ผลกระทบของสารลดแรงตึงผิวเกลือฟอสเฟตที่มีต่อสมบัติของพอลิโพรพิลีน/ดินเหนียวนาโนคอมพอสิทคาสท์ฟิล์ม

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THE EFFECT OF PHOSPHATE SALT SURFACTANT ON THE PROPERTIES OF POLYPROPYLENE/CLAY NANOCOMPOSITE CAST FILMS

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วิโรจน์ แซ่เจียง: ผลกระทบของสารลดแรงตึงผิวเกลือฟอสเฟตที่มีต่อสมบัติของพอลิโพรพิลีน/ดินเหนียวนาโนคอมพอสิทคาสท์ฟิล์ม. (THE EFFECT OF PHOSPHATE SALT SURFACTANT ON THE PROPERTIES OF POLYPROPYLENE/CLAY NANOCOMPOSITE CAST FILMS) อ.ที่ปรึกษาวิทยานิพนธ์หลัก: ผศ.ดร. อนงค์นาฎ สมหวังธนโรจน์, 93 หน้า

งานวิจัยนี้มุ่งเน้นการพัฒนาสมบัติของฟิล์มบรรจุภัณฑ์ เช่น สมบัติเชิงกล สมบัติทางความร้อน และการลดการซึมผ่านของก๊าซออกซิเจน โดยนำดินเหนียวอนุภาคระดับนาโนเมตรที่ได้รับการปรับแต่งสภาพพื้นผิวด้วยสารลดแรงตึงผิว เติมลงไปในเนื้อพอลิโพรพิลีนและเติมสารประสานเพื่อช่วยให้การผสมและการกระจายตัวของดินเหนียวดีขึ้น ดินเหนียวระดับนาโนเมตรมีคุณสมบัติเป็นสารเสริมแรงเมื่อเติมลงไปในเนื้อพอลิเมอร์ เพราะดินเหนียวสามารถช่วยรับแรง นอกจากนี้ดินเหนียวขนาดนาโนเมตรสามารถลดการซึมผ่านของก๊าซออกซิเจนได้เนื่องจากโครงสร้างของดินเหนียวที่มีลักษณะเป็นชั้นซึ่งสามารถสกัดกั้นทางเดินผ่านของก๊าซได้อย่างดี ทั้งนี้ดินเหนียวนาโนจะสามารถประพฤติตัวเป็นสารเสริมแรงและตัวสกัดกั้นก๊าซได้ดีเมื่อดินเหนียวมีการกระจายตัวในเนื้อพอลิเมอร์ที่ดี ซึ่งขึ้นกับประสิทธิภาพของสารลดแรงตึงผิวและความสามารถในการแลกเปลี่ยนไอออนบวกกับสารลดแรงตึงผิวของดิน ในงานวิจัยนี้ได้ศึกษาผลของสารลดแรงตึงผิวสองตระกูลหลัก อันได้แก่ สารลดแรงตึงผิวชนิดเกลือของแอมโมเนียมโครงสร้างใหญ่ และ สารลดแรงตึงผิวชนิดเกลือของฟอสเฟตซึ่งมีลักษณะโครงสร้างต่างกันจากเล็กไปใหญ่ 3 ชนิด, ชนิดของดินเหนียวที่มีความสามารถในการแลกเปลี่ยนไอออนและลักษณะทางกายภาพต่างกัน 2 ชนิด และปริมาณของดินเหนียวที่ได้รับการปรับแต่งแล้ว ต่อคุณสมบัติต่าง ๆ ของพอลิโพรพิลีน/ดินเหนียว นาโนคอมพอสิท ซึ่งขึ้นรูปด้วยหัวไดแบบคาสท์ฟิล์ม

จากผลการศึกษาพบว่า ฟิล์มนาโนคอมพอสิทที่ถูกเติมแต่งด้วยดินเหนียวความละเอียดไม่มากที่ปรับสภาพพื้นผิวด้วยสารลดแรงตึงผิวที่มีลักษณะโครงสร้างใหญ่เช่น เกลือของแอมโมเนียม เกลือของฟอสเฟตที่มีโครงสร้างกลางและใหญ่ สามารถพัฒนาค่ามอดูลัสของยังและลดการซึมผ่านของก๊าซออกซิเจนของฟิล์มนาโนคอมพอสิทที่ได้มากกว่าฟิล์มที่เติมดินเหนียวชนิดอื่น ๆ เนื่องจาก สารลดแรงตึงผิวชนิดนี้ทำให้การกระจายตัวของดินเหนียวในพอลิเมอร์ดี อีกทั้งยังมีการรวมตัวกันของดินเหนียวน้อยกว่าดินชนิดอื่น ๆ อย่างไรก็ตามฟิล์มที่เติมดินเหนียวความละเอียดน้อยที่มีสารลดแรงตึงผิวชนิดเกลือของฟอสเฟตโครงสร้างระดับกลางแสดงลักษณะของฟิล์มดีกว่าชนิดอื่น ๆ นอกจากนี้ ฟิล์มที่เติมด้วยดินเหนียวดังกล่าว 5 % โดยน้ำหนักสามารถพัฒนาค่ามอดูลัสได้สูงสุดถึง 4 เท่าโดยเปรียบเทียบของฟิล์มพอลิโพรพิลีนบริสุทธิ์

ภาควิชา..........วิศวกรรมเคมี.........ลายมือนิสิต..
สาขาวิชา.........วิศวกรรมเคมี........ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก..............................
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WIROTE SAE-CHIENG: THE EFFECT OF PHOSPHATE SALT SURFACTANT ON THE PROPERTIES OF POLYPROPYLENE/CLAY NANOCOMPOSITE CAST FILMS. ADVISOR: ASST.PROF. ANONGNAT SOMWANGTHANAROJ, Ph.D., 93 pp.

The main focus of this research was the improvement on mechanical, thermal and gas barrier properties of packaging films by the addition of nanoclay that was surface treated by surfactant in polypropylene matrix, in which the compatibilizer was added to increase the degree of clay dispersion. Nanoclay can act as the reinforcing filler when it was filled in polymer matrix because it helped transferring. Furthermore, gas barrier properties of nanoclay was observed, which was caused by layered clay obstructed path way of gas. Therefore, nanoclay can efficiently acted as the good reinforcing agent and gas barrier filler when it exhibited the high degree of clay dispersion in polymer, which depended on the effect of surfactant that was used to treat nanoclay and cation exchange capacity (CEC) of clay. In this study, the effect of surfactant, which was the large structure of ammonium salt and several kind of phosphate salt, source of clay that was different in CEC and physical characteristics and the modified clay loading on the properties of polypropylene/clay nanocomposite cast films was studied.

Polypropylene/clay nanocomposite films with fined T-organoclay that was treated by large structured surfactant such as ammonium salt, medium and large structured phosphate salt, showed the improved tensile modulus and oxygen permeability when compared with those of other nanocomposite films. It could be due to the high degree of clay dispersion and low degree of clay agglomeration of these organoclay. Furthermore, ultra fined nanoclay, which had high CEC, showed clay agglomeration. However, nanocomposite film with fined nanoclay that was treated by medium structure phosphate surfactant showed the nice appearance of film than that of other films. Moreover, films containing 5 wt% of this organoclay showed 4 times higher tensile modulus than virgin polypropylene film.

Department :........Chemical Engineering........Student's Signature..Wirote S.......
Field of Study :.....Chemical Engineering........Advisor's Signature..............
Academic Year :.................2008..................

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LIST OF ABBREVAIATIONS

A2	Dimethyl dihydrogenatedtallow quaternary ammonium chloride (ARQUAD 2HT-75)
ASTM	American Society for Testing and Materials
CEC	Cation exchange capacity
DSC	Differential scanning calorimetric
MKA2	MMK with A2 surfactant
MKPL	MMK with PL surfactant
MKPM	MMK with PM surfactant
MKPS	MMK with PS surfactant
MMK, K-clay	Ultra fined sodium bentonite with high CEC (110 meq/100 g of clay)
MMT, T-clay	Fined sodium bentonite (SAC) with CEC of 60 meq/100 g of clay
MTA2	MMT with A2 surfactant
MTPL	MMT with PL surfactant
MTPM	MMT with PM surfactant
MTPS	MMT with PS surfactant
M.W.	Molecular weight
OM	Optical microscopy
O_2TR	Oxygen transmission rate
PO_2	Oxygen permeability
PL	hexadecyltributylphosphoniumbromide (CYPHOS 3472P)
PM	tetradecyltributylphosphoniumchloride (CYPHOS 3453W)
PP	Polypropylene
PPcomp	PP blended with 9wt% of PP-g-MA
PP-g-MA	Maleic anhydride graft polypropylene
PP-3KA2	PP containing 3 wt% of MKA2
PP-3KPL	PP containing 3 wt% of MKPL
PP-3KPM	PP containing 3 wt% of MKPM
PP-3KPS	PP containing 3 wt% of MKPS
PP-1TPM	PP containing 1 wt% of MTPM

PP-3TA2	PP containing 3 wt% of MTA2
PP-3TPL	PP containing 3 wt% of MTPL
PP-3TPS	PP containing 3 wt% of MTPS
PP-3TPM	PP containing 3 wt% of MTPM
PP-5TPM	PP containing 5 wt% of MTPM
PP-7TPM	PP containing 7 wt% of MTPM
PS	tetrabutylphosphoniumbromide (CYPHOS 442W)
XRD	X-ray diffraction

CHAPTER I

INTRODUCTION

1.1 General introduction

The packaging film is the important material in the several industrial applications. Normally, packaging film is usually processed from polyethylene (PE) or polypropylene (PP) which has high oxygen permeability. It affects the rate of product degradation. Nowadays, the addition of some filler such as platelet nanoclay in the polymer matrix can reduce the oxygen transfer rate because of the gas barrier properties of nanoclay [1].

In recent years, several researches in field of polymer/clay nanocomposites had published [1-14]. The variety of polymer are used as polymer matrix for the suitable application i.e., automotive, food packaging, and others [3, 5, 6]. When nanoclay was added, it helped to transfer the stress between clay and polymer matrix that made the nanocomposite become high stiffness [2-3, 5, 13-17]. Furthermore, some of researches found that nanoclay can be used to improve fire retardant properties [2].

Before using nanoclay as filler, it is important to treat the surface of nanoclay by the surfactant. The surfactant exchanges with natural cation in nanoclay during the cation exchange reaction. After the reaction, the increasing of d – spacing of clay layer occurs and the polarity of clay is changed to be more hydrophobic that is suitable and easy to mix with the non polar based polymer. We call this type of nanoclay as “organoclay”.

The structure of the surfactant, which uses in the cation exchange reaction, affects the degree of clay dispersion [1-3]. In the previous research, the large structure of surfactant can effectively help to enhance the d – spacing of clay layer more than that of small structure surfactant [2-3]. The examples of surfactants are the traditional ammonium salt and the new synthesis phosphate salt [18-19].

In this study, we focus on the study of the effect of the new type surfactant phosphate salt on the properties of polypropylene/clay nanocomposite cast films. Moreover, effect of several types of surfactants and organoclay loading were also discussed.

1.2 Objectives

This research aims to generate the technical knowledge of production of casting film and the mechanical, thermal and gas barrier properties such as tensile strength, tensile modulus, melting temperature and oxygen transferring rate, respectively of polyprppylene/nanocomposite cast films. The objectives of this work are

1. To study the effect of surfactant on clay dispersion in the polymer matrix.
2. To study the effect of surfactant and clay composition and clay loadings on the mechanical, thermal and gas barrier properties on the polypropylene/clay nanocomposite cast films.

1.3 Scopes of the research

1.3.1 The following parameters were studied:

a. Types of montmorillonite clay

- Thai montmorillonite clay (CEC 60 meq/100 g)
- Korean montmorillonite clay (CEC 110 meq/100 g)

b. Types of surfactant

- Ammonium salt (Dimethyl dehydrogenated tallow, quaternary ammonium)
- Phosphate salt (tetrabutylphosphoniumbromide, tetradecyltributylphosphoniumchloride and hexadecyltributylphosphoniumbromide)

c. Clay loading between 0 – 7% by weight.

1.3.2 The following properties were studied:

a. Degree of clay dispersion by means of XRD

b. Inorganic content in films

c. Mechanical properties

  - Tensile properties by universal testing machine according to ASTM D882

d. Thermal properties by means of DSC

  - Melting temperature
  - Degree of crystallinity

e. Oxygen transmission rate

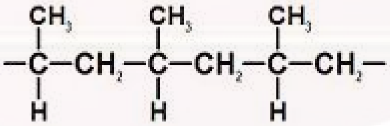
f. Appearance of nanocomposite films

CHAPTER II

THEORY

2.1 Polypropylene

Polypropylene or polypropene (PP) is a thermoplastic polymer and its structure is shown in figure 2.1. Most commercial polypropylene is isotactic polypropylene (the methyl group turns into the same side) and it has an intermediate level of crystallinity between that of low density polyethylene (LDPE) and high density polyethylene (HDPE). Its Young's modulus is also intermediate. Through the incorporation of rubber particles, PP can be made both tough and flexible, even at low temperatures. PP has a typical melting point of around 160°C (320°F), as determined by Differential Scanning Calorimetry (DSC). Many plastic items for medical or laboratory use can be made from PP because it can withstand the heat in an autoclave. Food containers made from it will not melt in the dishwasher, and do not melt during industrial hot filling processes.



$$-\overset{CH_3}{\underset{H}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2-$$

Figure 2.1 structure of PP [20]

PP has been used in a wide variety of applications, including packaging, textiles (e.g., ropes, thermal underwear and carpets), stationary, plastic parts and reusable containers of various types, laboratory equipment, loudspeakers, automotive components, and polymer banknotes [21-22].

2.2 Processing technique

2.2.1 The extrusion

The most common process in polymer industry is extrusion. This process can mix the component together under the shear force by screw in the extruder. It has been classified into two major types depending on the number of screw in the extruder. In this research, the co-rotating twin screw extruder was used to compound the based polymer and reinforcing agent because this type of extruder has the high efficiency of shear rate that was suitable to mix compound to be homogenous.

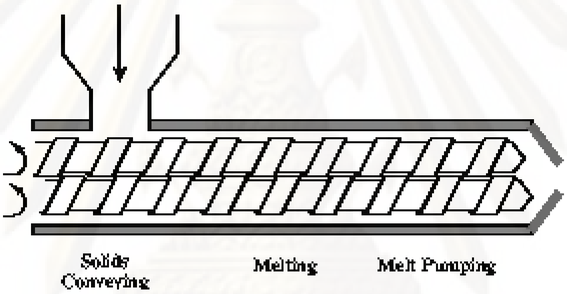


Figure 2.2 schematic of the twin screw extruder [23]

The cross sectional shape of the final product, which processed by extruder is designed by shape of die, for example, rod capillary die, blow film die and cast film die. In this research, we focus on casting the film so the cast film died is attached to the extruder.

2.2.2 Casting technique

In a cast film extrusion process, thin film is extruded through a slit onto a chilled, highly polished turning roll, where it is quenched from one side. The speed of the roller controls the draw ratio and final film thickness. The film is then sent to a second roller for cooling on the other side. Finally it passes through a system of rollers and is wound onto a roll. Thicker polymer sheets can be manufactured similarly. A sheet is distinguished from a film by its thickness, i.e., by definition a sheet has a thickness more than 2.50 mm. Otherwise, it is called a film.

The cast film process is used for very tight tolerances of thin film, or for low viscosity resins. Most flat dies are T-slot or coat hanger designs, which contain a manifold to spread the flowing polymer across the width of the die, followed downstream by alternating narrow and open slits to create the desired flow distribution and pressure drop. Most cast film lines manufactured today are coextrusion lines, combining layers from as many as 7 extruders into the product through multimanifold dies, or else single manifold dies with the aid of feedblocks [24].

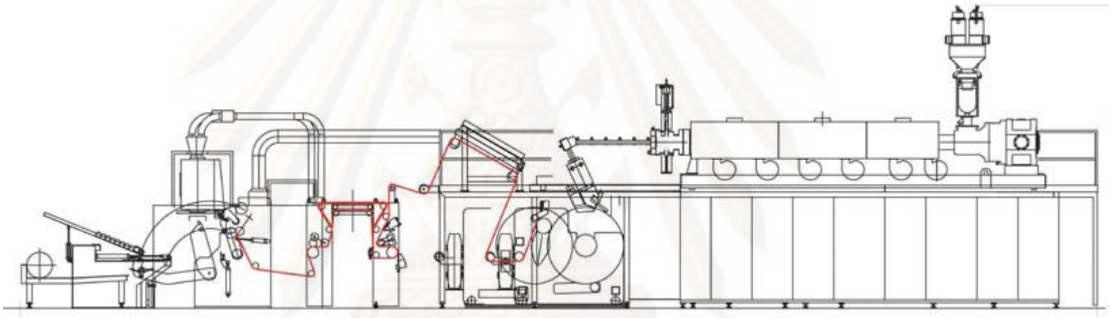


Figure 2.3 diagram of a cast film extrusion line [24]

2.3 Clay and organoclay

2.3.1 Montmorillonite (clay)

Montmorillonite is very soft phyllosilicate mineral that typically forms in microscopic sturcture. Montmorillonite, a member of the smectite family, is a 2:1 clay, meaning that it has 2 tetrahedral sheets sandwiching a central octahedral sheet. The particles are plate-shaped with an average diameter of approximately 1 micrometre.

Chemically it is hydrated sodium calcium aluminium magnesium silicate hydroxide $(Na,Ca)_{0.33}(Al,Mg)_2(Si_4O_{10})(OH)_2 \cdot nH_2O$. Potassium, iron, and other cations are common substitutes and the exact ratio of cations varies with source.

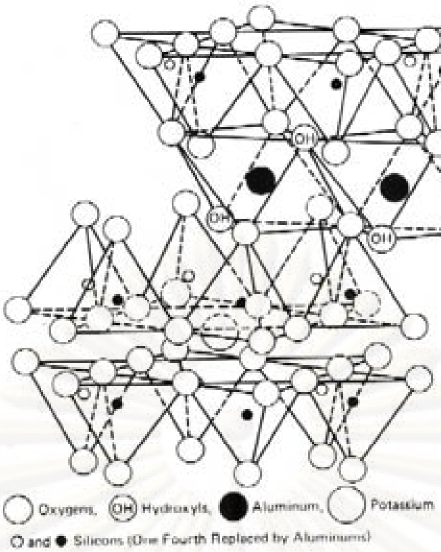


Figure 2.4 clay structure [25]

In natural, nanoclay has the exchangeable cation between the clay layers such as sodium ion, magnesium ion and calcium ion. The efficiency of cation exchanger can be measure by the CEC (cation exchange capacity) that relates to the source of clay.

2.3.2 Organoclay

In the present clay minerals are used as fillers in different products. The interactions between organic matter and clay minerals are among the most widespread reactions in nature. The interactions include cation exchange and adsorption of polar and nonpolar molecules. Smectites especially montmorillonite have been the most studied minerals of all clays. These minerals are able to swell and adsorb polar organic compounds into their interlayer space. The presence of small inorganic cations in the interlayer makes this space hydrophilic. However, inorganic exchangeable cation can also be replaced by a quaternary ammonium cation in the interlayer. This treatment is used to enhance the hydrophobic properties of the clay. These modified clays are commonly referred to as “organoclays”. There are two types of organoclay: those saturated with large quaternary ammonium cations with one or two long alkyl chains and those saturated with small quaternary ammonium aliphatic and aromatic cations. Some investigators use the term “organophillic clays” for the first type and the “adsorptive clays” for the organoclays saturated with small quaternary ammonium cations. For example, the exchange reaction between an inorganic metallic cation, M^{m+}, initially saturating a smectite mineral, M^{m+}-Smec, and an aqueous solution of an aliphatic ammonium salt such as ethylammonium chloride, $C_2H_5NH_3Cl$, can be formulated by the following equation:

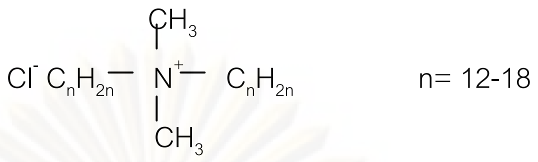
$$mC_2H_5NH_3Cl\,(aq) + M^{m+}\text{-smec}(s) \longleftrightarrow MCl_m(aq) + (C_2H_5NH_3^{+})_m\text{-smec}(s)$$

Figure 2.5 the treatment of clay by ion exchange with surfactant [10]

2.4 Surfactant

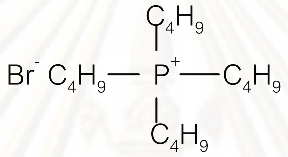
Normally, surfactant is a form of cation salt with the organic part. The large structure surfactant helps to increase the d-spacing of clay layers after the ion exchange reaction [1-3, 8, 12-14, 18-19]. In the previous work, the ammonium salt is the popular surfactant. Recently, the synthesized phosphate salt is developed. This kind of surfactant can improve the degradation temperature of organoclay [18-19], which interests us to study the effect of this surfactant on the polypropylene/clay nanocomposite cast films. Surfactants used in this study are the quaternary ammonium and phosphate salt, which can exchange cation with clay. Treating surface of clay makes the larger of d – spacing in clay than original clay.Types of salt affect the thermal properties of modified clay [8, 13, 15, 18-19]. The types of surfactants those used in this study are as follows.

