When compared with PP, PP/Si composite showed no significant change of $T_{5\%}$ and left char residue about 1.8%. This was because the sisal fiber as lignocellulosic fillers has a component called lignin, which formed char during thermal degradation. Char reduces the combustion rate of polymeric materials by act as a protective layer to not allowing the oxygen to reach the combustion zone easily resulting in the reduction in thermal degradation in the material [10]. In addition, the incorporation of OMMT into PP and PP/Si composite resulted in a significant improvement in thermal stability by increasing the $T_{5\%}$ and char residue. Biswal et al. (2009) also observed a remarkable enhancement in thermal stability of PP/pineapple leaf fiber composite in the presence of OMMT [9].

Table 3: TGA data of PP and PP composites.

Designation	$T_{5\%}$ (°C)	Char residue at 600°C (%)
PP	285	0.00
PP/Si	286	1.80
PP/OMMT	304	1.50
PP/Si/OMMT	297	3.59

Conclusions

Incorporation of sisal fiber increased the tensile properties but reduced the impact strength of PP.

Addition of OMMT into PP and PP/Si composites enables to achieve the nanocomposite. XRD patterns showed the intercalated nanostructure for PP/OMMT composite and presented the exfoliated nanostructure for PP/Si/OMMT composite.

Tensile properties, flame retardancy, and thermal stability of PP were increased in a presence of OMMT. Moreover, the mechanical properties and flame retardancy of PP/Si composite were improved by incorporating the OMMT.

Acknowledgements

The authors express their thanks to Suranaree University of Technology and Center for Petroleum, Petrochemicals, and Advanced Materials for financial supports, SCG Chemicals Co.,Ltd. for supplying P700J, Southern Clay Products Inc., USA for providing Cloisite®30B, and Chemical Innovation Co., Ltd. for supplying Fusabond®P MZ 109D.

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EFFECT OF ORGANOCLAY TYPES ON MECHANICAL PROPERTIES AND FLAMMABILITY OF POLYPROPYLENE/SISAL FIBER COMPOSITES

W. Chanprapanon^{1,2}, N. Suppakarn^{1,2} and K. Jarukumjorn^{1,2*}

¹ School of Polymer Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima, Thailand

² Center for Petroleum, Petrochemicals, and Advanced Materials, Chulalongkorn University, Bangkok, Thailand

* Corresponding author (kasama@sut.ac.th)

Keywords: *Polypropylene, Sisal fiber, Organoclay, Mechanical properties, Flammability*

1 General Introduction

Natural fiber reinforced polymer composites have received considerable attention, particularly in construction, automotive, and aerospace industries due to environmental and ecological concerns. The advantages of natural fibers are low density, acceptable specific strength, less tool wear, biodegradability, and renewability. Sisal fiber has been widely used as a reinforcing fiber in polymers due to high tensile strength and stiffness. In addition, the sisal fiber is locally planted in Thailand.

Polypropylene (PP) is a common thermoplastic used as a matrix in composites because of its low cost, low density, good mechanical properties, and ease of processing. However, natural fibers are not well compatible with PP leading to the composite with poor mechanical properties. Generally, maleic anhydride grafted polypropylene (MAPP) is used to improve the compatibility between the natural fibers and PP matrix [1,2]. Another critical drawback of PP/natural fiber composites is their high flammability. Flame retardants, e.g. ammonium polyphosphate (APP), magnesium hydroxide (Mg(OH)₂), have been used to improve flame retardancy of the composites. However, adding the flame retardants at high content is required to obtain effective performance.

In recent years, incorporation of an organoclay as nanofiller has been considered for overcoming the drawbacks of the polymers. Adding organoclay at very low loading (less than 5 wt%) has been an interesting approach of improving mechanical properties, thermal stability, flame retardancy, and water resistance of the composites [3-6]. However, to achieve the good property enhancement,

organoclay particles should be homogeneously dispersed and exfoliated within the polymer matrix [3,4]. Several types of commercial organoclays are currently available. In general, the main difference among of them concerns type and amount of organic modifiers used in the modification which influenced the final properties of the PP/clay nanocomposites [7].

