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SOLID-STATE MECHANICAL PROPERTIES AND MICROSTRUCTURE OF POLYPROPYLENE/NYLON-6 CLAY NANOCOMPOSITES

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นางสาววลัยลักษณ์ อยู่บ้านคลอง: การวิเคราะห์คุณสมบัติทางกลของสภาวะของแข็ง และ โครงสร้างจุลภาคของพอลิโพรพิลีน/ไนล่อน-6 ดินเหนียว นาโนคอมพอสิท (SOLID-STATE MECHANICAL PROPERTIES AND MICROSTRUCTURE OF POLYPROPYLENE/NYLON-6 CLAY NANOCOMPOSITES) อาจารย์ที่ปรึกษา: อ. ดร. อนงค์นาฎ สมหวังธนโรจน์, 76 หน้า. ISBN 974-17-4494-3

งานวิจัยนี้มีจุดมุ่งหมายเพื่อศึกษาคุณสมบัติทางกลและโครงสร้างจุลภาคของพอลิเมอร์ผสม และวัสดุประกอบแต่ง ซึ่งมีพอลิเมอร์ผสมระหว่างพอลีโพรพิลีน (PP) และไนล่อน-6 (Ny6) เป็นองค์ประกอบหลักและเพื่อเป็นการเพิ่มคุณสมบัติทางกลจึงได้มีการเติมสารประกอบแต่งขนาดอนุภาคนาโนเมตรซึ่งในงานวิจัยได้สนใจใช้ดินเหนียวที่ถูกปรับสภาพผิวด้วย Quaternary Ammonium Compound (Org-MMT) ซึ่งเป็นสารประกอบแต่งที่มีลักษณะโครงสร้างเป็นแผ่น ชั้น และในระบบยังมีสารช่วยผสม(PP-MA) ซึ่งทำหน้าที่ช่วยให้พอลิเมอร์ทั้งสองชนิดมีความเข้ากันได้มากขึ้นและยังช่วยเพิ่มระดับการกระจายตัวของดินเหนียวในเมตริกซ์อีกด้วย งานวิจัยนี้ศึกษาคุณสมบัติของพอลิเมอร์ผสมและนาโนคอมพอสิทเมื่อมีการเปลี่ยนแปลงปริมาณของสารประกอบแต่งและปริมาณของสารช่วยผสม โดยผ่านกระบวนการผสมด้วยความร้อน (Twin screw extruder) จากผลการทดสอบคุณสมบัติทางกลพบว่าเมื่อเพิ่มปริมาณของ PP-MA จะทำให้พอลิเมอร์ผสม (PP/Ny6) มีความแข็ง และระยะยืดก่อนการเกิดการแตกหักเพิ่มขึ้น 21% และ 99% ตามลำดับ นอกจากนั้นจากภาพถ่าย Scanning Electron microscopy (SEM) พบว่าสารช่วยผสมทำหน้าที่ปรับปรุงการยึดเหนี่ยวกันระหว่างโมเลกุลของ PP/Ny6 และช่วยในการกระจายตัวของ Ny6 เฟสใน PP เฟส ซึ่งทำหน้าที่เป็นองค์ประกอบหลักมีสาเหตุมาจากการเกิดปฏิกิริยาระหว่าง หมู่ฟังก์ชั่น Maleic anhydride ของ PP-MA และหมู่เอมายด์ของ Ny6 ซึ่งทำให้ความเป็นผลึกของ Ny6 ลดลง และจากผลการทดลองนี้สามารถสนับสนุนได้ว่ามีการเกิดปฏิกิริยาระหว่างหมู่ฟังก์ชั่น ส่วนผลกระทบที่เกิดจากการเพิ่มปริมาณของ PP-MA ในพอลิเมอร์ผสมและนาโนคอมพอสิท (PP/Ny6/PP-MA/Org-MMT)พบว่า ปริมาณ PP-MA เพิ่มขึ้นทำให้คุณสมบัติทางกลทั้งความแข็งแรง และระยะยืดก่อนการแตกหักของวัสดุต่ำลง ในขณะเดียวกันเมื่อมีการเพิ่ม ปริมาณของ ดินเหนียว ซึ่งทำหน้าที่เป็นสารเสริมแรงจะส่งผลให้วัสดุมีความแข็งแรงสูงขึ้น จากเดิม 30% และความหนืดสูงขึ้นเมื่อปริมาณของดินเหนียวเพิ่มขึ้น เป็นผลสืบเนื่องมาจากโครงสร้างและการกระจายตัวของชั้นดินเหนียวในเมตริกซ์ที่สามารถยืนยันได้จากผลการวิเคราะห์ เครื่องมือ X-ray diffraction (XRD) และ Transmission Electron Microscopey (TEM) ว่าสายโซ่พอลิเมอร์สามารถแทรกเข้ายึดเกาะระหว่างชั้นของดินเหนียวได้ดีทำให้ดินเหนียวมีการกระจายตัวที่ดีขึ้น นอกจากนั้นแล้วจากการวิเคราะห์โดย Dynamic mechanical analysis (DMA) ยังพบว่าการเติมสารประกอบแต่งส่งผลให้วัสดุมีความสามารถในการทนต่อความร้อนสูงหรือมีเสถียรภาพทางความร้อนสูงเมื่อเปรียบเทียบกับ PP ซึ่งเป็นองค์ประกอบหลักและมีความแข็งแรงสูงเมื่อต้องการ การใช้งานในอุณหภูมิต่ำได้ดีกว่าเมื่อเปรียบเทียบกับ พอลิเมอร์เมตริกซ์