2.4.1 Dimethyl bis(hydrogenated-tallow) ammonium chloride (ARQUAD ®2HT-75)



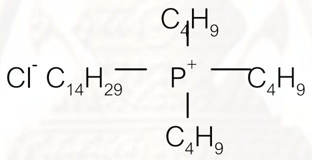
$$Cl^{-}\ C_nH_{2n}-\overset{CH_3}{\underset{CH_3}{N^{+}}}-C_nH_{2n} \qquad n= 12\text{-}18$$

2.4.2 Tetrabutylphosphoniumbromide (Cyphos 442W)



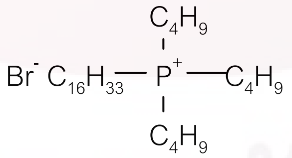
$$Br^{-}\ C_4H_9-\overset{C_4H_9}{\underset{C_4H_9}{P^{+}}}-C_4H_9$$

2.4.3 Tetradecyltributylphosphoniumchloride (Cyphos 3453W)



$$Cl^{-}\ C_{14}H_{29}-\overset{C_4H_9}{\underset{C_4H_9}{P^{+}}}-C_4H_9$$

2.4.4 Hexadecyltributylphosphoniumbromide (Cyphos 3472P)



$$Br^{-}\ C_{16}H_{33}-\overset{C_4H_9}{\underset{C_4H_9}{P^{+}}}-C_4H_9$$

The effect of the surfactant on the properties of polypropylene/clay nanocomposite cast films was studied.

2.5 Polymer/clay nanocomposites

Nowadays, there are many researches on nanocomposites are interested because clay can improve the properties of the nanocomposites. There are 3 levels of clay dispersion in polymer matrix, which is shown in figure 2.6. From figure 2.6, the clay fraction in conventional clay composites plays little or no functional role and acts mainly as a filling agent for economic considerations. Intercalated nanocomposites are formed when polymer chains are inserted into the clay galleries with fixed interlayer spacing. Exfoliated nanocomposites are formed when the silicate nanolayers are individually dispersed in the polymer matrix. Clay is a good reinforcement when it exfoliated.

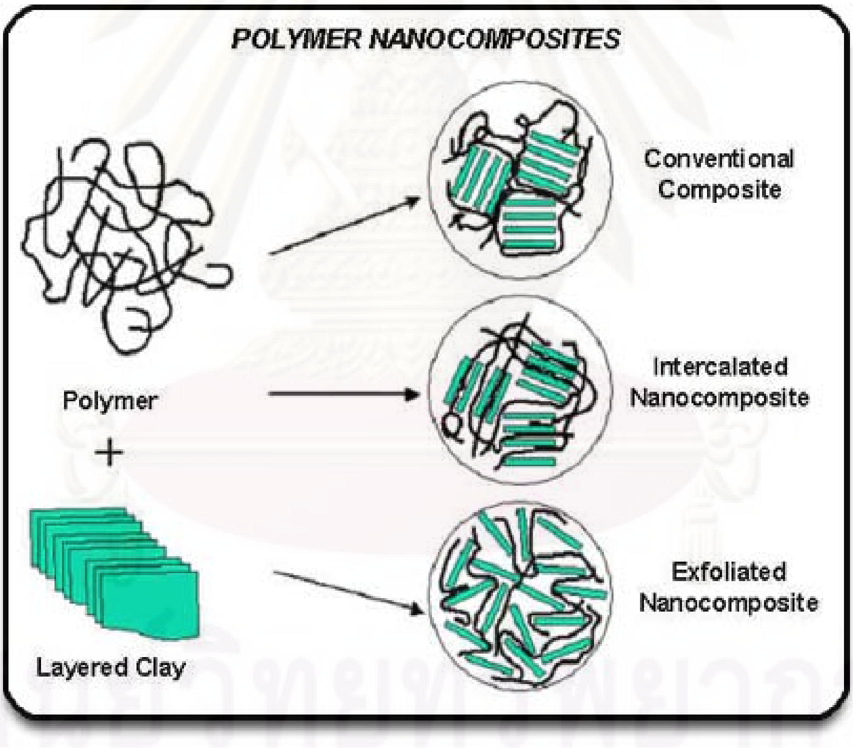


Figure 2.6 classifications of clay dispersion [26]

The way to classify the types of polymer nanocomposites is the X-ray diffraction (XRD) and TEM technique. The XRD pattern indicates the intercalated nanocomposites if the XRD graph show peak. On the other hand, the exfoliated nanocomposites do not show any peak in the XRD pattern.

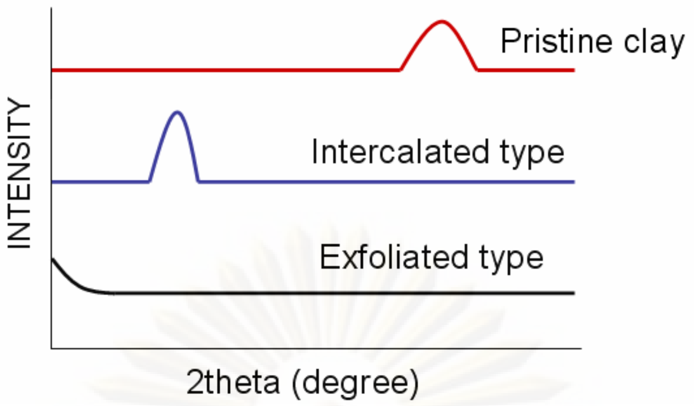


Figure 2.7 the XRD pattern

However, most of the polymer/clay nanocomposites is intercalated nanocomposites, in which some part of clay can disperse in the polymer matrix. Using organoclay and compatibilizer can improve the degree of clay dispersion [3-4, 8, 12-13, 15].

In general, polymer/clay nanocomposites can be prepared by several methods, i.e., solution method, in situ intercalative polymerization of monomers and melt mixing. Solution intercalation method is not an effective way to prepare commercial nanocomposites because of high costs of solvents, which are also environmental unfriendly. Furthermore, a compatible polymer/clay solvent system is not always available. In situ polymerization involves the insertion of a suitable monomer into the clay galleries followed by polymerization. Melt intercalation method is broadly applicable to many commodity and engineering polymers. Melt compounding is a flexible and commercial process capable of producing a variety of products on large volume scales [9].

2.6 Compatibilizer

Polymer and clay have the different of polarity; therefore, using of compatibilizer helps bonding between the two phases more tightly. When the polymer and clay are miscible mixed, the mechanical properties of nanocomposites enhance [1–8, 12-15]. Graft copolymers are also used as compatibilizer such as polyethylene graft maleic anhydride (PE-g-MA) and polypropylene graft maleic anhydride (PP-g-MA) as shown in figure 2.8.

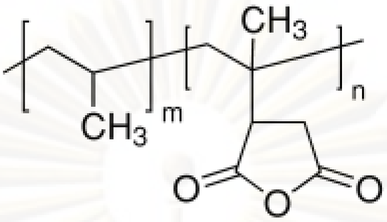


Figure 2.8 structure of PP-g-MA [27]

2.7 Characterizations

2.7.1 Mechanical measurement

Tensile properties indicate the behavior of material that reacts to forces applied in tension. The results are obtained from measuring the applied load and the elongation of specimen over some distance.

Normally, the specimens that are suitable to test the tensile properties are the dog bone shape or rectangular shape, which depend on the sample characteristic. In this research, the rectangular shape film specimens were tested under tension force accordance with ASTM D882 by using an Universal testing machine (Instron 5567, USA) in order to determine the modulus, tensile strength at yield and elongation at break shown in figure 2.9.

In tension test, the Young's modulus of the sample can be calculated from stress divide by its strain at the initial period which still linear relation. The ultimate elongation at break of engineering material obtains before it breaks. 100% ultimate elongation at break is common for polyolefin films. A high tensile Young's modulus and high elongation at break mean that the material is both rigid and tough.

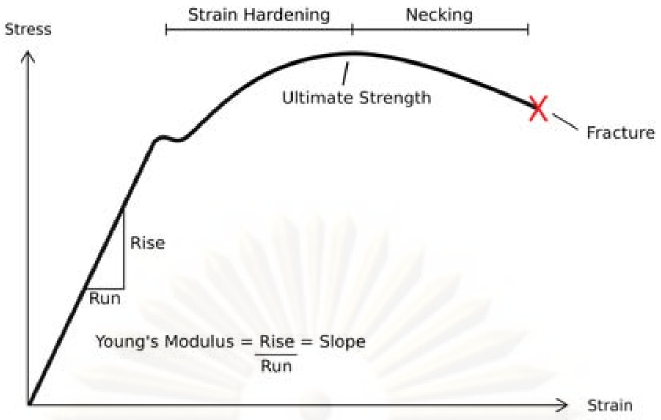


Figure 2.9 the diagram of stress/strain of sample under tension

2.7.2 Degree of clay dispersion analysis

The technique to analyze the interlayer spacing of clay and organoclay in polypropylene/clay nanocomposite cast film under X-ray irradiation of a known wavelength were proformed by mean of X-ray diffraction technique.

In this research, the D8 advance BRUKER German with CUKα radiation of wavelength 1.542 Å at 40 kV and 30mA at the ambient temperature were used to obtain the XRD pattern of the samples.

2.7.3 Thermal property testing

The melting temperature and degree of crystallinity of polypropylene/clay nanocomposite cast films were observed by mean of differential scanning calorimetry technique. The amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. The addition of energy to the samples were changed the form of partially crystalline polymer to amorphous form. The melting temperature showed as the endothermic peak.

The degree of crystallinity of the polypropylene/clay nanocomposite cast films can be calculated from the area of endothermic peak of the DSC curve.In this research, the crystallinity of the nanocomposite cast films were compared with the polypropylene film and compatibilizer to obtain relative degree of crystallinty of film.

2.7.4 Oxygen transmission rate

The measurement of the amount of oxygen gas that passed through the sample over a given period is the oxygen transmission rate (O_2TR). In this research, the oxygen transmission rate of polypropylene/clay nanocomposite cast films were observed by oxygen permeation analyzer (OX-TRAN 2/21, Mocon) following ASTM D1434.

CHAPTER III

LITERATURE REVIEWS

There were many researches regarding the effect of surfactant and compatibilizer on the mechanical and other properties of nanocomposites [1-5, 6-13]. A few of researches are focus on types of surfactants.

3.1 Casting film

There are several important parameters in the process of casting film such as temperature of chill roll, air gap between die and chill roll and draw ratio. Kenneth and Graham had studied the effect of those parameters on the thickness of film. Decreasing of draw ratio makes thicker film. Temperature profile of film is then slowly cooled. In addition, when air gap is wide, the widthness of film decreases because of the effect of neck in [28].

3.2 The effect of surfactant

Many researches showed the enhancement of mechanical and other properties [1–8, 12-15], when adding only small amount of clay into polymer matrix.

The exchanging of cation in mineral clay with surfactant can change the characteristic of clay such as enhancement of d-spacing of layered clay and changing the polarity of clay to be more hydrophobic. Furthermore, the interaction of quaternary alkylammonium cations with clay is affected by the size and structure of the alkyl group, the clay type, solution conditions and the nature of the exchanged cation. The longer chain of organic part made the better dispersion in nanocomposites. The preparation method of organoclay using the ammonium salt was reported in several researches [2-4, 8, 12-15].

The example of effect of surfactant are the used of ammonium salt such as alkyldimethylbenzylammonium chloride, cethyltrimethylammonium chloride, esthearildimethylammonium chloride and cethyltrimethylammonium bromide as surfactant to enhance the d-spacing of clay in nanocomposites, which was confirmed by X-ray diffraction (XRD). Surfactant helps decrease the burning rate of nanocomposites which was maximum at 17 % compared with that of pure PE [2].

Nowadays, the synthesis of new surfactant families was occurred. Phosphate salt which is the new kind of surfactant has the phosphorus ion with single alkyl group. It was reported that the use of phosphate salt such as tetrabutylphosphonium (TBP) – bromide, butyltriphenylphosphonium (BTPP) - bromide and hexadecyltributylphosphonium bromide for treated the surface of nanoclay enhances the thermal properties such as degradation temperature of organoclay [18, 19]. Using phosphate salt as surfactant increases the degradation temperature of organoclays batter than ammonium salt [18, 19].

3.3 The effect of compatibilizer

Even though, the treatment of clay helps changing the polarity of clay to be more hydrophobic but the mixing problem with PP still occurs. Therefore, the addition of compatibilizer, which acid group was grafted on PP chain, into the system helps to improve the efficiency of mixing. Moreover, the addition of compatibilizer shows the enhancement of mechanical properties of nanocomposites [3-4, 8, 12-13, 15]. Chemicals with meleic anhydride group are popular to use as a compatibilizer; however, chemical with other groups such as styrene –co- maleic anhydride, glycidyl methacrylate, acrylic acid are also used as compatibilizer [15]. The use of polypropylene grafted maleic anhydride (PP-g-MA) as compatibilizer reduced the reduction of spherulite site, which also decreases the strength in nanocomposites [13]. There were studies showing the effect of molecular weight of compatibilizer on the mechanical properties of nanocomposites [5, 13]. Although, low molecular and high percentage of maleic anhydride group of polypropylene grafted maleic anhydride (PP-g-MA) can enlarges the spherulite size of polymer but the PP-g-MA with high molecular weight (low % MA group) enhances the degree of clay dispersion that make the exfoliated clay in this system [13]. Thorefore, using PP-g-MA with high molecular weight showed better mechanical properties of polypropylene/clay nanocomposites than those using PP-g-MA with low molecular weight.

3.4 Polypropylene/clay nanocomposites

Several researches showed the preparation of nanocomposite such as via in situ intercalative polymerization of monomers, melt mixing method [1 -9, 12-14, 16], and solution method [17].

The previous researches reported the increasing of properties of nanocomposites such as mechanical and gas barrier property that was caused by the addition of organoclay in polymer matrix. The presence of organoclay helped to transfer stress between organoclay and matrix that made nanocomposites become stiffer [2-3, 5, 13-17]. Furthermore, the gas barrier properties of clay obstructed oxygen pathway, which was passed through nanocomposites, when it was used as the filler [1]. Moreover, the reduction of spherulite size in polypropylene/clay nanocomposites was investigated [13] that was caused by addition of organoclay dramatically reduced the degree of crystallinity and spherulite size [8]. However, adding compatibilizer can reduce the reduction of spherulite size and increase in degree of crystallinty [13], which enhances the mechanical and thermal properties of polypropylene nanocomposites compared with pure polypropylene.

Chapter IV

Experiments

4.1 Materials

Polypropylene resin (Grade P600F) was obtained from Siam Cement Group (SCG) Thailand as its properties listed in table 4.1. Sodium bentonite,T-clay (SAC) with 60 meq/100 g of clay of CEC, which had particle size of 51.412 μm, was provided by Thai Nippon Chemical Industry Co., Ltd., Thailand. Sodium bentonite (K-clay) with high CEC (110 meq/100 g) and it had particle size of 22.410 μm was provided by a company in South Korea. The CEC value of the clay was confirmed by methylene blue titration (ASTM C837) and the composition of the two sources of clay are showed in the table 4.2. Surfactants that were used for ion exchange reaction in this research were dimethyl dihydrogenatedtallow quaternary ammonium chloride (MW 585.5 g/mol, 95 % assay), tetrabutylphosphoniumbromide (MW 339.3 g/mol, 95 % assay), tetradecyltributylphosphoniumchloride (MW 435.1g/mol, 95 % assay) and hexadecyltributylphosphoniumbromide (MW 507.6 g/mol, 95 % assay) which provided by Akzo Nobel Co., Ltd., Thailand and Cytec Industries Inc., Canada, respectively. The structure of the surfactants was appeared in the table 4.3. Compatibilizer that was used in this study was maleic anhydride graft polypropylene grade MD511D (PP-g-MA) supplied by Du pont Singapore Holding Co.,Ltd. It has melt flow index of 24 g/10 min.

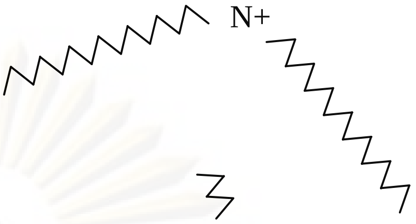
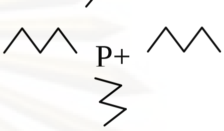
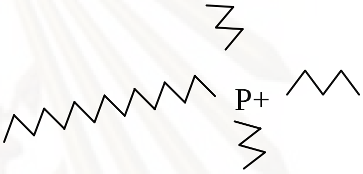
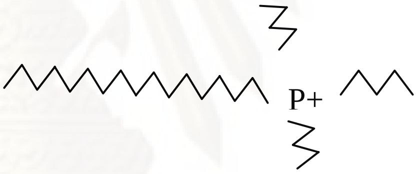
Table 4.1: Physical properties of PP (Data from SCG, Thailand)

Properties	PP (P600F)
1. Melt flow rate (g/10 min)	10.00
2. Density (g/cm^3)	0.91
3. Melting point (°C)	160
4. Softening point (°C)	155
5. Brittleness temperature (°C)	< - 10

Table 4.2: The composition of clay

T-clay	K-clay
Si, 80.078	Si, 55.71
Al, 12.329	Al, 12.91
Mg, 1.823	Mg, 5.82
Na, 1.619	Na, 5.60
Ca, 2.006	Fe, 3.72
Fe, 1.138	Ca, 2.43
K, 0.688	K, 0.38
Ti 0.204	Ti 0.28
P, 0.024	S, 0.17
Ba, 0.08	P, 0.13
Zr,0.12	Ba, 0.08
Sr, 0.02	Zr, 0.02

Table 4.3: The structure of surfactants

Surfactant	structure
ARQUAD 2HT-75 (A2)	
CYPHOS 442W (PS)	
CYPHOS 3453W (PM)	
CYPHOS 3472P (PL)	

4.2 Preparation of polypropylene/clay nanocomposite cast films

4.2.1 Preparation of organoclay

The replacing of natural cation in nanoclay structure with the surfactant is prepared by the simple ion exchange reaction. The different types of surfactant that was explained in the material section were used to study the effect of the surfactant on the degree of clay dispersion. After the ion exchange reaction, the polarity of clay was changed to more hydrophobic that was called “organoclay”. The steps of treating the clay to organoclay are shown as follow:

1) Dispersing the 400 g of clay was dispersed in the 20 L of pure water in the tank and stirred intensively for 3 hours at 70 ºC until the solution was homogeneous.

2) The other tank was filled with the 20 L of water and heated up to 70 ºC. After that surfactant was put into a tank and stirred intensively to dissolve it for about 10 minutes.

3) The solution of surfactant was put into the dispersed clay solution tank to ion exchange and stirred vigorously at 70 ºC for 1 hour.

4) After the ion exchange reaction was finished, the solid part was filtered by vacuum filter technique and washed with distilled water for several times.

5) The organoclay that was treated by ammonium surfactant was dried in an oven at 80 ºC for 3 to 4 days until it was dried and was then mortared and sieved respectively.

6) In the case of phosphate salt organoclay treatment, the wet slurry organoclay was dried in the freeze direr at -50 ºC for 2 days and was then gently crush and sieved respectively.