The objective of this work was to study the effect of organoclay type on mechanical, thermal, and flame retarding properties of PP/sisal fiber composites.

2 Material and Method

2.1 Materials

Polypropylene (PP, P700J) was supplied by SCG Chemicals Co., Ltd. Sisal fiber (SF) was purchased from the Sisal-Handicraft OTOP group, Nakhon Ratchasima, Thailand. The fiber was cut into an approximate length of 2 mm. Organoclays (organically modified montmorillonites, Cloisite[®]20 A (20A) and Cloisite[®]30B (30B)) were supplied from Southern Clay Products Inc., USA. The physical properties of organoclays used in this study are shown in Table 1. The chemical structures of organic modifiers of the modified montmorillonites are presented in Fig. 1. Maleic anhydride grafted polypropylene (MAPP, Fusabond[®]P MZ 109D, DuPont) was supplied from Chemical Innovation Co., Ltd.

Table 1. Physical properties of organoclays [8].

Organoclay	Organic modifier	Modifier concentration (meq/100g)
Cloisite [®] 20A	2M2HT ^a	95
Cloisite [®] 30B	MT2EtOH ^b	90

^a2M2HT: dimethyl, dehydrogenated tallow, quaternary ammonium

^bMT2EtOH: methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium



Fig. 1. Chemical structures of the organic modifiers of organoclay: (a) Cloisite[®]20A where HT is hydrogenated tallow (~65% C18; ~30% C16; ~5% C14) and (b) Cloisite[®]30B where T is tallow (~65% C18; ~30% C16; ~5% C14) [8].

2.2 Preparation of composites

Prior the composite preparation, sisal fiber and organoclay were dried in an oven at 70°C over night. PP compounds were prepared by melt blending using an internal mixer (Haake Rheomix, 3000p). The total mixing time was 15 min. The mixing temperature was 170°C and the rotation speed was 60 rpm. Test specimens were molded by an injection molding machine (Chuan Lih Fa, CLF 80T). Composition of PP composites and their designation used are shown in Table 2.

Table 2. Formulations of PP composites.

Designation	PP (phr)	Sisal (phr)	20A (phr)	30B (phr)	MAPP (phr)
PP/SF	100	30	-	-	-
PP/SF/20A	100	30	3	-	5
PP/SF/30B	100	30	-	3	5

2.3 Characterizations of materials

2.3.1 Structure characterization

The structure of organoclay and PP composites were determined by an X-ray diffractometer (XRD; Oxford, D5005) equipped with a Cu K α radiation source of wavelength 1.5406 Å operated at 40 kV and 40 mA at room temperature. Scanning rate and step size were 2.0°/min and 0.02° with 2 θ varying from 2° to 10°. XRD patterns were used to calculate the basal spacing or d-spacing from Bragg's law.

2.3.2 Mechanical test

Tensile properties of PP composites were measured according to ASTM D638 using a universal testing machine (UTM; Instron 5569). Impact test was performed on unnotched PP composites following ASTM D256 using an impact testing machine (Atlas, BPI). In all cases, average values from five specimens at least were taken for each sample.

2.3.3 Flammability test

Flammability of PP composites was characterized by a horizontal burning test according to ASTM D635 using a horizontal vertical flame chamber instrument (Atlas, HVUL). The sample was held horizontally and a flame was applied to light one end of the sample. The burning rate of the sample was calculated as follows:

$$V = 60L/t \quad (1)$$

Where V is the burning rate in millimeters per minute; L is the length the flame travels from the first reference mark (25 mm from the end) to the second reference mark, which is at 100 mm from the end; and t is the time in seconds for the flame to travel. Five measurements per sample were taken.

2.3.4 Thermal analysis

Thermal behaviors of PP composites were carried out on a thermogravimetric analyzer (TGA; TA Instrument, SDT2960) at a constant heating rate of 20°C/min under air flow. The temperature ranged from the room temperature to 700°C. The weight of each sample was kept within 10-15 mg.