ภาควิชา............วิศวกรรมเคมี................. ลายมือชื่อนิสิต...วลัยลักษณ์ อยู่บ้านคลอง...........

สาขาวิชา...........วิศวกรรมเคมี............... ลายมือชื่ออาจารย์ที่ปรึกษา.................................

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KEY WORDS: MECHANICAL/MICROSTRUCTURE/POLYPROPYLENE/
NYLON-6/NANOCOMPOSITES/

WALAILAK UBANKHLONG: SOLID-STATE MECHANCAL PROPERTIES AND MICROSTRUCTURE OF POLYPROPYLENE/NYLON-6 CLAY NANOCOMPOSITES. THESIS ADVISOR: ANONGNAT SOMWANGTHANAROJ, Ph.D., 76 pp. ISBN 974-17-4494-3.

This research aimed to study the mechanical properties and microstructure of polypropylene/nylon 6 nanocomposites. Polymer blends of polypropylene (PP) and nylon 6 (Ny6) were used as a matrix. The nano-filler used to improve the mechanical properties of polymer blends was organoclay. Organoclay(Org-MMT) was treated by quaternary ammonium compound acting as reinforcing filler. Compatibilizer, PP-MA, was used to improve the adhesion between phase and dispersion of Org-MMT in matrix. The mechanical properties and microstructure of the composite that processed by twin screw extruder were investigated at different amount of compatibilizer and Org-MMT. By adding 9.5wt% of PP-MA in polymer blends, tensile modulus and elongation at break increased by 21% and 99%, respectively. Improvement of adhesion and dispersion between PP and Ny6 was improved by adding PP-MA as shown in Scanning Electron Microscopy (SEM) micrograph. The result of physical reacting between maleic anhydride and amine of nylon 6 was supported by dynamic mechanical analysis (DMA). Moreover, by adding PP-MA, the crystallinity of Ny6 was decreased which confirmed by DSC thermograms and XRD results. The increasing of PP-MA in nanocomposites decreased tensile modulus and elongation at break of the composites. However, the presence of Org-MMT as reinforcement showed the decreasing of tensile modulus and viscosity as a function of Org-MMT due to the good dispersion of Org-MMT in matrix. X-ray diffraction (XRD) and Transmission electron microscopy (TEM) can be verified the insertion of polymer and dispersion between galleries. Furthermore, the thermal stability of nanocomposites observed by DMA showed higher glass transition temperature than polymer matrix.