NOTE : The weight of surfactant was calculated as follows:

$$g_{surf} = \frac{CEC \times conc \times Mw \times kg_{clay}}{\%assay}$$

Where g_{surf} = Weight of surfactant (g_{surf})

CEC = Cation exchange capacity of untreated clay (meq/g_{clay})

conc = Concentration of surfactant ($mmol_{surf}$)

Mw = Molecular weight of surfactant (g_{surf}/ mol_{surf})

kg_{clay} = Weight of untreated clay (kg_{clay})

%assay = Effectiveness of surfactant

The organoclay samples was identified as appeared in the table 4.5.

Table 4.4: The organoclay samples

Clay formula	name	Clay formula	name
Thai clay	MMT	Korean clay	MMK
MMT + A2	MTA2	MMK + A2	MKA2
MMT + PS	MTPS	MMK + PS	MKPS
MMT + PM	MTPM	MMK + PM	MKPM
MMT + PL	MTPL	MMK + PL	MKPL

4.2.2 Preparation of polypropylene/clay nanocomposites cast films

The melt mixing by co-rotating twin screw extruder (Thermo Haake Rheomex, Germany) that was attached to the cast die was used to proceed the polypropylene/clay nanocomposite cast films. The temperature of the extruder was set around the 210 – 235 ºC with the 230 rpm of screw speed. When the melting film was flowed through the cast die slit, it was instantly cooled down by using the chill rolls at 170 rpm speed to complete the film process. The types and loading of organoclay were varied to study their effects on the properties of polypropylene/clay nanocomposite cast films. The films were identified in this research as show in the table 4.6.

Table 4.5: The films samples names

Film formula	name
neat PP	PP
PP + 3% compatibilzer	PPComp
PP + 3% MTA2 + 9% compatibilizer	PP-3TA2
PP + 3% MTPS + 9% compatibilizer	PP-3TPS
PP + 3% MTPM + 9% compatibilizer	PP-3TPM
PP + 3% MTPL + 9% compatibilizer	PP-3TPL
PP + 3% MKA2 + 9% compatibilizer	PP-3KA2
PP + 3% MKPS + 9% compatibilizer	PP-3KPS
PP + 3% MKPM + 9% compatibilizer	PP-3KPM
PP + 3% MKPL + 9% compatibilizer	PP-3KPL
PP + 1% MTPM + 3% compatibilizer	PP-1TPM
PP + 5% MTPM + 15% compatibilizer	PP-5TPM
PP + 7% MTPM + 21% compatibilizer	PP-7TPM

4.3 Specimen characterization

4.3.1 The inorganic content in polypropylene/clay nanocomposites

The inorganic content of nanocomposite cast films was tested by burning samples. 2 g of sample were burnt in the ceramic crucibles in the furnace at 1200 °C for 4 hour to eliminate all organic material including the based polymer and surfactant. The percentage of inorganic content was calculated from the weight loss. This test was repeated for 3 times for each sample.

4.3.2 Degree of clay dispersion

The degree of clay particle dispersion in pristine clay, organoclay and polypropylene/clay nanocomposite cast films were determined by mean of XRD technique using a D8 advance, BRUKER X-ray diffractometer using CuKα radiation (wavelength 1.542 Å) with voltage of 40 kV and 30 mA. The 2 theta degree value can read from the XRD pattern. The interlayer spacing of clay was determined by the Bragg's equation that was shown below;

$$2d\sin\theta = n\lambda$$

where

λ = The wavelength of the X-ray radiation used in the diffraction experiment which is 1.542 Å.

d = The spacing between diffractional lattice planes

θ = The measured diffraction angle

n = Peaks correspond to the basal reflection {001} or n=1

From the Bragg's equation shows the low of measured 2 theta degree value corresponds to the high of d – spacing of clay layer.

4.3.3 Tensile measurement

The tensile properties such as tensile strength at yield, elongation at break and Young's modulus of the films and nanocomposite cast films were obtained by using Universal testing machine (Instron 5567, NY, USA) according to ASTM D 882. The rectangular dimensions of the specimens are 10 mm of width, 140 mm of length and 65 ± 10 μm of thickness. The initial grid length separation that requires for this standard is 100 mm. In this research, the films can suitably be tested only in the machine direction (MD). The 1 kN of load cells were attached to the testing machine to test the tensile properties with 50 mm/min speed.

4.3.4 The thermal properties

Thermal properties of neat polypropylene and polypropylene/clay nanocomposite cast films were determined by using a differential scanning calorimetry (DSC, Diamond PERKIN, USA) apparatus. All measurements were made under nitrogen atmosphere at heating rate of 10 ºC/min on sample weighing around 10 mg. The melting temperature (T_m) and degree of crytallinity of polymer were measured.

4.3.5 Oxygen transmission analysis

Oxygen permeability analysis of neat polypropylene and polypropylene/clay nanocomposite cast film were investigated by oxygen permeation analyzer (Mocon, OXTRAN 2/21, USA). All films were required in circular shape with thickness of 65 ± 10 μm. Each sample was repeated for 4 times. Polypropylene/clay nanocomposite cast films were attached to a diffusion chamber at oxygen (99 %) gas, chamber temperature 23 ºC, atmosphere pressure and 0 % RH (dry condition). Oxygen molecule was passed through films together with nitrogen, and was transported to sensor, which detect the amount of oxygen gas that was passed through nanocomposite cast films and displayed in the unit of cc/m^2.day according to ASTM D1434.

4.3.6 Appearance of films

The appearance of films was observed by optical microscopy (Nikon, ECLIPSE E600W, USA) with 50 x magnification.

CHAPTER V

RESULTS AND DISCUSSION

Polypropylene/clay nanocomposite cast films were prepared by co-rotating twin screw extruder attached to the cast die operated with high screw speed. The processing temperature of the extruder barrel was set around 210 – 230 ºC and 235 ºC at the cast die. In this research, the effect of surfactant types, clay source and organoclay content on the mechanical, thermal and gas barrier properties of polypropylene/clay nanocomposite cast films were studied.

5.1 Effect of surfactant types and clay source on the properties of polypropylene/clay nanocomposite cast films

The reason for investigating the effect of surfactant type, which was used to modify clay surface, was that the structure of surfactant differently affect the mechanical, thermal and gas barrier properties of polypropylene/clay nanocomposite cast films. Moreover, the new kind of surfactant such as phosphate salt was the main focus of this research. It was necessary to study the effect of phosphonium ion surfactant on the properties of nanocomposite cast films that can be compared with the traditional ammonium ion surfactant. The four surfactants that appeared in this research were divided into 2 families:

1. The traditional ammonium surfactant
    - Dimethyl bis(hydrogenated-tallow) ammonium chloride (ARQUAD ®2HT-75)
2. The phosphate salt surfactant
    - tetrabutylphosphoniumbromide (CYPHOS 442W)
    - tetradecyltributylphosphoniumchloride (CYPHOS 3453W)
    - hexadecyltributylphosphoniumbromide (CYPHOS 3472P)

Furthermore, the source of clay, which has some difference in inorganic composition, cation exchange capacity (CEC) and characteristics can affect the properties of the polypropylene/clay nanocomposite cast film. In this research, the ultra fined K-clay (CEC 110 meq/100 g) and 60 meq/100 g of fined T-clay were used to investigate an influence of clay source on the degree of clay dispersion and other properties of polypropylene/clay nanocomposite cast film.

To study the effect of type of surfactant and type of clay on the properties of nanocomposite films, the 3 wt% of organoclay loading and 9 wt% of compatibilizer, which were added in the based polymer, were fixed.

5.1.1 The inorganic content

The inorganic content of clay and organoclay was determined by the weight after the samples were burnt in the furnace for 4 hour at 1200 °C. The result showed that fined T-clay had the higher percentage of inorganic content than that of ultra fined K-clay. This result was consistent with the XRF result of these clays as reported in table 4.2. The MTA2, MTPS, MTPM and MTPL organoclay, with T-clay was used to modify surface showed higher inorganic content than that of MKA2, MKPS, MKPM and MKPL organoclay, comparing when using same type of surfactant. The types of surfactant, which had different molecular weight and structure, affected the inorganic content of organoclay. The using of large structured surfactant such as A2, PM and PL made clay lower containing inorganic content left in the system than that using PS surfactant that was shown in the table 5.1. Furthermore, the calculation of concentration value, which was fixed at 1.0 for this research, was found the error on some organoclay. It could be due to the error during the investigation such as washing process and pre-mixing process. The calculation of concentration value in table 5.1 was shown in appendix B.

Table 5.1: Percentage of inorganic content of clay and organoclay

Sample	Percentage of inorganic content (wt%)	Concentraion value ($mmol_{sur}$)
MMT	91.863 ± 0.186	-
MTA2	67.447 ± 3.754	0.979
MTPS	80.238 ± 3.401	0.648
MTPM	72.700 ± 1.595	0.952
MTPL	72.970 ± 4.213	0.808
MMK	84.532 ± 2.311	-
MKA2	61.125 ± 3.930	0.565
MKPS	67.570 ± 3.862	0.689
MKPM	62.230 ± 4.141	0.797
MKPL	61.728 ± 4.224	0.629

When organoclay was added in polypropylene to form the nanocomposite cast films, the trend of inorganic content in pellet that was used to form the polypropylene/clay nanocomposite cast films was similar to that of organoclay. The presence of high inorganic content can efficiently transfer stress when it exhibited high degree of clay dispersion. More over, the error of inorganic content in films occurred compared with calculation inorganic content. The determination of inorganic content in table 5.2 was shown in appendix B.

Table 5.2: Percentage of inorganic content of polypropylene/clay nanocomposites

Sample	Actual percentage of inorganic content (wt %)	Calculated percentage of inorganic content (wt %)
PP-3TA2	2.896 ± 0.051	2.023
PP-3TPS	2.885 ± 0.130	2.512
PP-3TPM	2.877 ± 0.027	2.181
PP-3TPL	2.720 ± 0.111	2.189
PP-3KA2	2.278 ± 0.121	1.834
PP-3KPS	2.372 ± 0.279	2.027
PP-3KPM	2.128 ± 0.148	1.667
PP-3KPL	1.980 ± 0.146	1.852

5.1.2 Degree of clay dispersion in interlayer spacing of clay and polypropylene/clay nanocomposite cast films

The first diffraction {001} peak that can be observed from the X-ray diffraction pattern can be used to identify the d-spacing of layered clay by using Bragg equation. Figure 5.1 showed the XRD pattern of pristine T-clay and T-organoclays that were surface treated by several surfactants. The {001} peak of pristine clay occurred at 7.22° corresponding to 1.22 nm of interlayer spacing of clay. The surface treated organoclays in which the natural cation was exchanged with quaternary ammonium ion or phosphonium ion surfactant showed the lower angles of {001} peak than that of pristine T-clay. The MTA2, MTPS, MTPM and MTPL peaks appeared at 2.66, 5.10, 3.45 and 3.23° corresponding to interlayer spacing of organoclays of 3.31, 1.73, 2.56 and 2.73 nm, respectively. This result can confirm that the replacement of cation in clay with surfactant enhancing the d-spacing of layered clay with consistent with Arau'jo et al and Arunvisut et al's work [2-3]. Furthermore, the MTPL organolcay showed broader peak with higher intensity compared with that of other T-organoclays.

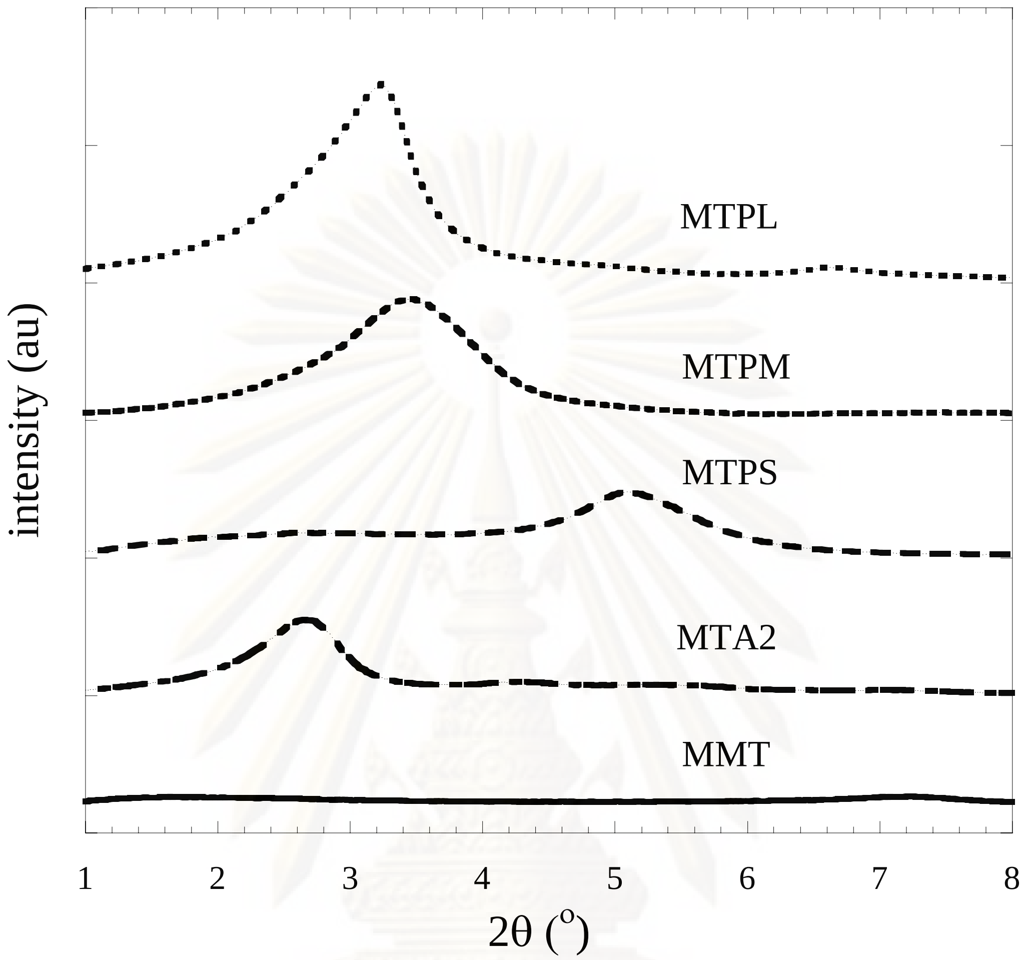


Figure 5.1 XRD patterns of pristine T-clay and modified T-clay, at 2θ = 1-8°

When the polypropylene was melt mixed with 3 wt% of organoclay and 9 wt% of compatibilizer by co-rotating twin screw extruder attached to cast die, the formation of polypropylene/clay nanocomposite cast films were occurred. The observation at 2θ = 1-8° of XRD patterns of nanocomposites were shown in figure 5.2. The 2θ peak of polypropylene/clay nanocomposite cast films such as PP-3TA2, PP-3TPS, PP-3TPM and PP-3TPL films, in which different types of organoclay were added in the based polypropylene, was observed at 2.06, 5.19, 2.63 and 2.45°, corresponding to an interlayer spacing of organoclays of 4.29, 1.70, 3.35 and 3.61 nm, respectively. The 2θ values of nanocomposite films were decreased from the 2θ value of organoclay that was added in each film except the PP-3TPS film. It obviously indicated that polypropylene chain which can penetrate between the layered clay as seen from the increasing of d-spacing of layered clay in most of nanocomposite cast films [2-3, 18-19]. In the case of PP-PS film, slight decrease of the distance between layered clay was found. It could be due to high degree of agglomeration in the macroscopic range that affected the degree of clay dispersion in polymer matrix. Furthermore, high order of layered clay orientation was observed in PP-3TPM films from high intensity and broad peak in XRD pattern. From the result, the intercalated nanocomposite cast films were formed, confirmed by XRD patterns. Moreover, the second peak of PP-3TA2, PP-3TPM and PP-3TPL films were observed at 4.40, 5.51 and 5.01°, corresponding to an interlayer spacing of organoclays of 2.01, 1.60 and 1.76 nm, respectively. It might be due to the variation of surfactant orientation between layered silicates in organoclay with is consistent with Limpanart's research [11].

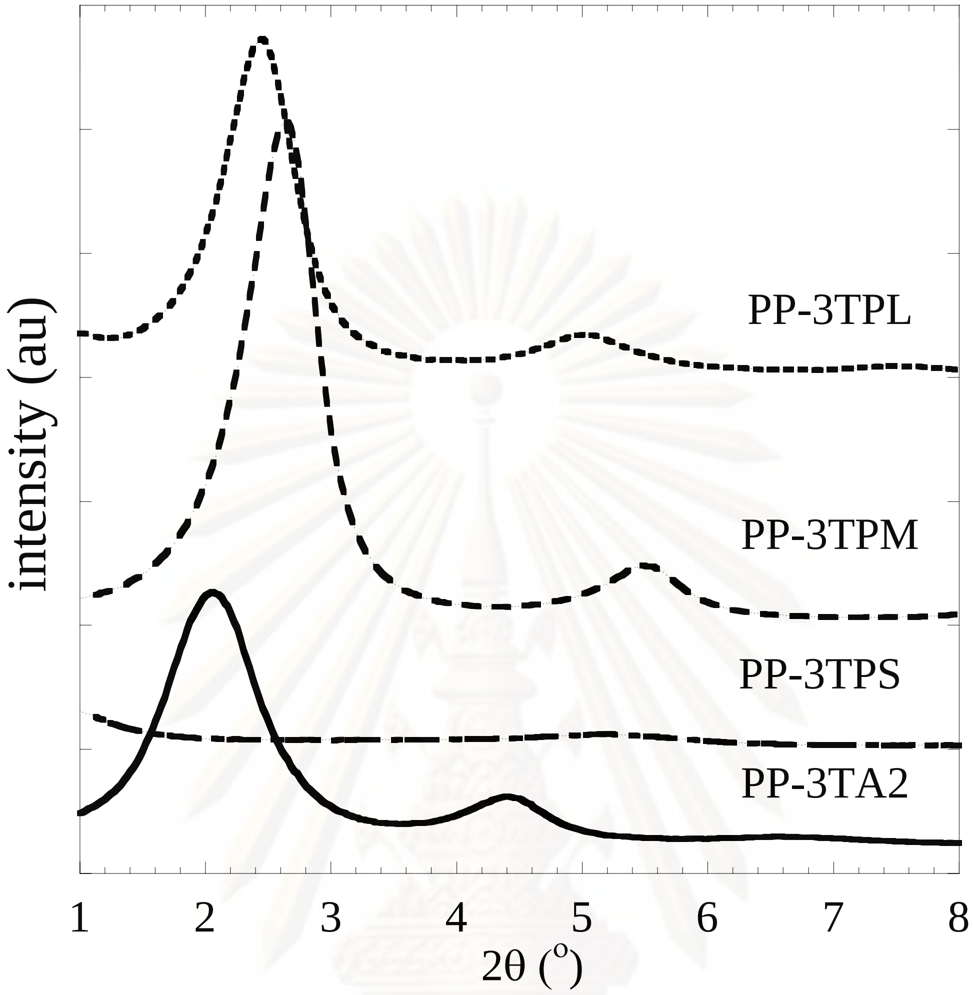


Figure 5.2 XRD patterns of polypropylene/clay nanocomposite cast films by using the 3wt% of T-organoclay loading, at 2θ = 1-8°

In the case of using ultra fined K-clay, the XRD patterns of pristine K-clay and modified K-clay were similar to those of T-clay which means that the surfactant can be exchanged with natural cation in clay and enhancing the d-spacing of layered clay on MKA2, MKPS, MKPM and MKPL compared with pristine K-clay (MMK). The result showed that their 2θ values were 2.57, 5.30, 3.80, 3.56 and 7.20°, which corresponded to the interlayer d-spacing of organoclay and clay of 3.44, 1.67, 3.44, 2.32, 2.48 and 1.23 nm, respectively. The figure 5.3 showed the broad peak with low intensity of K-organoclay compared with T-organoclay. It indicates that K-organoclay, which was surface treated by phosphate surfactant, showed better interlayer spacing enhancement than that of T-organoclay because K-clay had higher CEC value than that of T-clay. However, the ultra fined characteristic of K-clay made clay agglomeration in polymer matrix much more than the fined T-clay as seen in figure 5.5.