3 Results and Discussion

3.1 Clay structure

XRD patterns of organoclays and PP composites are shown in Fig. 2. XRD patterns of 20A and 30B showed a peak at $2\theta = 3.32$ with a d-spacing of 2.66 nm and at $2\theta = 4.77$ with a d-spacing of 1.85 nm, respectively. PP/SF/20A composite presented a shifted peak to a lower angle at $2\theta = 2.74^\circ$ which corresponds to d-spacing of 3.22 nm, indicating the formation of an intercalated structure. For PP/SF/30B composite, the peak was disappeared. This implied that the silicate layers could be exfoliated and dispersed in PP matrix [9]. The observed difference between 20A and 30B may be due to the nature of organic modifiers.

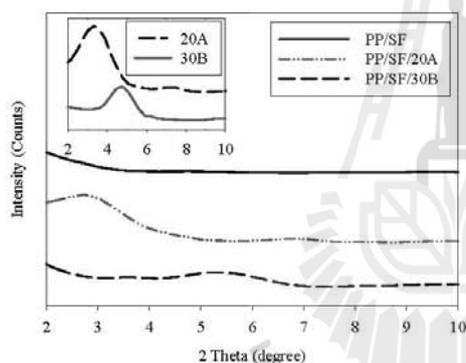


Fig. 2. XRD patterns of organoclays and PP composites.

3.2 Mechanical properties

Tensile properties of PP composites are listed in Table 3. Tensile strength of PP/SF/30B composite was higher than that of PP/SF/20A composite. This was because the organic modifier of 30B had hydroxyethyl group and showed higher polarity than that of 20A. Therefore, 30B had larger interaction capacity with the polar group of MAPP leading to the delamination in individual platelets [10]. However, the addition of organoclay did not show substantial increase in Young's modulus when compared with PP/SF composite.

Impact strengths of PP composites are presented in Table 3. The addition of organoclay slightly

improved the impact strength of PP/SF composites. Lee and Kim [4] also reported that incorporating 1 phr of organoclay slightly increased impact strength of wood/PP composites. However, organoclay type insignificantly affected the impact strength of PP/SF composites.

Table 3. Mechanical properties of PP composites.

Designation	Tensile strength (MPa)	Young's modulus (GPa)	Impact strength (kJ/m^2)
PP/SF	30.60 ± 0.37	2.32 ± 0.04	11.39 ± 0.25
PP/SF/20A	27.00 ± 0.92	2.31 ± 0.05	12.70 ± 0.36
PP/SF/30B	31.82 ± 1.60	2.36 ± 0.03	12.79 ± 0.50

3.3 Flammability

Fig. 3 shows burning rate of PP composites. The flame retardancy mechanism of organoclay involves a high performance carbonaceous silicate char, which built up on the surface during burning. The addition of 20A and 30B showed 15.5% and 37.5% reduction in burning rate of PP/SF composites, respectively. PP/SF/30B composite showed better improvement in flame retardancy than PP/SF/20A composite because PP/SF/30B composite achieved the formation of exfoliated nanostructure. Similarly, Lee et. al.[3] found that the presence of clay at a small amount decreased the burning rate of HDPE/wood fiber composites and also suggested that achieving a higher degree of exfoliation of nano clay is the key to enhance the flame retarding properties of natural fiber/polymer composites.

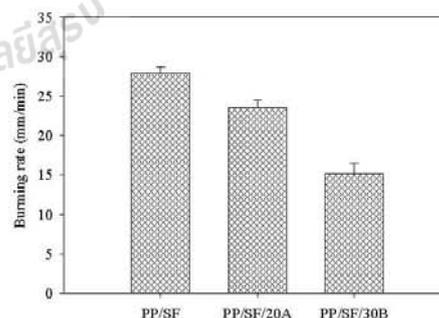


Fig. 3. Burning rate of PP composites.