Department…Chemical Engineering… Student's signature...วลัยลักษณ์ อยู่บ้านคลอง...

Field of study....Chemical Engineering… Advisor's signature.............................

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Finally, I would like to dedicate this paragraph to my parents who give their unfailing love, understanding, and generous encouragement during my studies.

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CHAPTER I

INTRODUCTION

1.1 General Introduction

Polymeric materials are inexpensive, exhibit good physical and thermal properties and can be processed easily; therefore, they have been widely used in automotive, packaging and aerospace applications. In addition, polymers are lighter than many inorganic materials such as metal and cement. Hence, they were used to substitute these materials in many applications.

However, sometimes, polymers, which are available in the market, do not meet the criteria. Blending two or more polymers together or polymer with inorganic fillers to obtain polymer blend and polymer composite, respectively, could be a way to improve the properties of these materials. Polymer blends can be obtained by either solution blending or melt mixing method. Solution blending method is used only when each polymer is readily available in solution form, as a result of the polymerization process. On the other hand, melt mixing method, which two or more polymers are mixed with an extruder or a mixer can be done easier than solution blending. Many pairs of polymers are almost impossible to mix or disperse in one another, and attempt to do so yield, at best, rather useless coarse aggregates with little or no cohesion between phases. The minor component forms domains, whose size and shape greatly depend on several factors, such as melt viscosities of component, interfacial tension, adhesion and processing condition. Polystyrene (PS) and polypropylene(PP), for example, are reputed to behave in this manner because of the difference in their molecular weight, interaction and polarities between phases. Therefore, such pairs of polymers are often referred as “incompatible”. There are several methods to increase the compatibility between polymer pairs. The copolymerization or grafting of one or both components, with segments of the other component or co-blending with a polymer, which is compatible with both major components (compatibilizer) and the reactive compatibilizer can produce in situ graft or block copolymer that contains segments miscible or compatible with both components of the blend.

In this study, polypropylene-graft-maleic anhydride (PP-MA) was used as a compatibilizer because the PP grafted with highly electrophilic MA reacted with the amine end groups of nylon through hydrogen bonding and improved the miscibility of PP and nylon-6 (Ny6) blend. Not only did compatibilizers be able to improve interfacial interaction between polymers, but they also increased the surface area and promoted compatibility between polymers and reinforcing fillers that mechanical and thermal properties were improved over unmodified PP and solvent permeation resistance were also enhanced.

Reinforcing fillers that were added into polymer in order to form composite material enhanced mechanical properties, reduced cost, provided a good resistance against moisture, chemical and temperature, ensured good processability and could be recycled. Therefore, sizes of filler that were macro-, micro- and nanometer size affected composite’s properties. Especially nanometer size filler would have more surface area than macro- or microfillers; therefore, it increased interfacial interaction between polymer and nano-particles. Nanoparticles that were used to add in polymer nanocomposite were sodium montmorillonite clay. Each layers of clay constructed of tetrahedral coordinated Si atoms fused into an edge shared octahedral plane of either $Al(OH)_3$ or $Mg(OH)_2$, which could be found in nature. Clay was often surface-treated by adding quaternary ammonium compound to enhance adhesion between polymer and fillers. While mixing, polymer chains intercalated between clay platelets and made clay platelets exfoliated through out polymer matrix. Due to their advantages, polymer nanocomposites have been intensively investigated both in industrials and academic fields. Most research have been done on homopolymer nanocomposites such as polyethylene(1), polyurethane(2), polystyrene(3).

In this study, nanocomposites of polymer blend between PP and Ny6 were developed. An effect of compatibilizer and clay loading on solid-state mechanical properties, melt-state processibility and their microstructure were investigated. PP/Ny6 clay nanocomposites were prepared by twin screw extruder and followed by injection molding machine. The degree of clay dispersion was evaluated by means of X-ray diffraction and TEM microscopy. The compatibility between PP and Ny6 phase was observed by SEM micrograph. The degree of crystallinity and phases of polymers were characterized by DSC and X-ray diffraction respectively. Possible effects of clay on the enhancement of solid-state mechanical properties of nanocomposites were discussed in details.