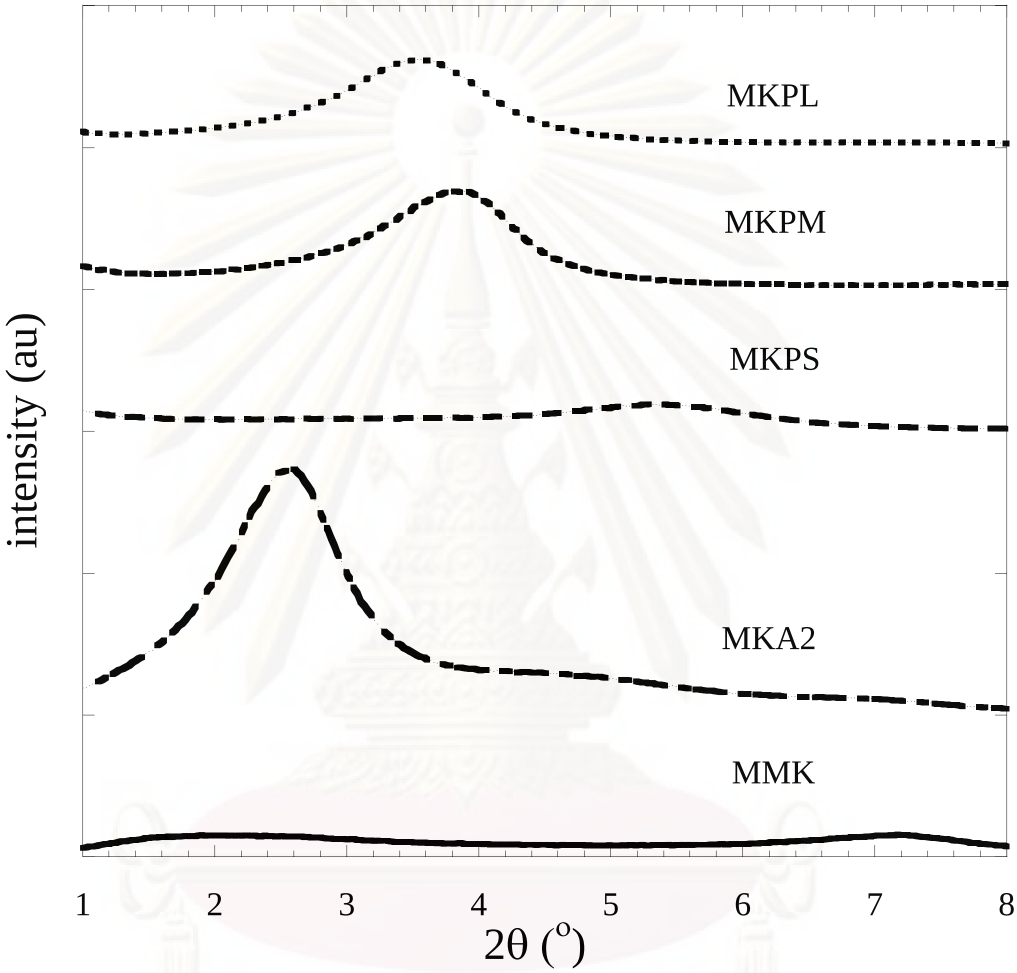


Figure 5.3 XRD patterns of pristine K-clay and modified K-clays, at 2θ = 1-8°

When the 3 wt% of K-organoclay was melt mixed with polypropylene and 9 wt% of compatibilizer, they formed the intercalated nanocomposite cast films which can be confirmed by XRD pattern as shown in figure 5.4. The d-spacing of layered clay in PP-3KPS, PP-3KPM and PP-3KPL was 1.74, 3.25 and 3.47 nm, respectively. Furthermore, the {001} peak of these films was flat compared with those of T-films, However, clay agglomeration occurred which affected the mechanical properties of films that were discussed in the next part.

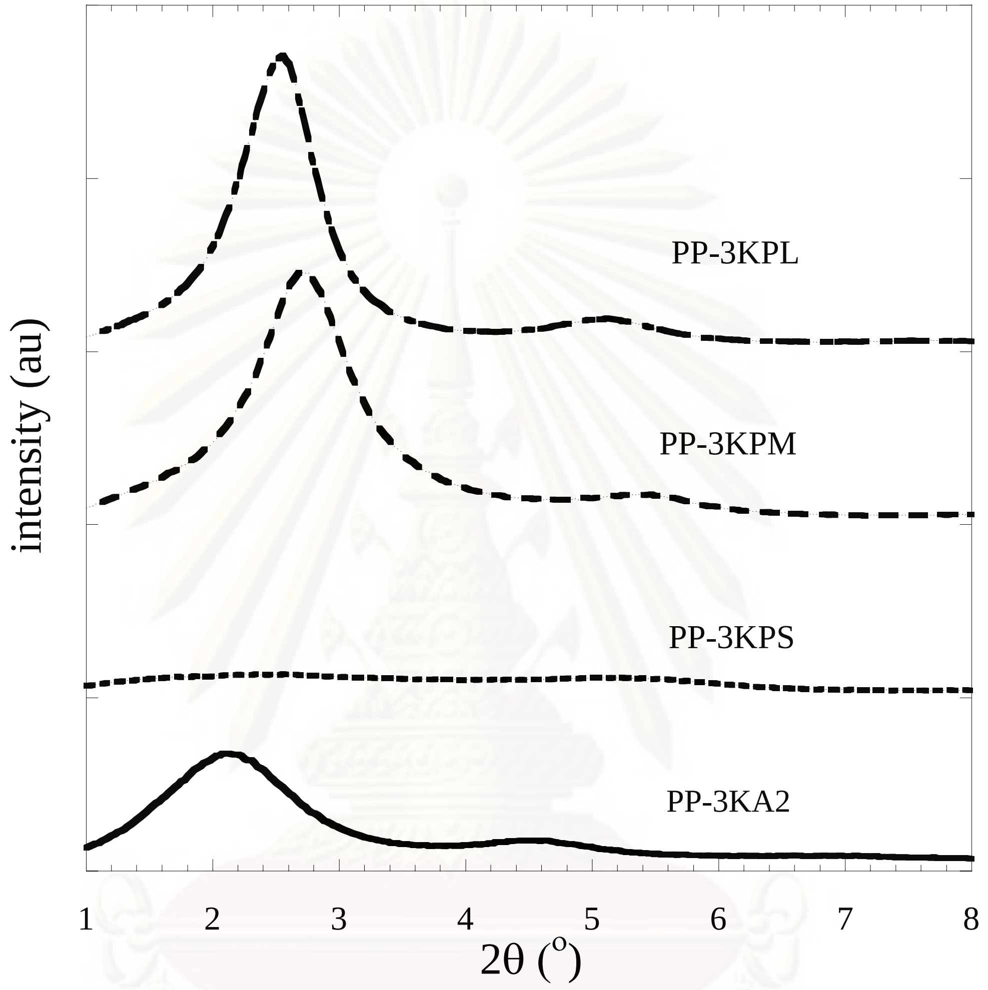
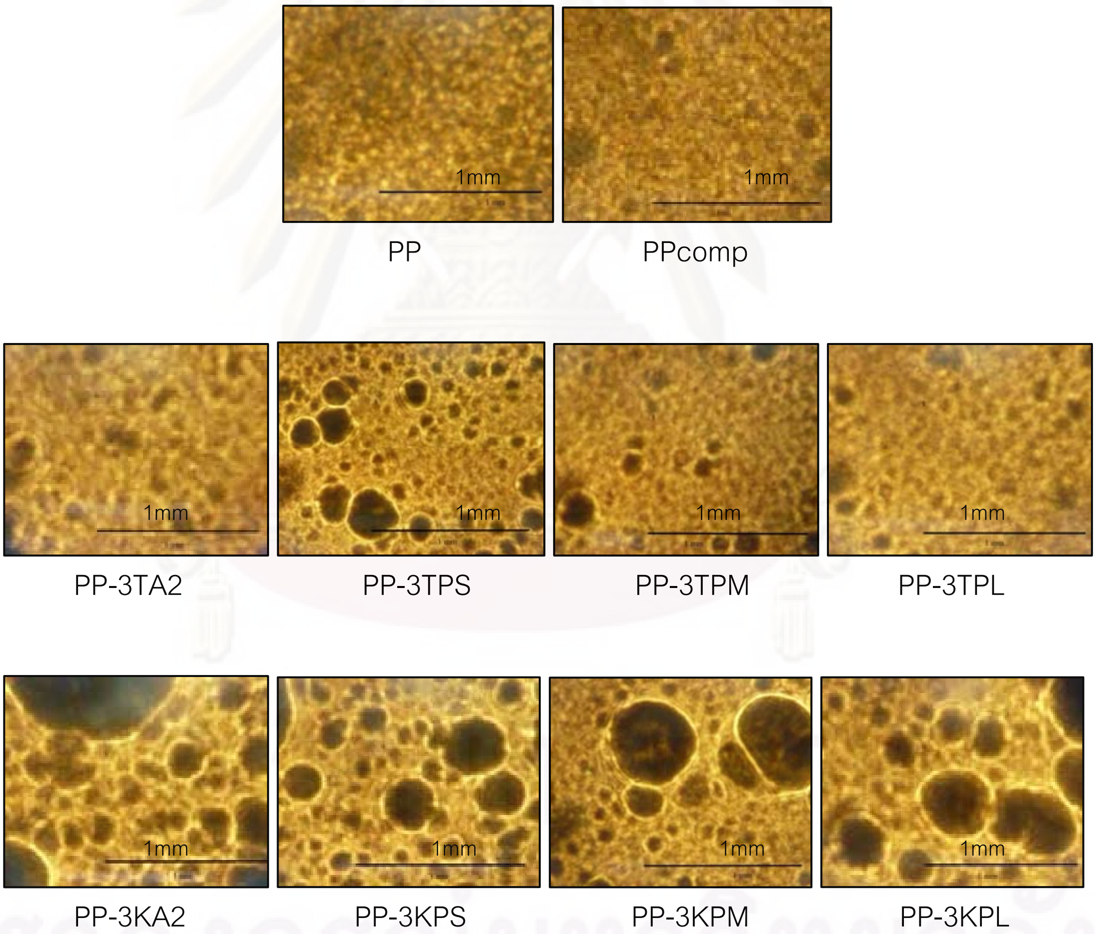


Figure 5.4 XRD patterns of polypropylene/clay nanocomposite cast films with 3wt% of K-organoclay, at 2θ = 1-8°

From XRD results, the types of surfactant affected the degree of clay dispersion in polypropylene matrix. The result showed that the large structured surfactant such as A2, PM and PL could help clay disperse in polymer matrix better than that of small structured surfactant (PS) which is consistent with Arau'jo et al, Arunvisut et al, and Hedley et al's work [2-3, 18]. It could be due to the large organic part in A2, PS, PL effectively increased the d-spacing of layered silicate [2, 18-19]. Furthermore, the second peak was observed for all of films which could be due to the variation of surfactant orientation in the layered silicates occurred [11].

The films appearance that was observed by optical microscope (OM) was shown in figure 5.5. The result shown in the set of K-films had high degree of clay agglomeration that was caused by ultra fined K-clay that was easily to agglomerate more than that of T-clay and the unsuitable treatment technique of K-clay. Considering the effect of surfactant types, it indicated that the using of PS surfactant extremely made high degree of clay agglomeration in film than that of other surfactants. In high degree of clay agglomerated films, poor properties were observed.



PP PPcomp

PP-3TA2 PP-3TPS PP-3TPM PP-3TPL

PP-3KA2 PP-3KPS PP-3KPM PP-3KPL

Figure 5.5 Appearance of films

5.1.3 Melting temperature and degree of crystallinity

The observation in term of thermal properties such as melting temperature and degree of crystallinity of neat polypropylene, compatibilizer (PP-g-MA) and polypropylene/clay nanocomposite cast films containing 3 wt% organoclay were obtained by endothermic peak and area under endothermic curve that were determined by mean of differential scanning carolimetry (DSC) technique at heating rate of 10 °C/min from 50 to 180 °C.

In this study, the degree of crystallinty of nanocomposite cast films was compared with that of neat PP film and PP-g-MA to obtain the relative degree of crystallinity. The result that appeared in the table 5.3 showed area under endothermic peak of polypropylene/clay nanocomposite cast. From table 5.3, it can be seen that the relative degree of crystallinity of nanocomposite cast film decreased in which the crystalline formation was obstructed by the presence of organoclay. Furthermore, the types of organoclay differently affected the degree of crystallinity of polymer. The result showed that organoclay that had low degree of clay dispersion such as MTPS and MKPS dramatically reduced the degree of crystallinity of film around 40 and 45 %, respectively. Although, XRD pattern of these films showed flatted {001} peak but clay agglomeration extremely occurred in the microscopic range as confirmed by figure 5.5. It affected the reduction of relative degree of crystallinity. More over, relative degree of crystallinity of nanocomposite films with K-organoclay was lower than that of T-nanocomposite films, comparing when using same type of surfactant. It could be due to high degree of clay agglomeration in the set of K-nanocomposite films dramatically reduced the relative degree of crystallinity.

Table 5.3: Relative degree of crystallinity of samples

Samples	Relative degree of crystallinity (%)
PP	-
PPcomp	99.02
PP-g-MA	-
PP-3TA2	74.29
PP-3TPS	60.16
PP-3TPM	79.21
PP-3TPL	81.02
PP-3KA2	64.90
PP-3KPS	56.07
PP-3KPM	76.92
PP-3KPL	77.11

From figure 5.6, the result showed that the endothermic peak corresponding to the melting temperature of polypropylene/clay nanocomposite cast films decreased around 5 ºC compared with virgin polypropylene film. It could be due to the presence of organoclay in polypropylene/clay nanocomposite cast films in which clay inhibited the formation of crystalline phase which is consistent with Lee et al and Perrin – Sarasin et al's work [8, 13].

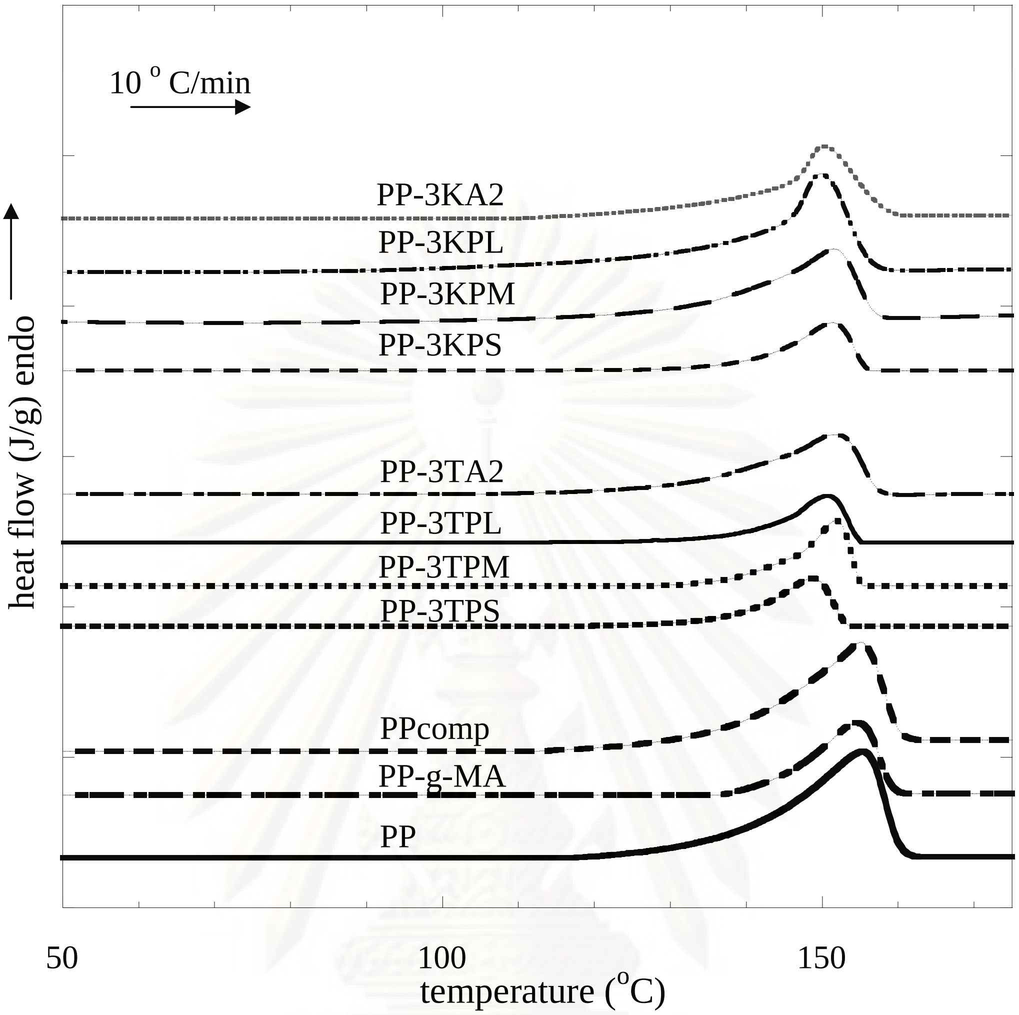


Figure 5.6 DSC profiles of virgin polypropylene, PP-g-MA, polypropylene containing 9 wt% of PP-g-MA and polypropylene/clay nanocomposite cast films containing 3 wt% of different organoclay, at 10 °C/min heating rate

5.1.4 The mechanical properties

The tensile properties of the samples such as tensile strength at yield, elongation at break and tensile modulus were determined by Universal testing machine (Instron 5567) following ASTM D882. The tensile strength can be observed by the maximum tensile stress at yield, the elongation at break was determined by the maximum strain at rapture point and the tensile modulus or Young's modulus was calculated by the linear slope at the first period of stress vs strain curve, respectively.

5.1.4.1 Tensile strength at yield

In this research, the tensile strength at yield was used to analyze the result because it was suitable for packaging application. Figure 5.8 showed the tensile strength at yield of virgin polypropylene, polypropylene blended with 9 wt% of compatibilizer and polypropylene/nanocomposite cast films containing 3 wt% organoclay of PP-3TA2, PP-3TPS, PP-3TPM, PP-3TPL, PP-3TPS, PP-3KA2, PP-3KPS, PP-3KPM and PP-3KPL. The result indicated that the presence of PP-g-MA in polypropylene reduce the tensile strength at yield around 11 % compared to pure PP film that was caused by the decreasing in degree of crystallinity of PPcomp, low mechanical properties of PP-g-MA and polymer chain scission can be occurred (Solomon et al.). Furthermore, the addition of organoclay decreased the tensile strength at yield of polypropylene/clay nanocomposite cast films compared with neat polypropylene film. Normally, organoclay could act as reinforcement when it was well dispersed but in this study, the high degree of clay agglomeration resulted in several weak points in the material. The texture of PP-3TPS, PP-3KA2, PP-3KPS, PP-3KPM and PP-3KPL films were rough which caused dramatic decreasing in tensile strength which was consistent with the work of Chuan et al [16]. The example of voids in PP-3KPM film was shown in figure 5.7.