3.4 Thermal stability

The temperature at 5% weight loss ($T_{5\%}$), the temperature at 90% weight loss ($T_{90\%}$), and weight residue at 600°C of PP and PP composites are shown in Table 4. PP showed $T_{5\%}$ and $T_{90\%}$ at 285°C and 396°C, respectively, and left no char residue. When compared with PP, PP/SF composite showed no significant change of $T_{5\%}$, $T_{90\%}$, and left char residue about 1.8%. Incorporation of organoclay into PP/SF composite increased the $T_{5\%}$, $T_{90\%}$, and char residue. This result indicated that thermal stability of the PP composite increased with the presence of organoclay. It may be due to some interaction between polymer matrix and organoclay which stabilized the composite. The well dispersed individual layers of intercalated/exfoliated clay sheets led to a decrease in volatile degradation products permeability [11]. In addition, char reduced the combustion rate of polymeric materials by act as a protective layer to limit the oxygen to easily reach the combustion zone [12].

Table 4. Thermal properties of PP and PP composites.

Designation	$T_{5\%}$ (°C)	$T_{90\%}$ (°C)	Char residue at 600°C (%)
PP	285	396	0.00
PP/SF	286	400	1.80
PP/SF/20A	288	414	3.44
PP/SF/30B	297	407	3.59

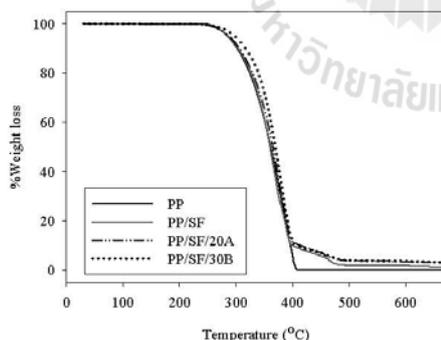


Fig. 4. TGA thermograms of PP and PP composites.

4 Conclusions

PP/SF/organoclay composites were prepared by melt blending. Two organoclays (Cloisite®20A and Cloisite®30B) were introduced into PP/SF composites. According to XRD analysis, PP/SF/20A composite showed intercalated structure while PP/SF/30B composite showed exfoliated structure. Adding 30B slightly improved mechanical properties of the PP/SF composite. Using a small content of organoclay improved flame retarding properties of PP/SF composites. PP/SF/30B composite with exfoliated structure showed better flame retarding properties than PP/SF/20A composite with intercalated structure. The addition of organoclay resulted in increased $T_{5\%}$, $T_{90\%}$, and char residue.

Acknowledgements

The authors express their thanks to Suranaree University of Technology and Center for Petroleum, Petrochemicals, and Advanced Materials for financial supports, SCG Chemicals Co., Ltd. for supplying polypropylene (700J), Southern Clay Products Inc., USA for providing Cloisite®20A and Cloisite®30B, and Chemical Innovation Co., Ltd. for supplying Fusabond®P MZ 109D.

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Advanced Materials Research Vol. 410 (2012) pp 47-50
 Online available since 2011/Nov/29 at www.scientific.net
 © (2012) Trans Tech Publications, Switzerland
 doi:10.4028/www.scientific.net/AMR.410.47

Flame Retardancy, Thermal Stability, and Mechanical Properties of Sisal Fiber/Organoclay/Polypropylene Composites

Wichuda Chanprapanon^{1,2,a}, Nitinat Suppakarn^{1,2,b}
 and Kasama Jarukumjorn^{1,2,c*}

¹School of Polymer Engineering, Institute of Engineering, Suranaree University of Technology, Nakhon Ratchasima 30000, Thailand

²Center for Petroleum, Petrochemical and Advanced Materials, Chulalongkorn University, Bangkok 10330, Thailand

^awchanprapanon@gmail.com, ^bnitinat@sut.ac.th, ^ckasama@sut.ac.th

Keywords: Natural fiber/polymer composites, Organoclays, Flame retardancy, Thermal stability, Mechanical properties

Abstract. Composites based on polypropylene (PP) and sisal fiber (SF) were prepared by melt blending. Sisal fiber content was 30 phr. Organoclay (OMMT; Cloisite®30B) (1-7 phr) was incorporated into the composites. In addition, maleic anhydride grafted polypropylene (MAPP) was used as a compatibilizer to enhance the interfacial adhesion between PP matrix and sisal fiber and also to improve the dispersion of the organoclay in PP matrix. The addition of OMMT had insignificantly affected mechanical properties of SF/PP composites. However, flame retardancy and thermal stability of SF/PP composites were improved dramatically with the presence of OMMT.