1.2 Objectives of the Present Study

1. Investigate the effect of clay loading and the amount of compatibilizer on solid-state mechanical properties, i.e., tensile strength, tensile modulus, flexural modulus, impact resistance and thermal properties of polymer blends and nanocomposites.
2. Determine the effect of compatibilizer on the degree of clay dispersion and morphology of polymers blends and nanocomposites by using X-ray diffraction (XRD), Transmission electron microscope (TEM) and scanning electron microscope (SEM) respectively.
3. Evaluate the relationship between the morphology of nanocomposites and their mechanical properties.
4. Study the effect of clay on flow properties of these materials.

1.3 Scopes of the Present Study

1. Polymer blends have been used as polymer matrix, in which PP was a major component and Ny6 was dispersed phases.

2. Organoclay, which was used in this study, has been obtained from company and was used without any modification.

3. The weight ratio of Ny6 and compatibilizer, PP-MA has been varied to obtain the suitable composition of polymer blends before adding organoclay to obtain polymer/clay nanocomposites.

4. The amount of clay has been varied to determine the effect of clay on the mechanical and thermal properties of nanocomposites.

5. The effect of clay on the rheological properties has been studied.

CHAPTER II

THEORY

2.1 Polymer Blends

Mixing two or more polymers together to produce polymer blends is a well-established for achieving of physical properties, without chemical reaction. Polymer blends provide a straightforward and relatively inexpensive method to develop polymeric materials with desirable properties. In many cases it can be cost effective to improve material's properties through the blending of existing materials. Not only can the cost of new materials reduce but can also improve properties and processability which are major considerations in the assessment of potential benefits. For example, ABS, which is a blend of acrylonitrile, butadiene and styrene, shows major commercial success nowadays. This is driven by consideration of the difficulty in developing new polymeric materials from monomer. The development of polymeric materials has four basic techniques, i.e., solution blending, emulsion blending, powder dry blending and pellet dry blending. Solution blending is normally feasible only if each polymer is readily available in solution form, as a result of the polymerization process. It is good mixing at the molecule level. Emulsion blending requires that the components are in emulsion (latex) form as a result of emulsion polymerization. In latex, very small polymer particles are suspended, and kept from coalescing by soapy water (as in latex paints). Mixing of latexes of different polymers and subsequent removal of the water can lead to an excellent dispersion and distribution of discrete phase. Powder dry blending achieves good initial distribution of the materials, but normally the powder particle size is still larger than the final desired size of the discrete domains. Pellet dry blending only gives a very coarse initial dispersion. In the case of dry blended polymers, in particular, the final blend structure is achieved only after the melt processing stage.

In generally, each polymer has different properties such as density, molecular weight and polarity, which will exist as two separate phases or immiscible polymer blends. Immiscible polymer blends form dispersions of two or more phases, in the same way as oil and water, resulting in an uneven and poorly bonded structure in the final product. Illustration of phase dispersion and distribution were depicted in figure 2.1. Dispersion (fine to coarse) of the dispersed phase reflects primarily their sizes and numbers. However, distribution (good to poor (agglomerates)) reflects the uniformity throughout a sample.

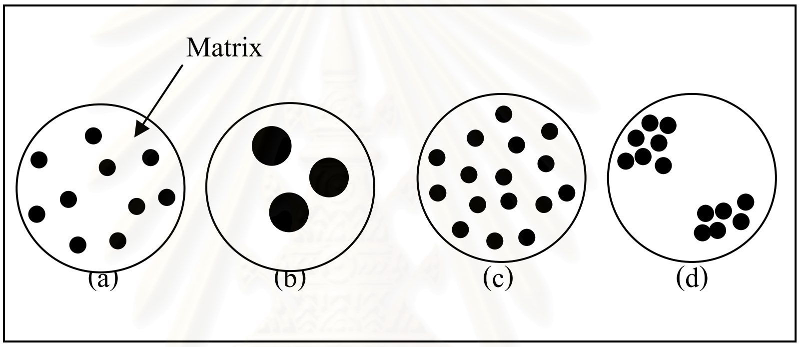

Figure 2.1 Phase dispersion and distribution (a) Fine dispersion, (b) Coarse dispersion, (c) Good distribution, (d) Agglomerates.