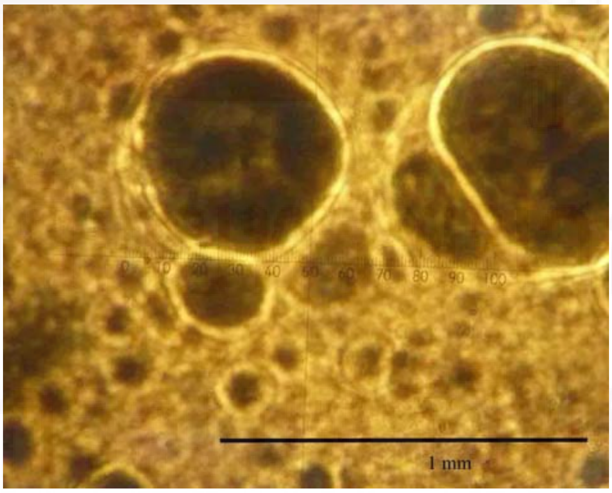


Figure 5.7 Voids in PP-3KPM film

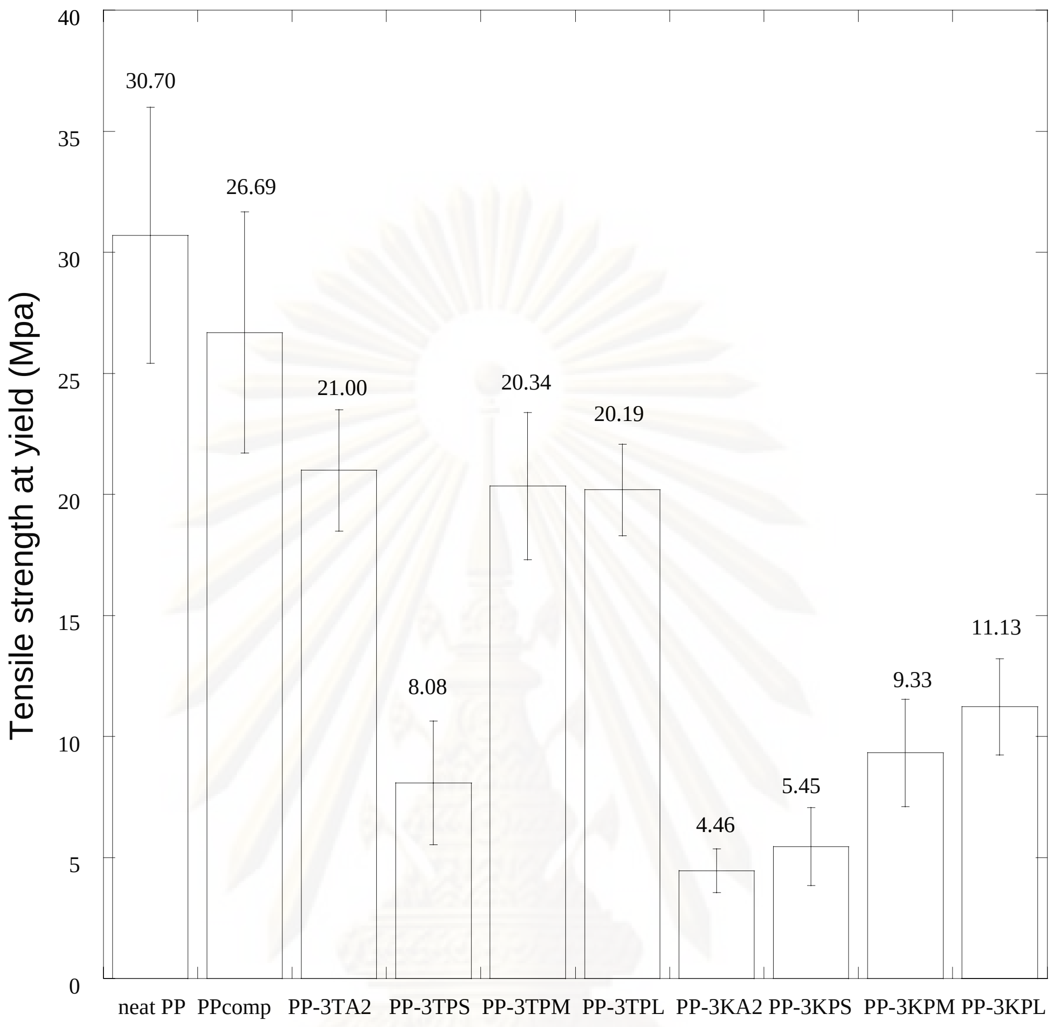


Figure 5.8 Tensile strength at yield of polypropylene, polypropylene containing 9 wt% PP-g-MA and polypropylene/clay nanocomposite cast films

5.1.4.2 Elongation at break

The elongation at break of samples that were observed by the maximum strain was shown in figure 5.10. The addition of 9 wt% of PP-g-MA in polypropylene reduced the elongation at break around 13 % compared with that of neat PP film. Moreover, the result indicated the reduction of elongation at break of PP-3TA2, PP-3TPM, PP-3TPL and PP-3KPL films compared with virgin polypropylene film around 2 times that the schematic in figure 5.9 shows the rapture of PP film and nanocomposite films. Over wise, the elongation at break of other nanocomposite cast films such as PP-3TPS, PP-3KA2, PP-3KPS and PP-3KPM films significantly decreased compared to that of pure PP which were 73, 65, 57, 45 and 37 %, respectively. The agglomeration of clay made the nanocomposite cast films became stiffer and there were several voids between interfacial surface of clay and polypropylene matrix as well as the presence of PP-g-MA. Furthermore, the type of surfactant as well as clay had different influence on the elongation at break of polypropylene/clay nanocomposite cast films. The PP-3TA2, PP-3TPM and PP-3TPL, which was used large structured surfactant such as A2, PM and PL to treat the T-clay as filler, showed the high degree of clay dispersion, low degree of clay agglomeration and high degree of crystallinity than those of other nanocomposite films. Therefore, the elongation at break of PP-3TA2, PP-3TPM and PP-3TPL films was higher than that of other films.

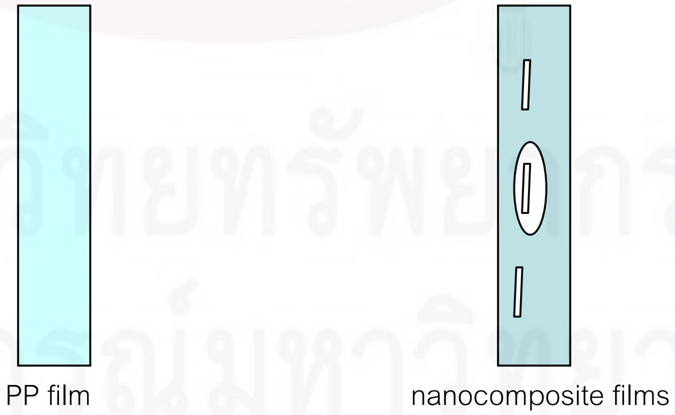


Figure 5.9 The rapture point of PP film and nanocomposite films

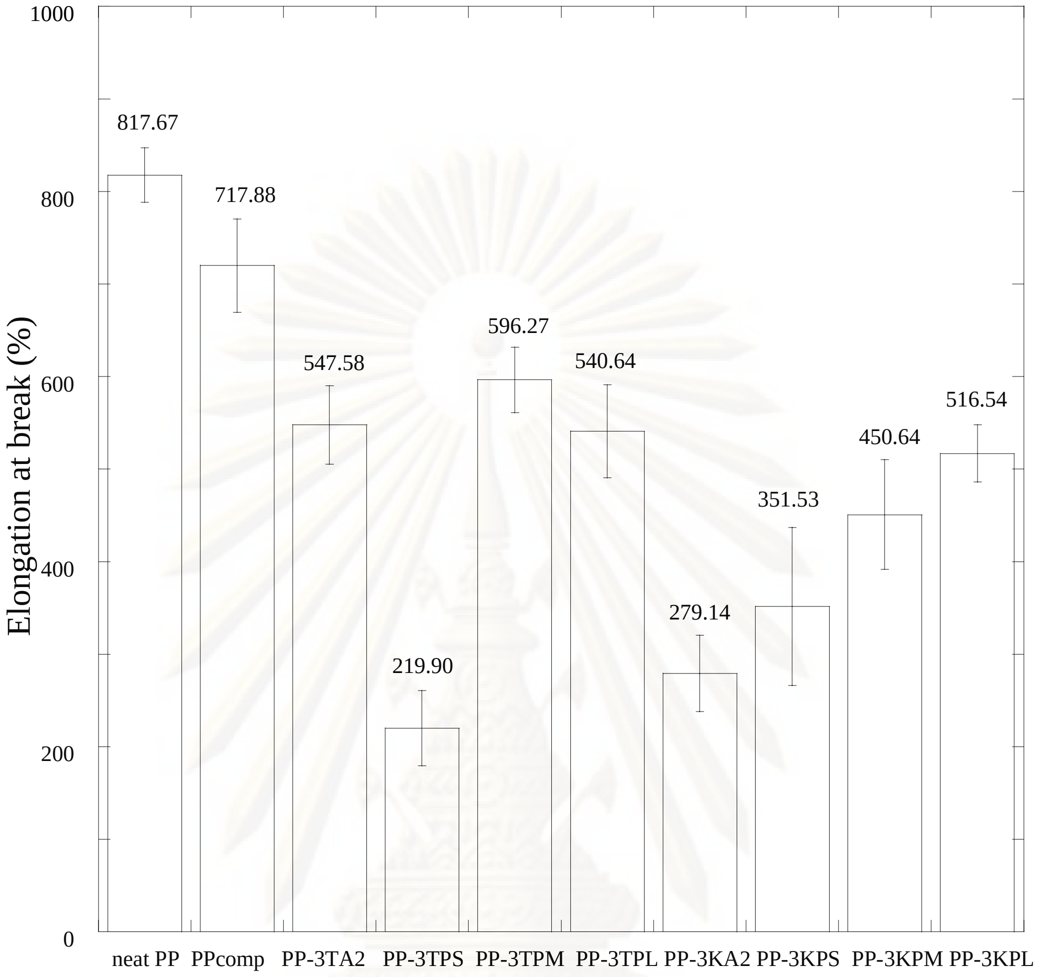


Figure 5.10 Elongation at break of pure polypropylene, polypropylene containing 9 wt% PP-g-MA and polypropylene/clay nanocomposite cast films

5.1.4.3 Tensile modulus (Young’s modulus)

The tensile modulus or Young’s modulus of pure polypropylene and polypropylene/clay nanocomposite cast films has been shown in figure 5.11. The addition of organoclay and PP-g-MA can improve the Young’s modulus because the presence of organoclay in polypropylene/clay nanocomposite cast films helped to transfer the stress between organoclay and polypropylene matrix [2-3, 5, 13-17]. Furthermore, the polypropylene/clay nanocomposite cast films that 3 wt% of T-organoclay with A2, PM and PL surfactant significant enhanced Young’s modulus with 137, 122 and 160 % of that of neat polypropylene film, respectively. This result indicated that high effectiveness of surface treatment, which was confirmed by XRD pattern of these films, extremely affected the tensile modulus. Even though, the {001} peak of PP-3TA2, PP-3TPM and PP-3TPL showed the high intensity with broad peak which means clay was high ordered orientation but these films performed low clay agglomeration that helped to perform high efficiency of stress transferring between organoclay and polypropylene. Over wise, for the other films such as PP-3TPS, PP-3KA2, PP-3KPM and PP-3KPL, the tensile modulus increased around 11 – 27 % compared with that of virgin polypropylene film, respectively. It could be due to high degree of clay agglomeration of these films which makes low effectiveness of stress transferring which is consistent with work of Chuan et al [16].

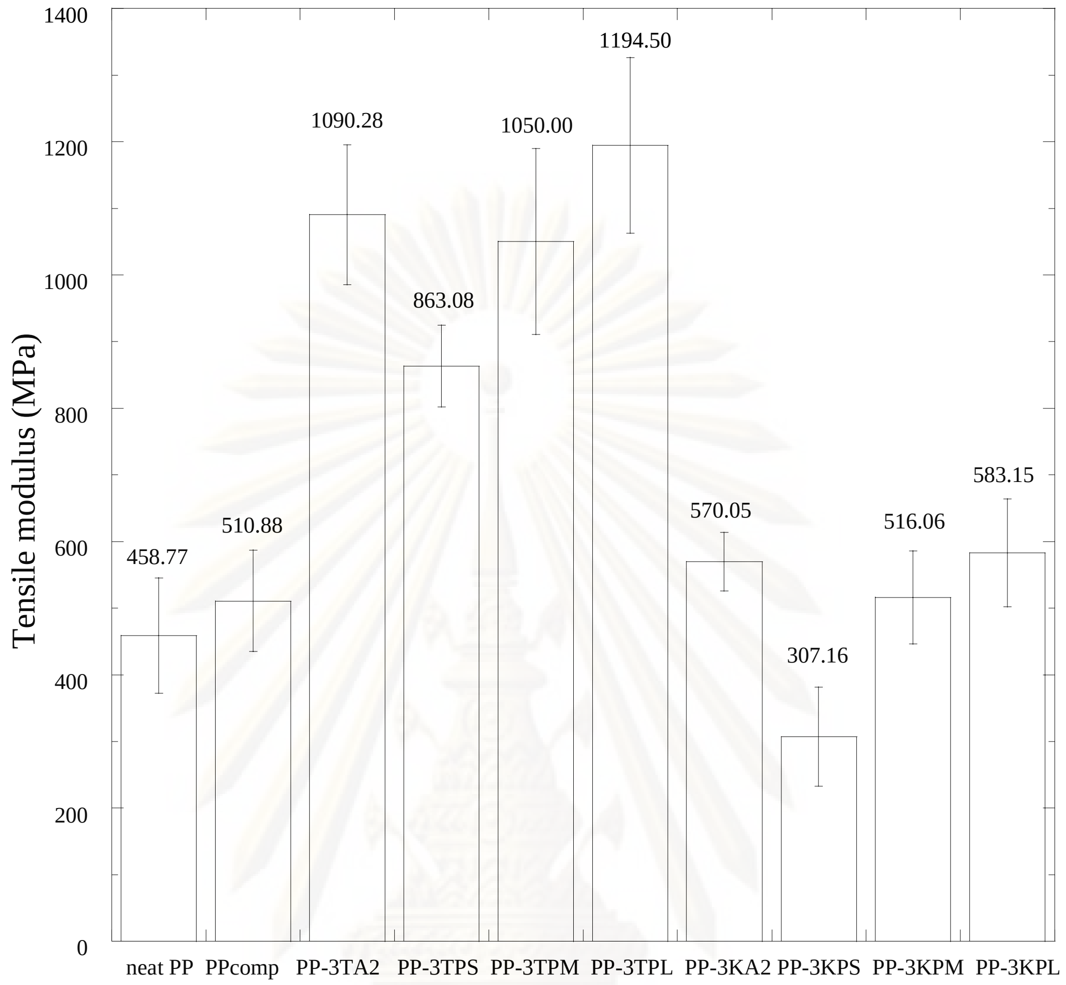


Figure 5.11 Tensile modulus of pure polypropylene, polypropylene containing 9 wt% PP-g-MA and polypropylene/clay nanocomposite cast films

Moreover, the inorganic content of polypropylene/clay nanocomposite cast films that was shown in table 5.2 showed that polypropylene/clay nanocomposite cast films, in which treated organoclay with large structured surfactant such as A2, PM and PL was added, had similar inorganic content to those contained small structured surfactant. However, the degree of clay agglomeration of PP-3TA2, PP-3TPM and PP-3TPL were lower than that of other films. Therefore, organoclay can act as good reinforcing agent when it was added in polypropylene matrix.

5.1.5 The oxygen permeability (PO_2) of polypropylene/clay nanocomposite cast films

The oxygen permeability of polypropylene/clay nanocomposite cast films, which was added 3 wt% of organoclay, was observed by MOCON OX-TRAN® 2/21 following ASTM D1434. All of films were tested at 23 ºC, 1 atm and dry condition (0 % RH).

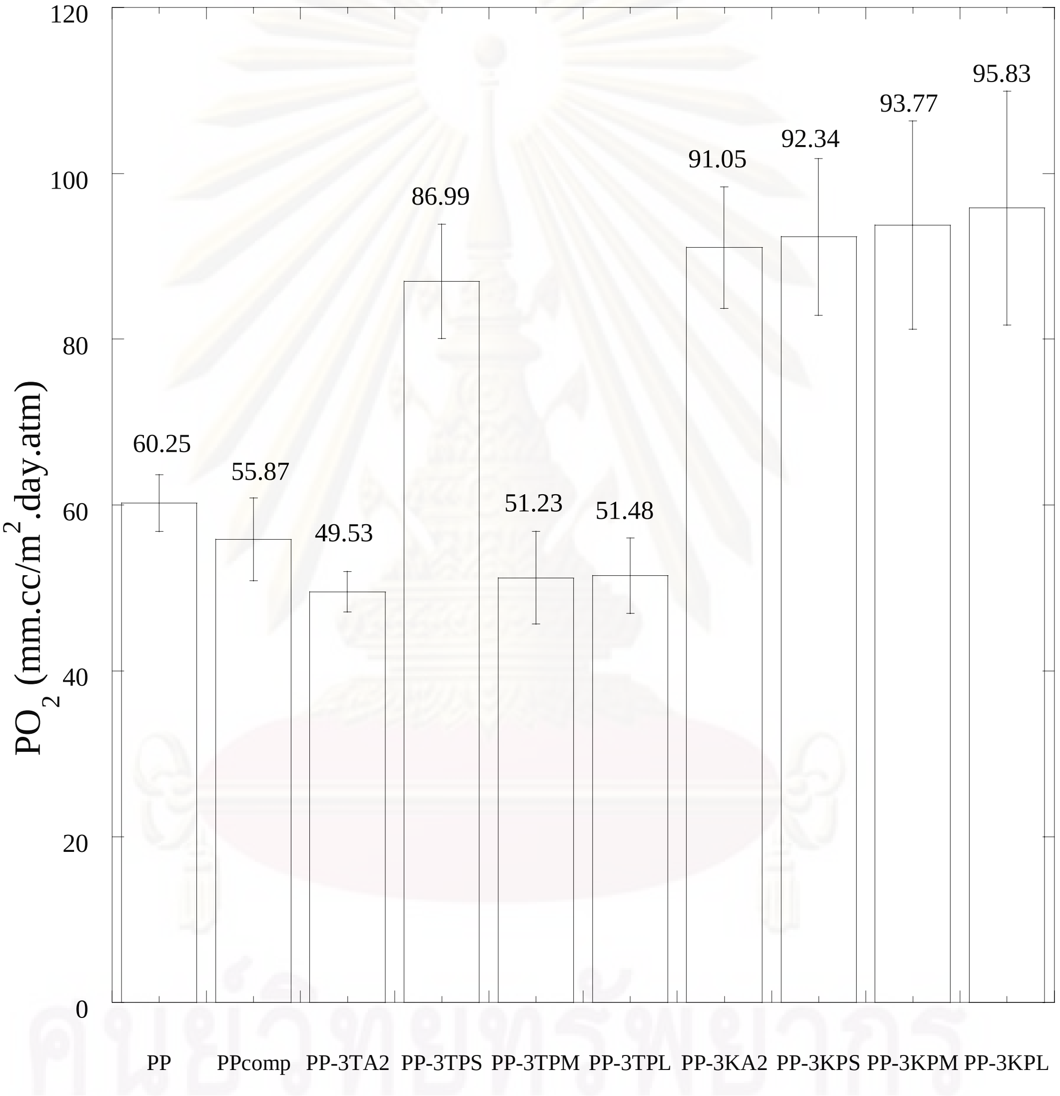
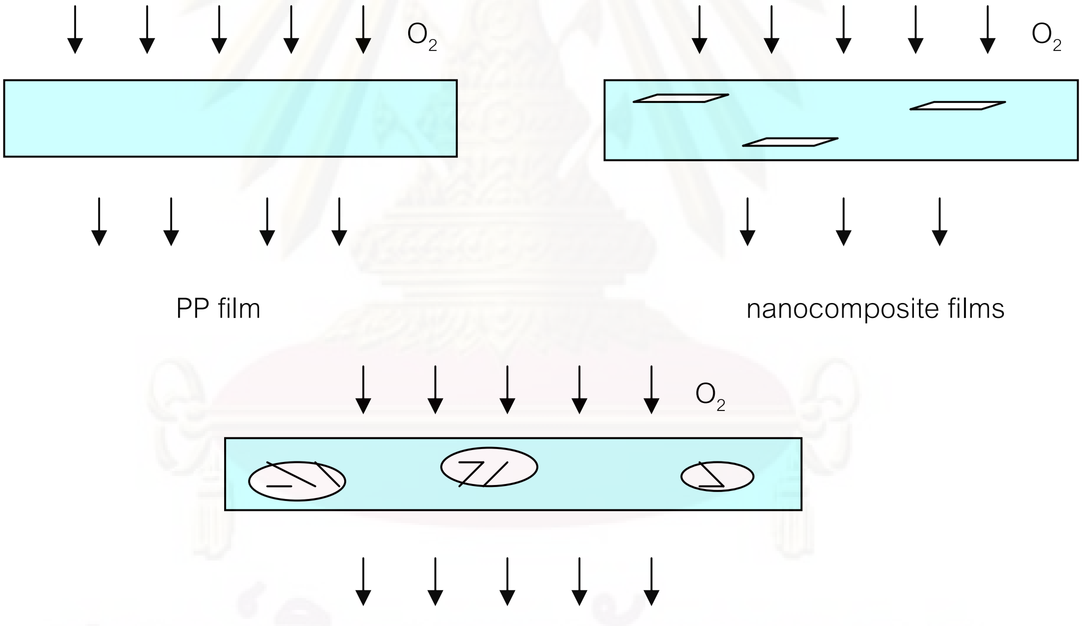


Figure 5.12 Oxygen permeability of pure PP, PP mixed with 9 wt% of PP-g-MA and polypropylene/clay nanocomposite cast films containing 3 wt% of different organoclay

Figure 5.12 showed the oxygen permeability of polypropylene/clay nanocomposite cast films containing 3 wt% organoclay, at 23 ºC, 1 atm and 0 % RH.