Introduction

The use of natural fibers as reinforcing filler for polymers has gained significant interest in the last decade both in industry and academia. Advantages of natural fibers over inorganic fillers are light weight, low cost, biodegradability, renewable nature, absence of toxic by-products, and high specific strength and modulus.

Polypropylene (PP) is one of the most popular thermoplastic polymers for producing natural fiber reinforced composites because of its low cost, low density, good mechanical properties, and ease of processing. The combination of natural fibers e.g. flax, hemp, sisal, jute, kenaf, or ramie with PP provides materials that can be used in construction, automotive, and aerospace industries. However, hydrophilic natural fibers and hydrophobic PP are not well compatible resulting in poor mechanical properties of the composites. Several studies showed that adding maleic anhydride grafted polypropylene (MAPP) as a compatibilizer at low concentration improves the fiber-polymer matrix adhesion [1]. In addition, high flammability is another drawback of natural fiber/PP composites due to their structure and chemical composition. Improving their flame retardancy can expand the range of their applications.

During the last decade, many researchers have reported that the incorporation of organoclays at very low loading (<5 %wt) into polymer can dramatically improve mechanical, thermal, and processing properties as well as enhance flammability resistance and barrier properties [2,3]. These property improvements are achieved through a good dispersion of clay in polymer to form an intercalated or exfoliated nanostructure [3,4]. It has been also found that MAPP acts as a dispersant and compatibilizer to enhance the melt intercalation of PP into the galleries of clay platelets [5].

The aim of this work was to study the effect of organoclay contents on mechanical, thermal, and flame retarding properties of SF/PP composites.

Materials and Method

Materials. Polypropylene (PP; P700J) was supplied from SCG Chemicals Co.,Ltd. Sisal fiber (SF; *Agave sisalana*) was purchased from the Sisal-Handicraft OTOP group in Tambon Ban Kao, Amphur Dan Khun Thod, Nakhon Ratchasima, Thailand. The sisal fiber was cut into approximate length of 2 mm. Maleic anhydride grafted polypropylene (MAPP; Fusabond[®]P MZ 109D, DuPont) provided by Chemical Innovation Co., Ltd. was used as a compatibilizer. Organoclay, montmorillonite modified with a methyl, tallow, bis-2-hydroxyethyl, quaternary ammonium, (OMMT; Cloisite[®]30B) was supplied from Southern Clay Products Inc., USA.

Composite Preparation. The sisal fiber and OMMT were dried in an oven at 70°C overnight before composite preparation. Composites were prepared using an internal mixer (Haake Rheomix, 3000p) for 15 min. The compounding temperature was 170°C and a rotation speed was 60 rpm. Then test specimens were molded by an injection molding machine (Chuan Lih Fa, CLF 80T). Composition of PP composites and their designation used are shown in Table 1.

Characterization. Tensile and flexural properties were measured according to the ASTM D638 and D790, respectively, using a universal testing machine (Instron, 5565). Impact test was performed on unnotched PP composites followed by ASTM D256 using an impact testing machine (Atlas, BPI). Flammability of PP composites was studied by a horizontal burning test according to ASTM D635, which gives a quantitative measure of rate of burning of the material, using a horizontal vertical flame chamber instrument (Atlas, HVUL). The thermal stability of PP composites were investigated using a thermogravimetric analyzer (TA Instruments, SDT2960) under air flow with samples of 10-15 mg.

Table 1. Designation and composition of SF/PP composites.