2.2 Compatibilization

It was point out earlier that few polymer pairs were readily miscible (homogeneous) or even compatible (heterogeneous). There are several methods to increase compatibility between pairs of polymers, i.e., improving thermodynamic stability, adding block or graft copolymer, using reactive blending and adding functional polymers. *Achievement of thermodynamic miscibility* was recognized that Miscibility between polymers was determined by a balance of enthalpy and entropic contributions to the free energy of mixing ($\Delta G = \Delta H - T\Delta S$). Therefore, to *achieve thermodynamic miscibility*, ΔG must be negative. *Addition of block and graft copolymer* is one way to assure miscibility between copolymer segments and corresponding blend component. This method provides the copolymer to meet certain structure and molecular weight requirements. Copolymers usually locate at interfaces as shown in figure 2.2. *Reactive blending*, which differed from other compatibilization routes in that the blend components themselves were either chosen or modified so that reaction occurred during melt blending, with no need for addition of a separate compatibilizer. The other compatibilization method which is widely used in commercial applications was an *addition of functional polymers*. Polymer was modified to have certain functional group via chemical reaction, or via physical interaction such as the formation of ionic bonds. Figure 2.3 showed the method of compatibilization, this included grafting of maleic anhydride or similar compounds to polyolefin, resulting in pendant carboxyl group that had the ability to form a chemical linkage with nylons via their terminal amino groups.

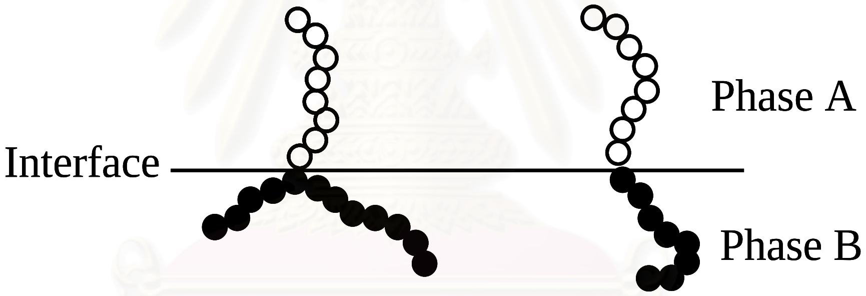

Figure 2.2 Schematic diagram showing location of block and graft copolymers at phase interfaces

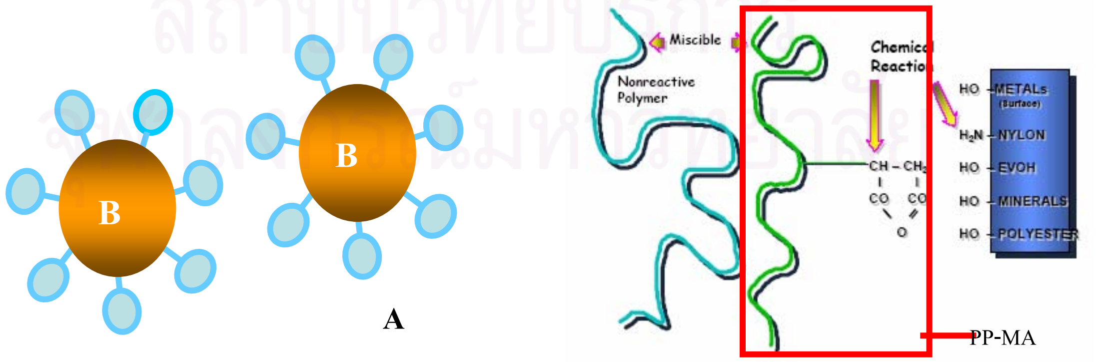

Figure 2.3 Adding functional polymers as a compatibilizer (4)