The result showed that the oxygen permeability of virgin PP film was less than that of PP-3TPS, PP-3KA2, PP-3KPS, PP-3KPM and PP-3KPL films. It might due to the agglomeration of clay in polypropylene matrix in which the void at the polymer and clay interface occurred. Furthermore, the reduction of degree of crystallinity of nanocomposite films allowed oxygen permeated through the films. However, some films such as PP-3TA2, PP-3TPM and PP-3TPL films showed slightly lower oxygen permeability than that of neat PP film that was caused by low of degree of clay agglomeration, which was confirmed by surface roughness and appearance. This reason can make organoclay acted as good gas barrier filler in PP-3TA2, PP-3TPM and PP-3TPL films. Moreover, these films had higher inorganic content than that of other films, which can be slightly helped to obstruct the oxygen path way as seen in figure 5.13.



PP film

nanocomposite films

Highly clay agglomerated nanocomposite films

Figure 5.13 Schematic of oxygen permeability in films

5.2 Effect of organoclay content on the properties of polypropylene/clay nanocomposite cast films

From the first experimental part, we found that the PP-3TPM film exhibited high Young's modulus and smooth texture. Therefore, MTPM organoclay was chosen to observe the effect of organoclay loading. In this research, 1, 3, 5 and 7 wt% of MTPM organoclay was added in the polypropylene to form the polypropylene/clay nanocomposite cast films. From previous work, this parameter affected the properties of polymer/clay nanocomposite such as mechanical, thermal and gas barrier properties [3]. Therefore, the effect of organoclay loading on the properties of polypropylene/clay nanocomposites cast films was also studied.

5.2.1 The inorganic content

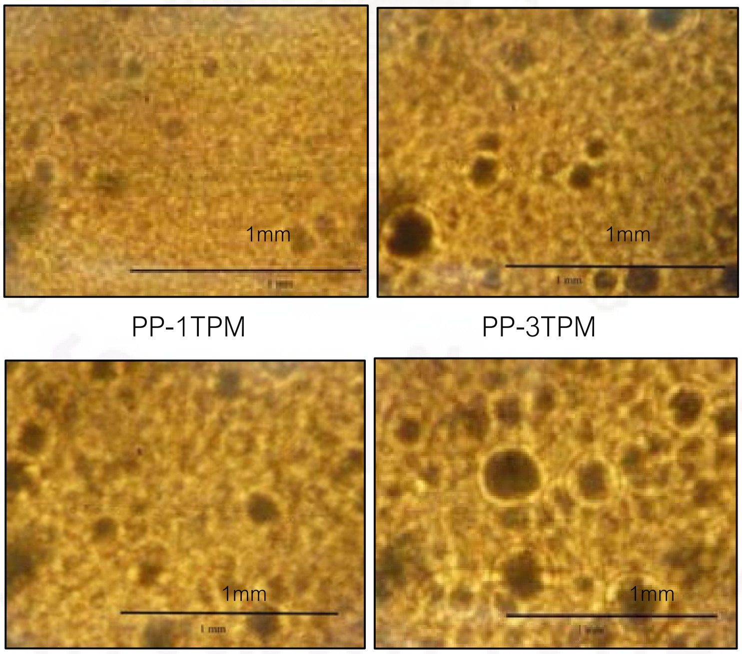
The inorganic content of polypropylene/clay nanocomposite cast films containing different MTPM organoclay loading was shown in table 5.4. The result showed that inorganic content was increased with increasing organoclay loading, which affected the properties of nanocomposite cast films.

Table 5.4: Percentage of inorganic content in the films

films	Actual Percentage of inorganic contents (wt %)	Calculated percentage of inorganic content (wt %)
PP-1TPM	0.933 ± 0.228	0.727
PP-3TPM	2.877 ± 0.027	2.181
PP-5TPM	3.873 ± 0.100	3.635
PP-7TPM	4.702 ± 0.275	5.108

5.2.2 Degree of clay dispersion of polypropylene/clay nanocomposite cast films

Figure 5.10 showed the XRD pattern of polypropylene/clay nanocomposite cast films with different MTPM organoclay loading. Nanocomposite films which contained 1 wt% of MTPM (PP-1TPM film) showed broad peak with low intensity at 2.23°, corresponding to 4.00 nm of d-spacing of layered clay. However, this situation might occur because of low quantity of modified clay addition. For PP-3TPM, PP-5TPM and PP-7TPM films in which 3, 5 and 7 wt% of MTPM was added, the diffraction peak shifted to higher 2θ degree as the clay content increased that was 2.63, 2.73 and 2.91 ° corresponding to 3.35, 3.23 and 3.04 nm of d-spacing of layered clay in polypropylene/clay nanocomposite cast films, respectively. Furthermore, the XRD patterns of nanocomposite cast films showed small second peak at 4.54, 5.51, 5.61 and 5.69°, corresponding to an interlayer spacing of 1.94, 1.60, 1.57 and 1.55 nm of 1, 3, 5 and 7 wt % nanocomposite films, respectively. This result could be due to the variation of orientation of organic part of surfactant between layered clay.



PP-1TPM PP-3TPM

PP-5TPM PP-7TPM

Figure 5.14 Film appearances

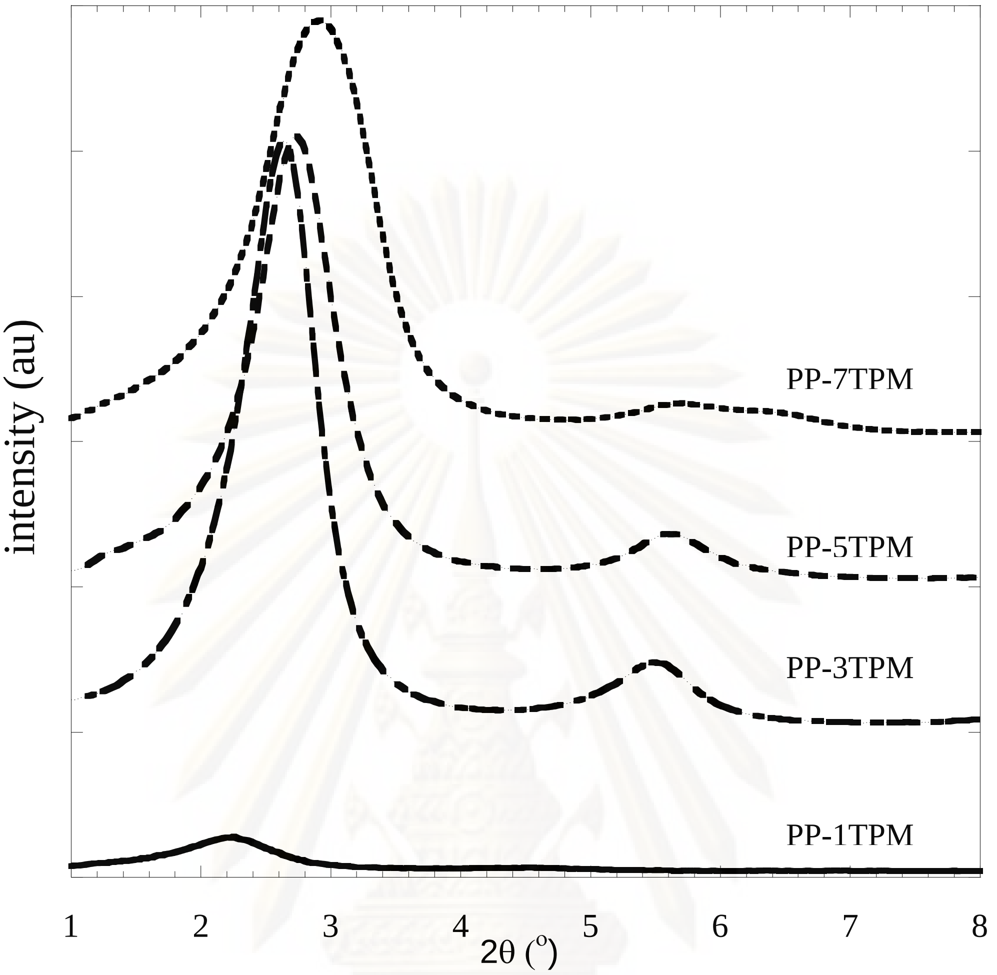


Figure 5.15 XRD patterns of polypropylene/clay nanocomposite cast films containing 1, 3, 5 and 7 wt% of MTPM loading, at 2θ = 1-8°

5.2.3 Melting point and degree of crystallinity of polypropylene/clay nanocomposite cast films

The degree of crystallinity of pure polypropylene, nanocomposite cast films containing 1, 3, 5 and 7 wt% of MTPM films and PP-g-MA that was tested by DSC, at heating rate of 10°C/min was shown in table 5.5. The result indicated the reduction of degree of crystallinity in polypropylene/clay nanocomposite cast films compared with neat polypropylene film. Furthermore, when organoclay loading increased, the relative degree of crystallinty decreased. The formation of crystalline phase was obstructed by the presence of organoclay in polymer matrix. High quantity of organoclay loading added in polypropylene/clay nanocomposite cast films also extremely affected the reduction of degree of crystallinty [13].

However, the crystalline-melting temperature (T_m) of PP-1TPM, PP-3TPM, PP-5TPM and PP-7TPM films slightly decreased with increasing organoclay loading compared with neat polypropylene film which was around 3°C, as shown in figure 5.16. Therefore, the organoclay loading did not significantly affect the T_m of polypropylene/clay nanocomposit cast films.

Table 5.5: Relative degree of crystallinity of polypropylene, PPcomp, polypropylene/clay nanocomposite cast films, containing1, 3, 5 and 7 wt % of MTPM organoclay, and PP-g-MA

Samples	Relative degree of crystallinity (%)
PP	-
PPcomp	99.02
PP-g-MA	-
PP-1TPM	95.67
PP-3TPM	79.21
PP-5TPM	71.84
PP-7TPM	62.80

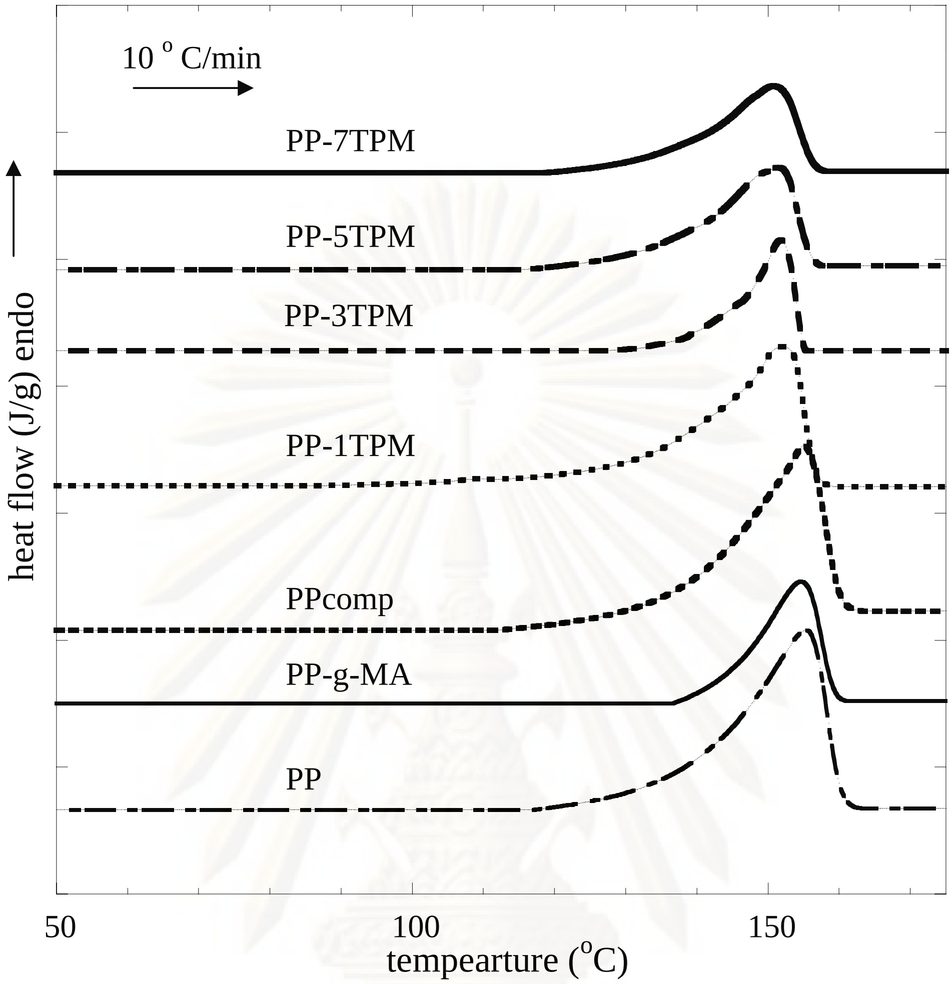


Figure 5.16 DSC profiles of virgin polypropylene, PP-g-MA, polypropylene containing 9 wt% of PP-g-MA and polypropylene/clay nanocomposite cast films containing different MTPM organoclay loading

5.2.4 The mechanical properties of polypropylene/clay nanocomposite cast films

5.2.4.1 Tensile strength at yield

The tensile strength of polypropylene/clay nanocomposite cast films, in which the organoclay loading was varied, was shown in figure 5.17. Tensile strength at yield of PP-1TPM, PP-3TPM and PP-5TPM films was around one third lower than that of neat polypropylene film. In addition, from DSC technique, the addition of organoclay reduced the degree of crystallinity. Furthermore, when 7 wt% of MTPM organoclay was added into nanocomposite film. The high organoclay content obviously decreased the tensile strength at yield of PP-7TPM film. This could be due to the immiscibility between polypropylene and large amount of clay loadding in which 37.20 % reduction of relative degree of crystallinity and turbid film appearance compared with other films was occurred [9].

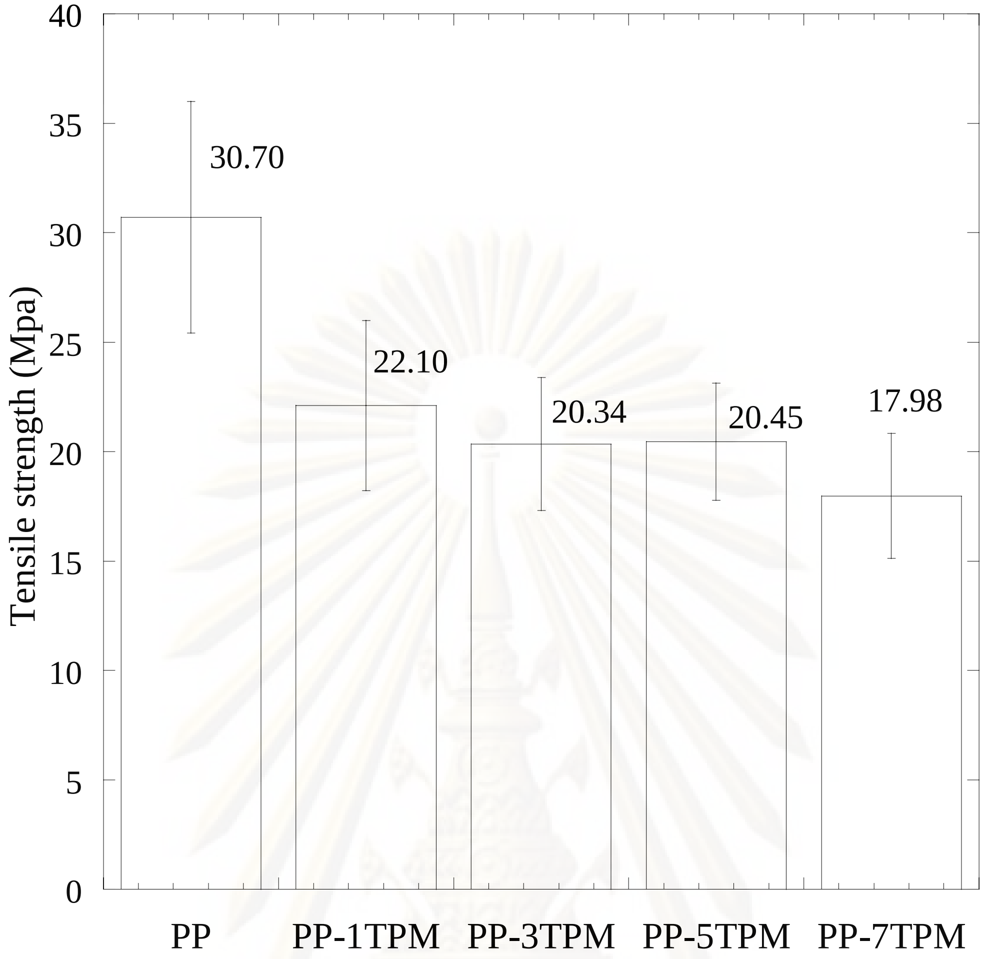


Figure 5.17 Tensile strength at yield of pure polypropylene and polypropylene/clay nanocomposite cast films, containing 1, 3, 5 and 7 wt% of MTPM organoclay

5.2.4.2 Elongation at break

The elongation at break of polypropylene/clay nanocomposite cast films deceased when organoclay loading was increased. The presence of clay in nanocomposite cast films made several weak points in polymer matrix that affected the performance of films as shown in figure 5.18. Moreover, the increasing of organoclay contents in polypropylene/clay nanocomposite cast films over 3 wt% dramatically decreased the elongation at break of films which was around 64 % compared with neat polypropylene films. The reason was that increasing organoclay loading extremely made high degree of clay agglomeration in polymer matrix as can be seen in figure 5.5, which made high critical rapture point in PP-5TPM and PP-7TPM films compared with other films as shown in figure 5.19. Therefore, the elongation at break of PP-5TPM and PP-7TPM films decreased more than that of PP-1TPM and PP-3TPM films which was about 2 times.