Designation	PP [phr]	Sisal fiber [phr]	Cloisite [®] 30B [phr]	MAPP [phr]
SF/PP	100	30	0	5
SF/PP/OMMT1	100	30	1	5
SF/PP/OMMT3	100	30	3	5
SF/PP/OMMT5	100	30	5	5
SF/PP/OMMT7	100	30	7	5

Results and Discussion

Mechanical Properties. Tensile properties of SF/PP composites are shown in Table 2. The tensile strength of the SF/PP composites decreased with increasing OMMT content. This may be because OMMT particle could not well disperse in the polymer matrix [6]. Additionally, Young's modulus of SF/PP composites insignificantly changed with increasing OMMT content.

Flexural properties of SF/PP composites are presented in Table 2. Increasing OMMT content exhibited little effect on the flexural properties of SF/PP composites because of the poor dispersion of clay in PP.

Impact strength of SF/PP composites also are listed in Table 2. Impact strength of SF/PP composites was retained with adding OMMT. Similar investigations have also been reported for natural fiber/organoclay/PP composites [1,2]. However, Nourbaskhsh and Ashori (2009) showed that the impact strength of bagasse/PP composites was lowered by the addition of organoclay because the presence of clay particles in the PP matrix provides points of stress concentrations, thus providing sites for crack initiation [7].

Table 2. Mechanical properties of SF/PP composites.

Designation	Tensile strength [MPa]	Young's modulus [GPa]	Flexural strength [MPa]	Flexural modulus [GPa]	Impact strength [kJ/m ²]
SF/PP	35.10 ± 0.44	1.986 ± 0.066	56.23 ± 0.60	2.768 ± 0.066	11.48 ± 0.94
SF/PP/OMMT1	32.83 ± 0.32	2.016 ± 0.038	55.15 ± 0.88	2.785 ± 0.040	11.89 ± 0.71
SF/PP/OMMT3	32.39 ± 0.47	2.055 ± 0.079	55.38 ± 0.38	2.987 ± 0.034	12.57 ± 0.78
SF/PP/OMMT5	32.28 ± 0.69	2.161 ± 0.039	55.77 ± 0.93	3.003 ± 0.035	12.39 ± 0.12
SF/PP/OMMT7	31.74 ± 0.34	2.049 ± 0.060	54.41 ± 0.81	2.863 ± 0.057	11.93 ± 0.26

Flammability. Burning rate of SF/PP composites measured by a horizontal burning test are shown in Fig. 1 and Table 3. Among all composites, SF/PP composite without OMMT had the highest burning rate. The SF/PP composite with OMMT 7 phr showed the lowest burning rate (28% reduction). Increasing OMMT content decreased the burning rate of SF/PP composites. This was because during the burning, OMMT could form a high-performance carbonaceous-silicate char on the surface [8].

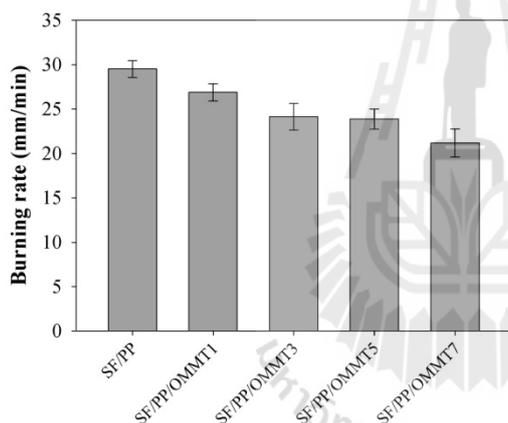


Table 3. Burning rate of SF/PP composites.

Designation	Burning rate [mm/min]
SF/PP	29.51 ± 0.94
SF/PP/OMMT1	26.88 ± 0.97
SF/PP/OMMT3	24.15 ± 1.50
SF/PP/OMMT5	23.88 ± 1.13
SF/PP/OMMT7	21.18 ± 1.58

Fig. 1 Burning rate of SF/PP composites.