Most polymer blends were immiscible; therefore, they formed weak interfaces and poor mechanical coupling between phases were observed. Compatibilizer, which was prepared by an adding the third component, inducing an in-situ chemical reaction or using reactive blending, could improve the interphasal interaction and stress transfer. Hence, the mechanical properties and phase's morphology were also improved. Therefore, it played an important role in the development of polymer blend. Blend of polycarbonate, polyesters, and toughened nylons could be done by adding nylon with graft-functional polyolefin elastomers. Graft-functionalized elastomers, produced by melt modification, were also commercially available for toughening nylons. Polymer blend containing nylon was carried out commercially with a number of objectives. The main purpose was to increase its toughness. Chemical modification of the polyolefin can be used to inducing compatibility between nylon and polyolefin. It was done by adding pendent carboxyl groups or grafting polyolefin with maleic anhydride (MA) or similar compounds. This functional group would form chemical linkages to the nylon via the terminal amino group. Idle and Hasegawa added various levels of polypropylene grafted maleic anhydride (PP-MA) into PP/Ny6 blend via extrusion process (5). Addition of PP-MA caused a dramatic size reduction in the dispersed phase of blends containing 20% by weight Ny6 and improved tensile strength, elongation and impact strength. These improvements were also seen in Ny6 rich blends. The reaction between MA group and Ny6 amino end-groups was verified by DSC analysis of PP phase after solvent extraction of the Ny6 phases (6). An addition of 3% by weight PP-MA resulted in substantial size reduction, which was more than 10 times in the size of dispersed phase but it also caused dramatic reduction in the phase growth which was observed in the binary blends on annealing for up to 1.5 hours at 230°C (7).

The development of compatibilization of polymer blends are in three main areas, i.e., engineering polymer blends, superior performance commodity polymers and polymer recycling. In first two areas, the primary objective is to produce a material where some specific property is enhanced. Polymer blending method is very significant in cost-effective aspect to produce a better material than synthesizing a completely new kind of polymer. The properties of commodity polymers can be improved by blending method in many aspects such as mechanical properties such as toughness and stiffness, thermal properties such as melting and glass transition temperatures, gas permeation and chemical resistance. Applications for improved performance commodity polymers include automotive parts, business machines and household.

2.3 Composite Materials

A composite material can be defined as an inorganic combination with polymeric materials in the form of polymer composites. Inorganic components are normally referred to “reinforcing fillers,” if their role is primarily increasing the stiffness of polymeric material, sometimes with an associated cost advantage. Reinforcing fillers usually are chosen to create composites with tailored properties; for example, high modulus but brittle carbon are added to low-modulus polymers to create a stiff, light weight composites with some degree of toughness. Nowadays these materials are used as consumer products and infrastructure materials(8). Recently, nanocomposites, which are nanometer-size particle filled polymer composites, have been developed to overcome limitations of traditional micrometer-scale polymer composites. Nanofillers are the filler that are less than 100 nm in at least one dimension. The small size of nanofillers leads to unique properties of the particles themselves. For example, when polymer/clay nanocomposites and fiber reinforced composites are compared in the low filler content, nanocomposites exhibit better properties than conventional fiber composites. It was observed that nanocomposites exhibit higher Young’s modulus than fiber composites (9). In addition to the effect of filler size on mechanical properties, the small size of the fillers leads to an exceptionally large interfacial area in the composites. As seen in figure 2.4, nanoscale fillers can be divided into three categories according to their shapes and sizes, i.e., particle or sphere, fiber and disk. Three dimensional (3D) nanofillers are relatively equi-axed particles less than 100 nm in their largest dimension. Fiber or tube filler have a diameter less than 100 nm and an aspect ratio of at least 100. The other shape is disk (plates, flakes), which includes mica, glass flakes, aluminum flakes and aluminum diboride, which are layered materials typically with a thickness in the order of 1 nm.