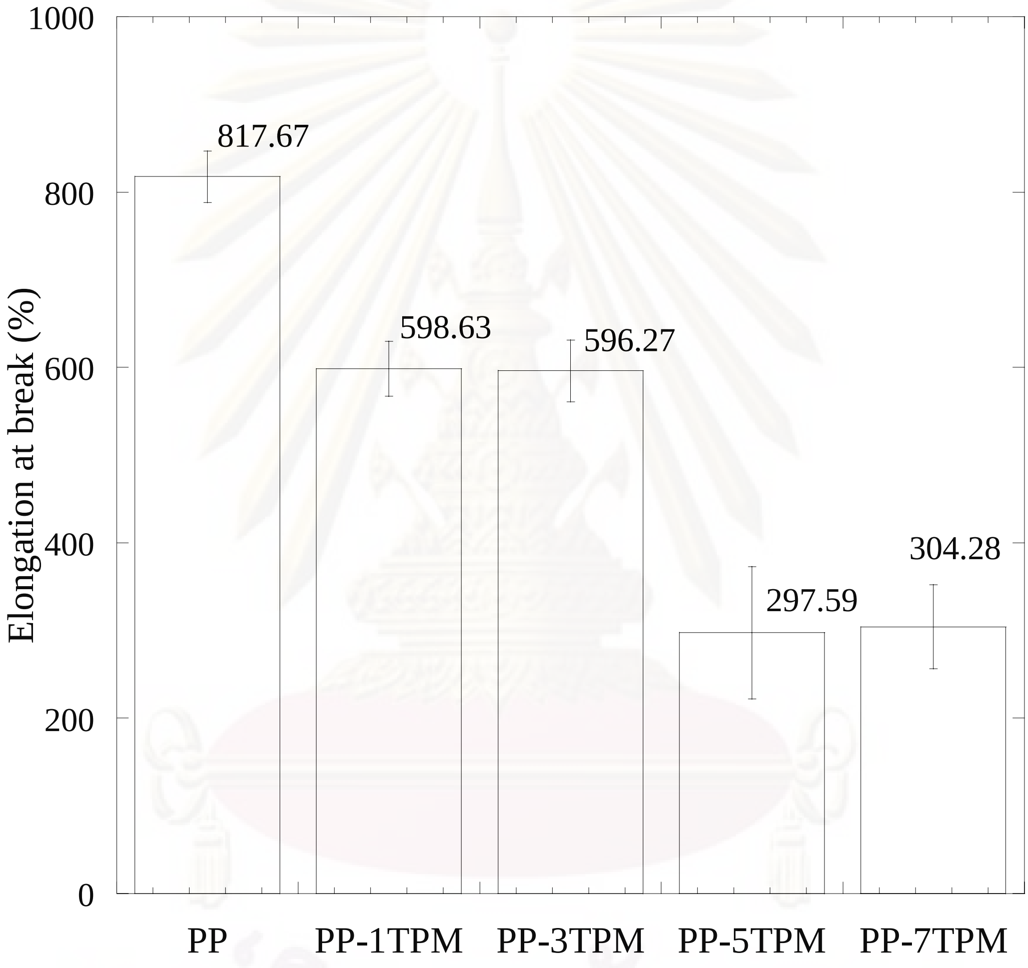


Figure 5.18 Elongation at break of pure polypropylene and polypropylene/clay nanocomposite cast films, containing 1, 3, 5 and 7 wt% of MTPM organoclay

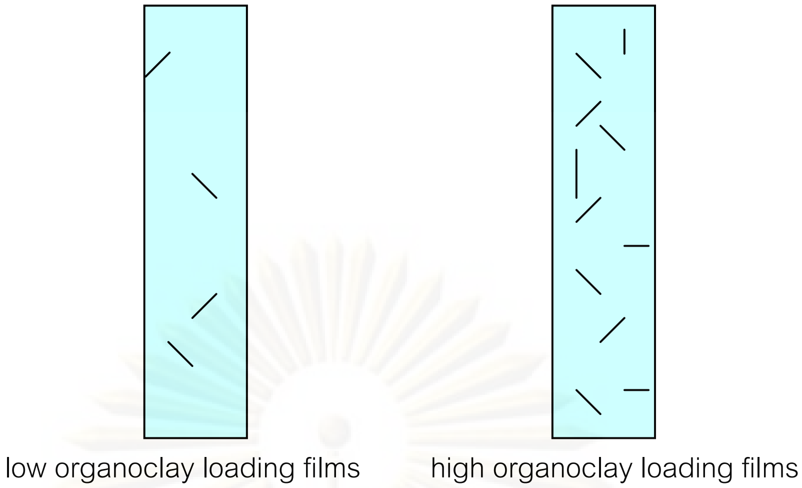


Figure 5.19 Critical rapture points in films

5.2.4.3 Tensile modulus

The increase in tensile modulus of polypropylene/clay nanocomposite cast films was found as the clay loading increased as shown in figure 5.20. The result showed that tensile modulus of PP-1TPM and PP-3TPM films was double when compared with that of pure polypropylene films. Over wise, the tensile modulus of PP-5TPM and PP-7TPM films was four times compared with that of neat polypropylene. This result indicated that the presence of organoclay in polypropylene/clay nanocomposite cast films helped transfer the stress [2-3, 5, 13-17]. Furthermore, the increasing of inorganic contents in the PP-1TPM, PP-3TPM, PP-5TPM and PP-7TPM films after burning test as shown in table 5.4 affected the increasing of tensile modulus except the addition of 7 wt% of organoclay, which means that the optimum value of organoclay contents at 5 wt%.

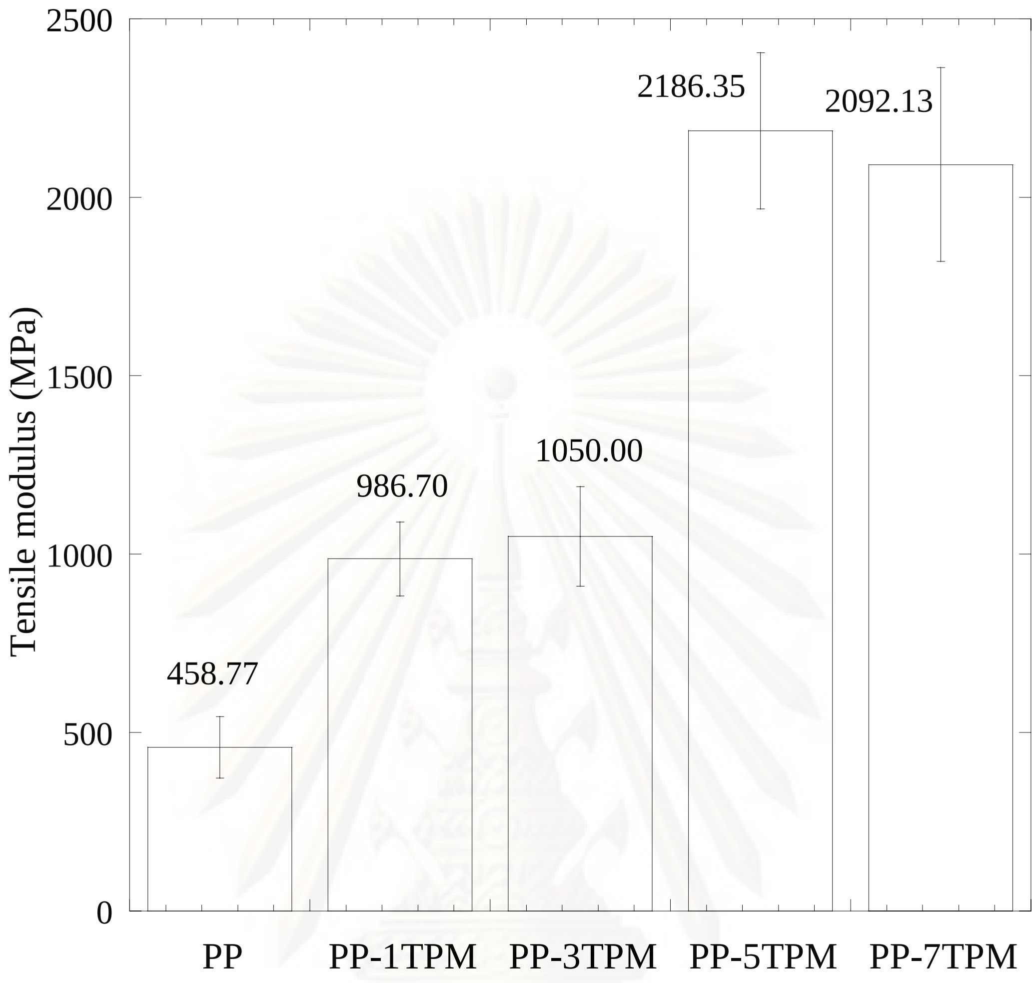


Figure 5.20 Tensile modulus of pure polypropylene and polypropylene/clay nanocomposite cast films, containing 1, 3, 5 and 7 wt% of MTPM organoclay

5.2.4 The oxygen permeability of polypropylene/clay nanocomposite cast films containing different of organoclay loading

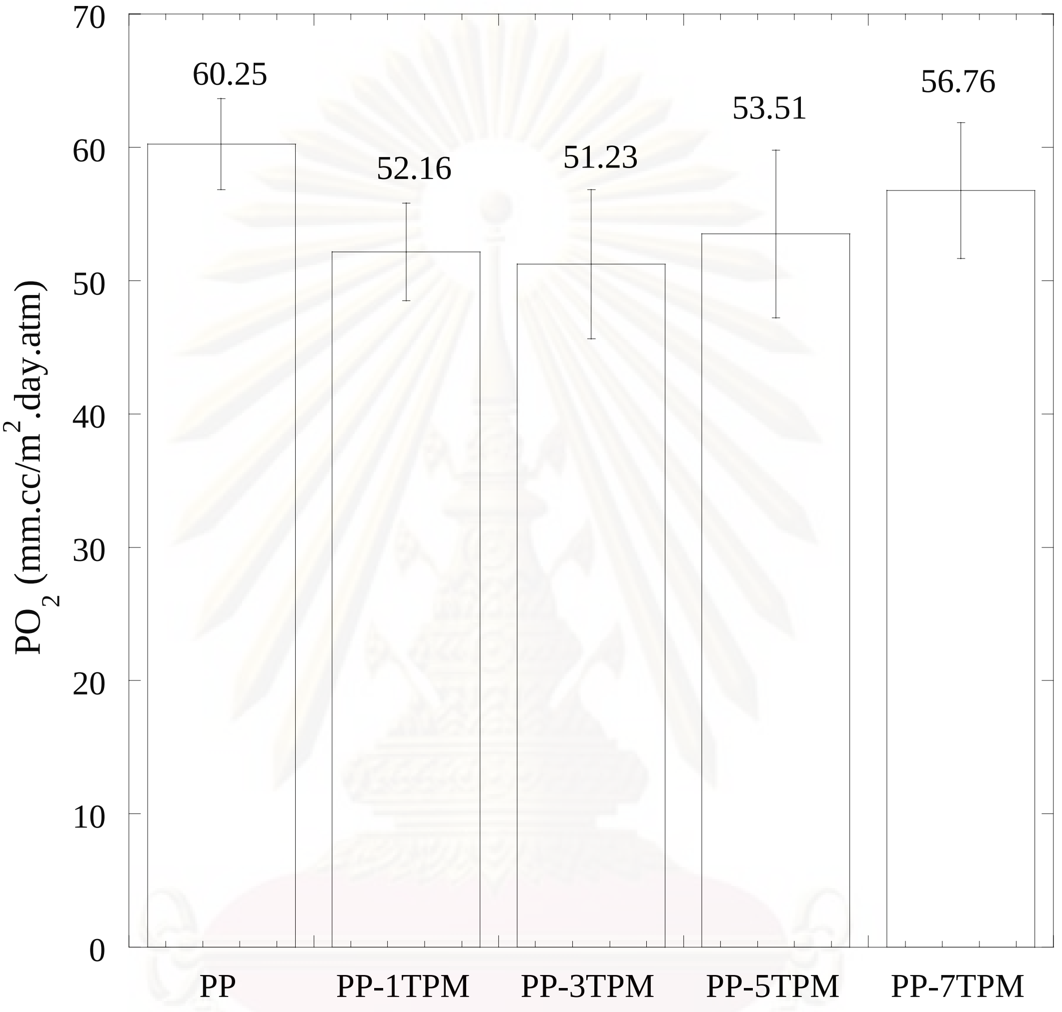


Figure 5.21 Oxygen permeability of pure PP and polypropylene/clay nanocomposite cast films with different organoclay loading

Figure 5.21 showed the oxygen permeability (PO_2) of polypropylene/clay nanocomposite cast films that contained different MTPM organoclay loading at 23 °C, 1 atm and 0 %RH (dry condition). The result indicated that PO_2 of nanocomposite films was lower than that of pure PP film. It could be due to gas barrier function of organoclay, when it was completely mixed with polymer matrix [1]. However, the PP-5TPM and PP-7TPM showed that PO_2 value was higher than that of PP-1TPM and PP-3TPM films. It could be due to high degree of clay agglomeration in PP-5TPM and PP-7TPM made voids in nanocomposites structure that allowed oxygen pass through films. Even though, the degree of crystallinity of nanocomposite films was deceased that affected the high of PO_2 but the influence of high degree of clay dispersion in polymer matrix made clay acted as gas barrier filler and performed the low PO_2 in nanocomposite films.

CHAPTER VI

CONCLUSION

Polypropylene/clay nanocomposite cast films were prepared by co-rotating twin screw extruder attached to cast die. The processing temperature was set around 210 – 235 ºC. The effect of type of surfactant and organoclay as well as organoclay content on the mechanical, thermal and gas barrier properties of polypropylene/clay nanocomposite cast film were studied.

In this research, the addition of small amount of organoclay in polypropylene can improve their properties such as mechanical and gas barrier properties. Tensile moduli of polypropylene/clay nanocomposite cast films were increased compared with that of neat PP film. It could be due to the presence of organoclay which can help stress transferring between clay and polypropylene. In addition, the increase of tensile modulus was the result of the presence of inorganic particles in polypropylene/clay nanocomposite films. Therefore, the addition of organoclay into polypropylene matrix can change the characteristic of film to be stiffer. Moreover, the addition of organoclay slightly reduced the oxygen permeability because the presence of organoclay can obstructed\ oxygen path way when it performed low degree of clay agglomeration. Furthermore, the large structured phosphate surfactant such as PM and PL can be used to treat the nanoclay similar to traditional ammonium surfactant that the improvement of Young’s modulus and gas barrier properties of these films was the clear evidence. However, the appearance of nanocomposite cast film, which was filled with MTPM organoclay was clear and smooth than that with of MTPL organoclay. In the case of ultra fined K-clay, although it had high CEC but this type of nanoclay was easy to agglomerate; therefore, the properties of films decreased PP-5TPM film containing 5 wt% of MTPM organoclay showed the highest enhancement of Young’s modulus that was caused by high inorganic content, In addition, the PP-3TPM film, which 3 wt% of MTPM was added in PP matrix, showed the lowest PO_2 but it was only 4.26 % better than that of PP-5TPM film. Therefore, this research can conclude that 5 wt% of MTPM organoclay were suitable to improve the polypropylene/clay nanocomposite cast films.

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APPENDICES

APPENDIX A

Calculation of surfactant loading

The replacement of surfactant with natural cation in nanoclay was used for organoclay treatment. Surfactant loading was calculated as follows:

$$g_{surf} = \frac{CEC \times conc \times Mw \times kg_{clay}}{\%assay}$$

Where g_{surf} = Weight of surfactant (g_{surf})

CEC = Cation exchange capacity of untreated clay (meq/g_{clay})

conc. = Concentration of surfactant ($mmol_{surf}$)

Mw = Molecular weight of surfactant (g_{surf}/ mol_{surf})

kg_{clay} = Weight of untreated clay (kg_{clay})

%assay = Effectiveness of surfactant

For example: the preparation of organoclay based on dimethyl dihydrogenatedtallow quaternary ammonium (A2), which had 585.5 of MW, at stoi ratio of clay and surfactant 1.0 by using 400 g of T-clay (CEC of clay = 0.6 meq/g of clay), showing as follow:

$$\text{Surfactant loading} = \frac{0.6 \times 1.0 \times 585.5 \times 0.4}{0.95}$$

$$= 147.9158 \text{ g}$$

APPENDIX B

Calculation of percentage of inorganic content, concentration value and calculation percentage of inorganic content in organoclay and films

The percentage of inorganic content in polypropylene/clay nanocomposite cast films was calculated by equation:

$$\% \text{ inorganic content} = \frac{\text{final weight}}{\text{initial weight}} \times 100\ \%$$

In this study, we fixed initial weight at 2 g.

The concentration (conc) value of organoclay was determined by equation

$$conc = \frac{g_{surf} \times \%assay}{CEC \times Mw \times kg_{clay}}$$

For example: the calculation of MTA2 organoclay conc value, which 24.417 g_{surf}*, 95 % assay and 585.5 of MW by using 67.447 g of T-clay (CEC of clay = 0.6 meq/ g of clay), showing as follow:

$$conc = \frac{24.417 \times 0.95}{0.6 \times 585.5 \times 0.067447} = 0.979$$

**Note* g_{surf} = inorganic of MMT - inorganic of MTA2 = 91.683 – 67.447

The calculation percentage of inorganic content of nanocomposite cast films determined by equation:

calculation % inorganic content = wt % organoclay loading x % inorganic content of clay

For example: the calculation of PP-3TA2 films calculation % inorganic content that was 3 wt % of organoclay loading and 67.447 of inorganic of MTA2 showing as follow:

calculation % inorganic content = (3/100) x 67.447 = 2.023

Table B.1: Inorganic content and percentage of inorganic content of clay and organoclay

	Final weight (g)			Percentage of inorganic content (wt%)	Concentraion value (mmol$_{sur}$)
	1	2	3		
MMT	1.8386	1.8410	1.8322	91.863 ± 0.186	-
MTA2	1.3214	1.4515	1.2739	67.447 ± 3.754	0.979
MTPS	1.6120	1.6844	1.5179	80.238 ± 3.401	0.648
MTPM	1.4944	1.4511	1.4164	72.700 ± 1.595	0.952
MTPL	1.4841	1.5480	1.3461	72.970 ± 4.213	0.808
MMK	1.6576	1.7560	1.6583	84.532 ± 2.311	-
MKA2	1..1322	1.2115	1.3238	61.125 ± 3.930	0.565
MKPS	1..796	1.2459	1.4287	67.570 ± 3.862	0.689
MKPM	1.1578	1.2199	1.3561	62.230 ± 4.141	0.797
MKPL	1.1424	1.3465	1.2148	61.728 ± 4.224	0.629

Table B.2: Inorganic content and percentage of inorganic content of polypropylene/clay nanocomposite cast films containing 3 wt% of different organoclay

	Final weight (g)			Actual percentage of inorganic content (wt %)	Calculated percentage of inorganic content (wt %)
	1	2	3		
PP-3TA2	0.0578	0.0567	0.0592	2.896 ± 0.051	2.023
PP-3TPS	0.0550	0.0569	0.0612	2.885 ± 0.130	2.512
PP-3TPM	0.0571	0.0583	0.0572	2.877 ± 0.027	2.181
PP-3TPL	0.0514	0.0567	0.0551	2.720 ± 0.111	2.189
PP-3KA2	0.0432	0.0446	0.0489	2.278 ± 0.121	1.834
PP-3KPS	0.0409	0.0543	0.0453	2.372 ± 0.279	2.027
PP-3KPM	0.041	0.0400	0.0467	2.128 ± 0.148	1.667
PP-3KPL	0.038	0.0437	0.0371	1.980 ± 0.146	1.852

Table B.3: Inorganic content and percentage of inorganic content of polypropylene/clay nanocomposite cast films containing different of organoclay loading

	Final weight (g)			Actual percentage of inorganic content (wt%)	Calculated percentage of inorganic content (wt %)
	1	2	3		
PP-1TPM	0.0144	0.0166	0.0250	0.933±0.228	0.727
PP-3TPM	0.0571	0.0583	0.0572	2.877±0.027	2.181
PP-5TPM	0.0777	0.0798	0.0749	3.873±0.100	3.635
PP-7TPM	0.0864	0.0992	0.0965	4.702±0.275	5.108

APPENDIX C

Determination of d-spacing of layered silicate of clay

The d-spacing of layered clay and organoclay that was corresponded to the degree of clay dispersion is calculated by the Bragg's equation, which is derived by physicists W.H. Bragg and his son. It was determined the interlayer spacing between silicate planes of clay as shown below;

$$n\lambda = 2d\sin\theta$$

where n = Peaks corresponded to the {001} basal reflection (n=1)

λ = The wavelength of X-ray radiation that equals to 1.542 Å with CuKα

d = The interlayer spacing between plane in atomic lattice (Å)

θ = The angle between the incident ray and the scattering planes (degree)

The X-ray diffractometer determine double diffraction angle (2θ). For example, 2θ peak of MTA2 was 2.66° in which d-spacing of layered clay can be determined as follow:

$$(1)(1.542) = 2d \sin (2.66/2)$$

$$d = 3.31 \text{ Å}$$

Table C.1: The degree of clay dispersion of nanoclay and organoclay

	2θ = 1-8°			
	First peak of 2θ position (°)	D-spacing of layered clay (nm)	Second peak 2θ position (°)	D-spacing of layered clay (nm)
MMT	7.22	1.22	-	-
MTA2	2.66	3.31	-	-
MTPS	5.10	1.73	-	-
MTPM	3.45	2.56	7.73	1.14
MTPL	3.23	2.73	4.86	1.82
MMK	7.20	1.23	-	-
MKA2	2.57	3.44	-	-
MKPS	5.30	1.67	-	-
MKPM	3.80	2.32	-	-
MKPL	3.56	2.48	-	-

Table C.2: The degree of clay dispersion of polypropylene/clay nanocomposite cast films, which contained 3 wt% of different organoclays

	2θ = 1-8°			
	First peak of 2θ position (°)	D-spacing of layered clay (nm)	Second peak 2θ position (°)	D-spacing of layered clay (nm)
PP-3TA2	2.06	4.29	4.40	2.01
PP-3TPS	5.19	1.70	-	-
PP-3TPM	2.63	3.35	5.54	1.60
PP-3TPL	2.45	3.61	5.01	1.76
PP-3KA2	2.13	4.15	4.50	1.96
PP-3KPS	5.09	1.74	-	-
PP-3KPM	2.72	3.25	5.42	1.63
PP-3KPL	2.54	3.47	5.11	1.72

Table C.3: The degree of clay dispersion of polypropylene/clay nanocomposite cast films, which contained different organoclays loading

	2θ = 1-8°			
	First peak of 2θ position (°)	d-spacing of layered clay (nm)	Second peak 2θ position (°)	d-spacing of layered clay (nm)
PP-1TPM	2.23	4.00	4.54	1.94
PP-3TPM	2.63	3.35	5.54	1.60
PP-5TPM	2.73	3.23	5.61	1.57
PP-7TPM	2.91	3.04	5.69	1.55

APPENDIX D

The Crystalline-melting temperature (T_m), area under endothermic curve and relative degree of crystallinity

In this research, relative degree of crystallinity of nanocomposite films was evaluated by area under endothermic curve that was determined by DSC. The degree of crystallinity of polypropylene/clay nanocomposite cast films was compared with pure polypropylene film and pure PP-g-MA to obtain relative degree of crystallinity of nanocomposite films.