Thermal Stability. TGA curves of SF/PP composites are presented in Fig. 2. Temperature at 5% weight loss ($T_{5\%}$) and weight residue at 600°C of SF/PP composites are shown in Table 4. SF/PP composite showed $T_{5\%}$ at 292°C and left 1.97% char residue at 600°C. The addition of OMMT into SF/PP composites slightly increased the $T_{5\%}$ and left a greater amount of char residue than the SF/PP composite without OMMT. This result indicated that thermal stability of the SF/PP composites were improved with adding OMMT. It was reported that incorporation of clay into polymeric materials enhanced thermal stability by acting as a superior insulator and mass transport barrier to volatile products during decomposition as well as by assisting in the formation of char [3,9]. Char also reduced the combustion rate of polymeric materials by act as a protective layer to limit the oxygen to easily reach the combustion zone [10].

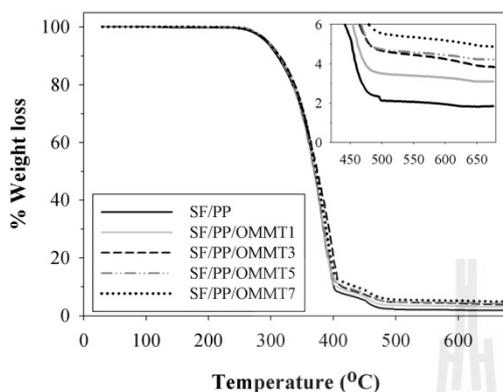


Table 4. TGA data of SF/PP composites.

Designation	T _{5%} [°C]	Residue at 600°C [%]
SF/PP	292	1.97
SF/PP/OMMT1	296	3.30
SF/PP/OMMT3	295	4.24
SF/PP/OMMT5	295	4.45
SF/PP/OMMT7	296	5.19

Fig. 2 TGA data of SF/PP composites.

Summary

In this paper, mechanical properties, flame retardancy, and thermal stability of sisal fiber/organoclay/PP composites were investigated. The incorporation of organoclay showed insignificant effect on Young's modulus, flexural properties, and impact strength of the SF/PP composites. However, flame retardancy and thermal stability of the SF/PP composites were enhanced with adding organoclay.

Acknowledgements

The authors express their thanks to Suranaree University of Technology and Center for Petroleum, Petrochemicals, and Advanced Materials for financial supports, SCG Chemicals Co., Ltd. for supplying PP (P700J), Southern Clay Products Inc., USA for providing organoclay (Cloisite®30B), and Chemical Innovation Co., Ltd. for supplying MAPP (Fusabond®P MZ 109D).

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BIOGRAPHY

Miss Wichuda Chanpranon was born on February 10, 1984 in Lopburi, Thailand. She completed a bachelor's degree in textile science and technology with 2nd class honors from Thammasat University, Thailand in 2005.

After a period of marketing textiles at Thanulux Public Company Limited, Thailand and then participating with Cultural Care Au Pair in the United States for one and a half years, she enrolled and was awarded a scholarship for graduate studies in polymer engineering at Suranaree University of Technology, Thailand.

During her master degree's study, she presented four poster presentations entitle: **“Effect of nanoclay on mechanical properties and flame retardancy of sisal fiber/polypropylene composites”** in the Pure and Applied Chemistry International Conference 2011 (PACCON 2011) in Bangkok, Thailand, **“Flammability and mechanical properties of polypropylene/sisal fiber composite containing organoclay”** in the 2nd Research Symposium on Petroleum, Petrochemicals and Advanced Materials and the 17th PPC Symposium on Petroleum, Petrochemicals, and Polymers (PPAM 2 and PPC 17) in Bangkok, Thailand, **“Effect of organoclay types on mechanical properties and flammability of polypropylene/sisal fiber composites”** in the 18th International Conference on Composite Materials (ICCM 18) in Jeju, Korea, and **“Flame retardancy, thermal stability, and mechanical properties of sisal fiber/organoclay/polypropylene composites”** in the 20th International Symposium on Processing and Fabrication of Advanced Materials (PFAM XX) in Hong Kong, People's Republic of China (PRC).