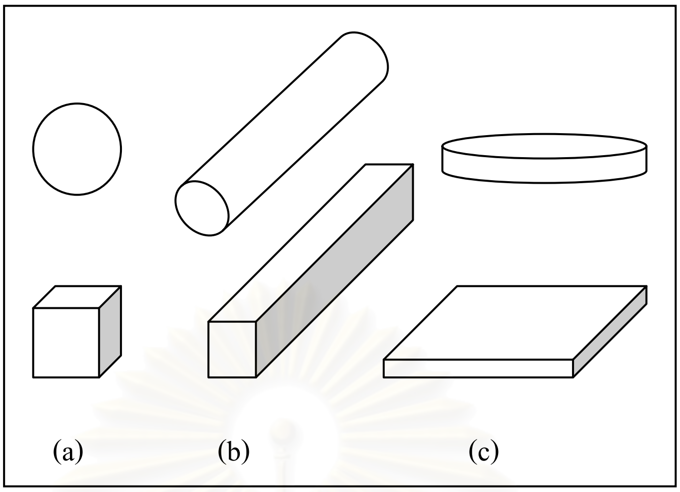

Figure 2.4 Shapes of reinforcing filler (a) Particle, (b) Short fiber, (c) Disk

2.4 Polymer/Clay Nanocomposites

Polymer/clay nanocomposites are made by mixing polymer with inorganic filler which is in nanometer size. If nanoscale dispersion can be achieved, the mechanical properties such as strength and impact resistance can be further improved, reduction of their electrical conductivity, oxygen permeability and good flame retardation are enhanced. For example, the mechanical properties of 5 wt % clay loading Ny6 nanocomposites were enhanced tramendously when compared with neat nylon 6. The nanocomposites exhibited 40% increase in tensile strength, and 126% increase in flexural modulus. The heat distortion temperature (HDT) was also increased from 65 to 152°C, and the impact strength were lower by 10%(10). These enhancements were obtained with low particle loading, typically in the range of 1-10wt%(11). To enhance the mechanical properties of nanocomposites, the polymer chain must intercalate between layered silicates and make layered silicates exfoliate through out polymer matrix. The increase in interfacial interaction between filler and polymer chains also affects properties of nanocomposite.

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2.5 The Effect of Clay on Polymer Nanocomposites Properties

2.5.1 The Nature of the Fillers

The layered silicates commonly used in nanocomposites belong to the structural family known as the 2:1 phyllosilicates. Their crystal lattice consists of two sheets of silica tetrahedral (corner shared) with an edge-shared octahedral sheet of either alumina (aluminosilicates) or magnesia (magnesium silicates) as shown in figure 2.5. Wall gap between them are called the interlayer or the gallery. Layered silicates that are used to produce nanocomposites need some surface modification. Silicate clays are inherently hydrophilic, but polymer tends to be hydrophobic; therefore, the surface modification of clay is necessary to make clay be organophilic. Clay which is modified surface is called organoclay. Organoclay can be laminated and dispersed better in polymer matrix than natural clay. Hence, mechanical, thermal and permeability properties are improved. The most popular methods for clay modification is cation exchange in which organic ammonium salt is used to convert surface of clay from being hydrophilic to organophilic.

To achieve nanoscale dispersion of clay in polymer, clay galleries must be opened and the polarity of polymer or monomer is matched with clay so that polymer chain can intercalate between layers. This is done by exchanging an organic cation for an inorganic cation such as sodium. The large organic cations swell the layers and make clay to be more hydrophobic, resulting in organically modified clay. The organically modified clay can then be intercalated by polymer chains by several routes such as solution processing, in situ polymerization and melt intercalation.