To obtain the relative degree of crystallinity of polypropylene/clay nanocomposite cast films, which had the ratio of polypropylene: PP-g-MA: organoclay as 88: 9: 3, the relative degree of crystallinity was determined as follow:

$$\text{Relative degree of crytallinity} = \frac{Area(sample)}{\left(\frac{88}{97}\right)\times Area(PP)+\left(\frac{9}{97}\right)\times Area(PP-g-MA)}$$

where area of pure PP = 441.596 mJ

area of pure PP-g-MA = 431.340 mJ

In this research, the effect of surfactant on the degree of crystallinity of polypropylene/clay nanocomposite cast films was neglected.

Table D.1: The crystalline-melting temperature (T_m), ΔH, area under endothermic curve and relative degree of crystallinity of polypropylene, polypropylene blending 9 wt% of PP-g-Ma, polyproprolene/clay nanocomposite cast films containing 3 wt% of different organoclays and PP-g-MA

	Heating scan (10ºC/min)			
	T_m (ºC)	ΔH (J/g)	Area (mJ)	Relative degree of crytallinity (%)
Pure PP	154.22	81.7771	441.596	-
PPcomp	154.25	79.8779	436.307	99.02
PP-g-MA	155.31	79.2545	431.340	-
PP-3TA2	151.50	78.8711	327.372	74.29
PP-3TPS	149.36	71.6444	265.084	60.16
PP-3TPM	151.95	75.0993	349.017	79.21
PP-3TPL	150.60	76.3225	357.019	81.02
PP-3KA2	149.36	64.9857	285.957	64.90
PP-3KPS	152.19	70.9999	247.052	56.07
PP-3KPM	150.91	74.2452	338.952	76.92
PP-3KPL	149.15	75.7341	339.776	77.11

Table D.2: The crystalline-melting temperature (T_m), ΔH, area under endothermic curve and relative degree of crystallinity of polypropylene, polypropylene blending 9 wt% of PP-g-Ma, polyproprolene/clay nanocomposite cast films containing different of organoclays loading and PP-g-MA

	Heating scan (10ºC/min)			
	T_m (ºC)	ΔH (J/g)	Area (mJ)	Relative degree of crytallinity (%)
PP-1TPM	152.00	78.9293	421.543	95.67
PP-3TPM	151.95	75.0993	349.017	79.21
PP-5TPM	151.66	74.6763	316.567	71.84
PP-7TPM	151.01	68.8667	276.720	62.80

APPENDIX E

The mechanical properties of the films

Table E.1: Tensile properties of pure PP film

	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
1	23.08	854.50	300.56
2	38.18	805.33	566.68
3	29.02	789.30	409.21
4	33.07	822.37	459.29
5	25.53	799.00	378.66
6	30.15	792.60	552.84
7	35.12	841.77	477.68
8	32.98	870.37	424.69
9	37.14	826.57	591.61
10	22.72	774.93	426.62
Avg.	30.70	817.67	458.77
SD	5.59	29.29	86.36

Table E.2: Tensile properties of polypropylene blending with 9 wt% of PP-g-MA film

	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
1	21.45	691.23	409.13
2	31.00	771.73	456.60
3	30.74	771.80	470.22
4	18.55	623.27	474.08
5	24.70	774.03	475.70
6	21.23	656.93	484.04
7	26.25	703.77	510.25
8	26.90	701.43	544.53
9	31.54	740.37	597.07
10	34.54	744.21	687.24
Avg.	26.69	719.88	510.88
SD	4.98	50.42	76.11

Table E.3: Tensile properties of polypropylene/clay nanocomposite film containing 3 wt% of MTA2 organoclay (PP-3TA2)

	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
1	23.70	627.90	1016.24
2	22.09	600.73	933.99
3	23.62	524.87	955.80
4	19.96	541.17	1154.35
5	18.81	525.60	1214.44
6	25.12	575.00	1047.00
7	19.10	559.57	1139.58
8	16.45	482.67	1176.11
9	20.27	541.4	1014.99
10	20.86	496.87	1250.30
Avg.	21.00	547.58	1090.28
SD	2.51	42.47	105.10

Table E.4: Tensile properties of polypropylene/clay nanocomposite film containing 3 wt% of MTPS organoclay (PP-3TPS)

	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
1	6.15	163.66	817.67
2	10.89	166.06	908.84
3	11.17	182.69	802.66
4	5.36	190.69	841.53
5	6.71	236.72	934.04
6	6.15	207.50	834.09
7	13.28	257.63	968.42
8	6.38	257.85	777.65
9	7.26	258.20	824.45
10	7.46	278.00	922.06
Avg.	8.08	219.90	863.08
SD	2.55	40.55	61.31

Table E.5: Tensile properties of polypropylene/clay nanocomposite film containing 3 wt% of MTPM organoclay (PP-3TPM)

	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
1	20.92	594.17	1006.47
2	22.14	576.67	1050.95
3	24.96	535.21	1240.21
4	17.82	584.20	1166.21
5	18.91	631.83	870.43
6	25.96	675.03	1108.20
7	18.11	594.17	834.88
8	17.64	573.77	1016.87
9	16.42	590.67	938.31
10	20.54	607.00	1267.46
Avg.	20.34	596.27	1050.00
SD	3.04	35.20	139.41

Table E.6: Tensile properties of polypropylene/clay nanocomposite film containing 3 wt% of MTPL organoclay (PP-3TPL)

	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
1	19.18	522.43	912.01
2	21.19	562.77	1370.99
3	23.00	584.83	1272.88
4	18.30	547.53	1322.22
5	22.51	590.97	1311.53
6	21.24	604.29	1161.33
7	18.67	564.85	1053.85
8	17.59	516.15	1130.90
9	18.31	442.81	1186.01
10	21.88	469.73	1223.31
Avg.	20.19	540.64	1194.50
SD	1.88	50.19	131.50

Table E.7: Tensile properties of polypropylene/clay nanocomposite film containing 3 wt% of MKA2 organoclay (PP-3KA2)

	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
1	4.55	271.00	559.37
2	2.87	272.39	558.30
3	4.98	322.86	561.78
4	5.04	327.76	549.58
5	3.26	227.59	631.64
6	4.06	242.15	547.67
7	4.44	326.81	522.08
8	5.87	264.18	486.51
9	3.96	214.63	643.93
10	5.54	322.08	609.60
Avg.	4.46	279.14	570.05
SD	0.90	41.13	44.00

Table E.8: Tensile properties of polypropylene/clay nanocomposite film containing 3 wt% of MKPS organoclay (PP-3KPS)

	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
1	7.94	291.27	438.61
2	7.97	300.61	367.12
3	4.44	265.90	218.98
4	6.84	265.05	337.36
5	6.36	529.03	203.09
6	4.02	344.86	254.08
7	4.31	308.57	361.97
8	5.15	362.53	370.85
9	4.04	485.00	254.61
10	3.41	362.53	264.90
Avg.	5.45	351.53	307.16
SD	1.61	85.14	74.04

Table E.9: Tensile properties of polypropylene/clay nanocomposite film containing 3 wt% of MKPM organoclay (PP-3KPM)

	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
1	12.00	534.38	679.12
2	8.07	353.86	477.19
3	9.46	371.61	571.99
4	8.87	519.88	544.42
5	15.25	509.36	438.27
6	8.96	516.17	613.96
7	8.90	424.58	424.58
8	8.04	495.88	519.64
9	6.99	426.65	442.15
10	9.39	437.63	612.37
Avg.	9.23	450.62	516.06
SD	2.22	59.27	70.08

Table E.10: Tensile properties of polypropylene/clay nanocomposite film containing 3 wt% of MKPL organoclay (PP-3KPL)

	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
1	12.39	526.24	484.85
2	13.77	478.77	615.42
3	13.95	563.25	506.61
4	10.65	521.58	479.56
5	12.17	540.49	624.20
6	13.07	517.96	689.10
7	9.34	543.33	541.61
8	9.78	465.00	651.41
9	8.53	476.56	709.64
10	8.66	534.17	529.07
Avg.	11.23	516.74	583.15
SD	1.98	30.96	80.94

Table E.11: Tensile properties of polypropylene/clay nanocomposite film containing 1 wt% of MTPM organoclay (PP-1TPM)

	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
1	26.32	616.33	1113.54
2	19.47	590.69	924.26
3	18.45	606.68	950.38
4	24.58	616.06	1059.29
5	20.65	633.49	932.82
6	29.78	556.71	1177.98
7	19.05	587.75	806.45
8	19.73	630.93	1033.17
9	17.64	531.30	918.86
10	25.35	616.33	950.27
Avg.	22.10	598.63	986.70
SD	3.88	31.19	103.27

Table E.12: Tensile properties of polypropylene/clay nanocomposite film containing 5 wt% of MTPM organoclay (PP-5TPM)

	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
1	20.41	413.17	2034.45
2	23.37	210.08	2383.21
3	21.57	217.18	1919.44
4	22.68	411.65	2437.89
5	17.58	338.76	1971.71
6	19.47	362.98	1805.92
7	18.13	267.62	2364.56
8	18.38	281.04	2369.41
9	25.72	204.57	2216.46
10	17.20	268.88	2351.43
Avg.	20.45	297.59	2186.35
SD	2.68	75.57	218.61

Table E.13: Tensile properties film of polypropylene/clay nanocomposite film containing 7 wt% of MTPM organoclay (PP-7TPM)

	Tensile strength (MPa)	Elongation at break (%)	Tensile modulus (MPa)
1	17.50	248.79	2117.68
2	16.67	299.57	2037.46
3	16.23	214.23	1930.91
4	22.41	321.29	2649.67
5	21.04	355.04	2315.35
6	22.87	364.55	2405.36
7	16.31	281.01	1771.51
8	15.63	273.21	1781.31
9	16.96	364.46	2026.91
10	14.14	320.67	1885.10
Avg.	17.98	304.28	2092.13
SD	2.86	48.07	271.10

APPENDIX F

The oxygen transmission rate of the films

Table F1: PO_2 of pure PP, PPcomp and polypropylene/clay nanocomposite cast films containing 3 wt% of different types of organoclay

	PO_2 (mm.cc/m^2.day.atm)					
	1	2	3	4	Avg.	SD
Pure PP	60.55	63.76	56.85	56.83	60.25	3.40
PPcomp	48.32	55.28	57.83	62.05	55.87	4.98
PP-3TA2	49.39	53.19	49.23	46.32	49.53	2.44
PP-3TPS	87.60	78.93	83.71	97.70	86.99	6.91
PP-3TPM	45.98	45.44	57.94	55.58	51.23	5.59
PP-3TPL	45.82	48.92	53.26	57.88	51.48	4.54
PP-3KA2	96.15	79.21	91.00	97.86	91.05	7.29
PP-3KPS	78.46	90.79	95.37	104.74	92.34	9.46
PP-3KPM	90.09	112.63	82.31	114.92	93.77	12.53
PP-3KPL	83.47	51.43	106.87	80.36	92.83	14.11

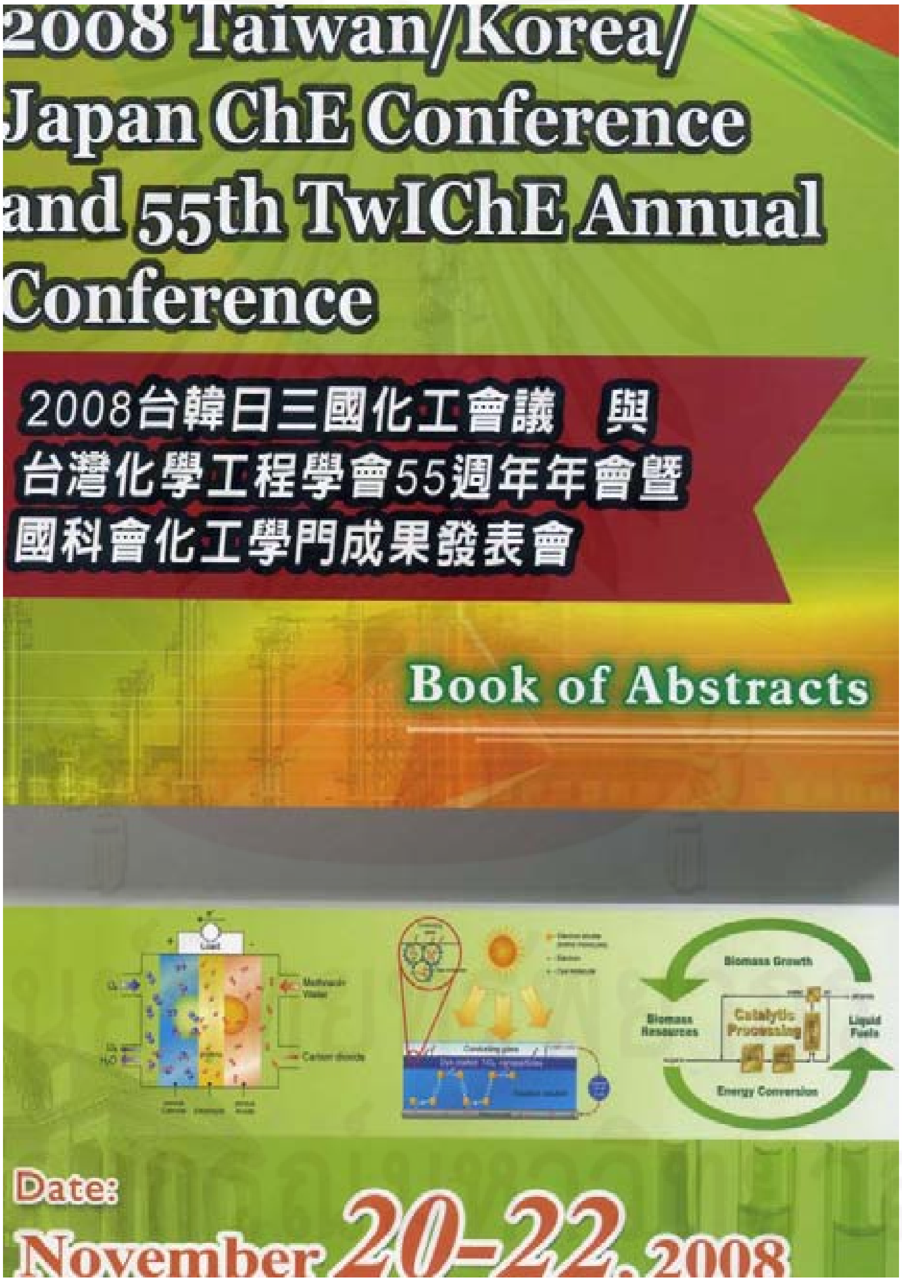
Table F2: PO_2 of pure PP, PPcomp and polypropylene/clay nanocomposite cast films containing different of MTPM organoclay loading

	PO_2 (mm.cc/m^2.day.atm)					
	1	2	3	4	Avg.	SD
PP-1TPM	58.13	51.43	50.88	48.22	52.16	3.65
PP-3TPM	45.98	45.44	57.94	55.58	51.23	5.59
PP-5TPM	52.42	45.08	53.74	62.79	53.51	6.29
PP-7TPM	56.76	62.86	58.57	48.85	56.76	5.07

APPENDIX G

Thesis presentation

This thesis was presented at 2008 Taiwan/ Korea/ Japan ChE conference and 55th TwIChE annual conference in Taipei city, Taiwan.



2008 Taiwan/Korea/
Japan ChE Conference
and 55th TwIChE Annual
Conference

2008台韓日三國化工會議　與
台灣化學工程學會55週年年會暨
國科會化工學門成果發表會

Book of Abstracts

Date:
November 20-22, 2008

Figure G.1 Book of abstract

Topic 6.
Polymer Science

OS6004 The effect of phosphate salt surfactant on the properties of polypropylene/clay nanocomposite cast films

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Polypropylene (PP)/clay nanocomposite films can be used in packaging application. The addition of the small amount of nanoclay (below 5 wt %) in polymer can improve the mechanical, thermal and gas barrier properties because the layered clay whose thickness is about 1 nm shows high aspect ratio and high surface area. Thus, the interaction between polymer and nanoclay help promoting the enhancement in solid-state properties of nanocomposites. Before mixing polypropylene with clay, clay must be treated surface by surfactant to change the polarity of clay to be hydrophobic. Surfactant would help nanoclay disperses in polypropylene matrix. The degree of clay dispersion can change the percent of crystallinity and crystalline phase of polypropylene in polypropylene/clay nanocomposite films that in turn affect mechanical and gas barrier properties of films. The traditional ammonium salt (double chain surfactant) and four types of phosphate salt whose chain length are varied the length are used in this research. In this research, the nanocomposite films are prepared by co-rotating twin screw extruder attach to a cast die. The mechanical properties of nanocomposite films are tested by the Universal testing machine. The thermal, gar barrier and degree of clay dispersion of nanocomposite films are tested by mean of DSC, OTR and XRD technique, respectively.

Keywords: Polypropylene, Nanocomposites, Film, Clay, Packaging.

OS6005 Effect of type of surfactant and the mixing sequence between nanoclay and monomer on properties of polyurethane/clay nanocomposite foams

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Polyurethane (PU) nanocomposite foams have attracted a great deal of attention in automotive industry such as car seat manufacture. Adding a small amount of nanoclay as a filler in the polyurethane has been found to reduce the amount of polyurethane, thereby lowering cost of polyurethane used in automotive industry and overcome some disadvantages properties of polyurethanes concerning with low thermal stability and low mechanical strength which limit their application. However the improvement of these properties will depend on clay dispersion ability in the polyurethane matrix. Therefore in the current study a series of alkyl ammonium were carefully selected to explore relationships between structure of surfactants and degree of clay dispersion i.e. (1) one long alkyl tail, (2) two long alkyl tail and (3) hydroxyl ethyl groups on the amine. Furthermore the effect of the mixing sequence between nanoclay and one monomer of polyurethane such as polyol or isocyanate on degree of clay dispersion were investigated. In all cases only 3 wt.% nanoclay are used. The degree of clay dispersion in PU nanocomposite foams were characterized by X-ray diffraction and the structure of PU foams were observed via scanning electron microscopy. In addition the mechanical properties of PU nanocomposite foams were investigated by indentation force deflection test, Resilience test and compression set test. Finally the functional groups were considered by FTIR. Nevertheless all the results will be discussed in a presentation.

Keywords: Polyurethane, Nanocomposite foam, Organoclay, Clay dispersion, Automotive.

Figure G.2 Thesis abstract

VITA

Mr. Wirote Sae-chieng was born in Bangkok, Thailand on November 18th, 1984. He is the first son of Mr. Surachai Sae-Chieng and Mrs. Nukent Namak and has one younger brother; Mr. Witchitpol Sae-Chieng. He completed high school at Chanpradittharam wittayacom school, Thailand in 2002 and received Bachelor degree from the department of chemical engineering, faculty of engineering, King Mongkut's University of North Bangkok, Thailand in 2006. After that, he decided to continue his study for master degree at department of chemical engineering, faculty of engineering, Chulalongkorn University. In November 2008, he had great opportunity to present his thesis in the subject of "The effect of phosphate salt surfactant on the properties of polypropylene/clay nanocomposite cast films" at 2008 Taiwan/ Korea/ Japan ChE conference and 55th TwIChE annual conference in Taipei city, Taiwan.