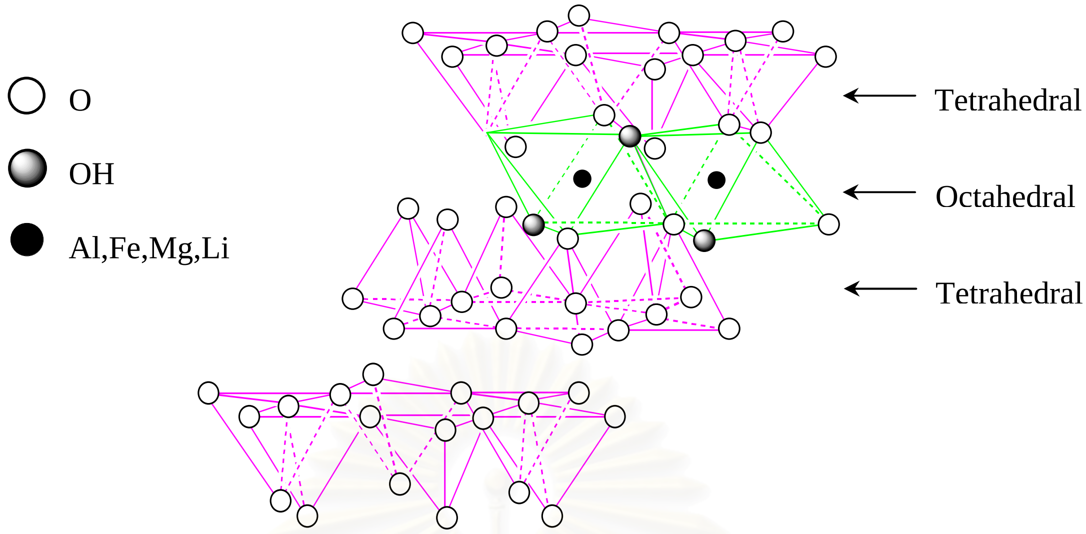


Figure 2.5 Three-dimensional structures of 2:1 phyllosilicates

2.5.2 The Method for Polymer/Clay Nanocomposite Preparations

Several routes have been developed to produce polymer/clay nanocomposites. Three methods were developed in the early stages of this field and have been widely applied, i.e., solution mixing, in situ polymerization and melt intercalation method. Solution mixing involves dispersion of both the organically modified clay and polymer in common solvent. Variations on this process include emulsion or suspension polymerization (12). In situ polymerization intercalates monomer directly into the organically modified clay galleries as shown in figure 2.6 (13). Polymerization of the monomer occurs in the interlayer of clay mineral, resulting in an expanded interlayer distance and layered silicate that are homogeneously dispersed in nanometer level at the end of polymerization. However, this method is not economically suitable for industrial production because it wastes large amount of solvent and energy. The most attractive mixing method is direct polymer melt intercalation which can be done by mixing clay and polymer melt with or without shear (14). Traditionally, melt-mixing or elastic mixing methods are feasible because they are the fastest method for introducing new products to market. The resulting nanocomposites obtaining from these methods can have several structures as discussed in the next session.

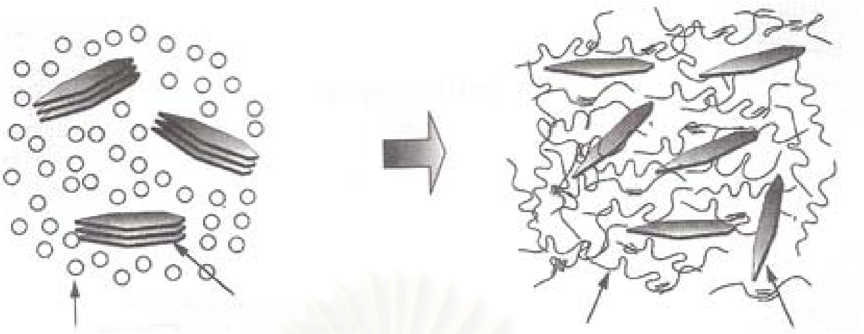
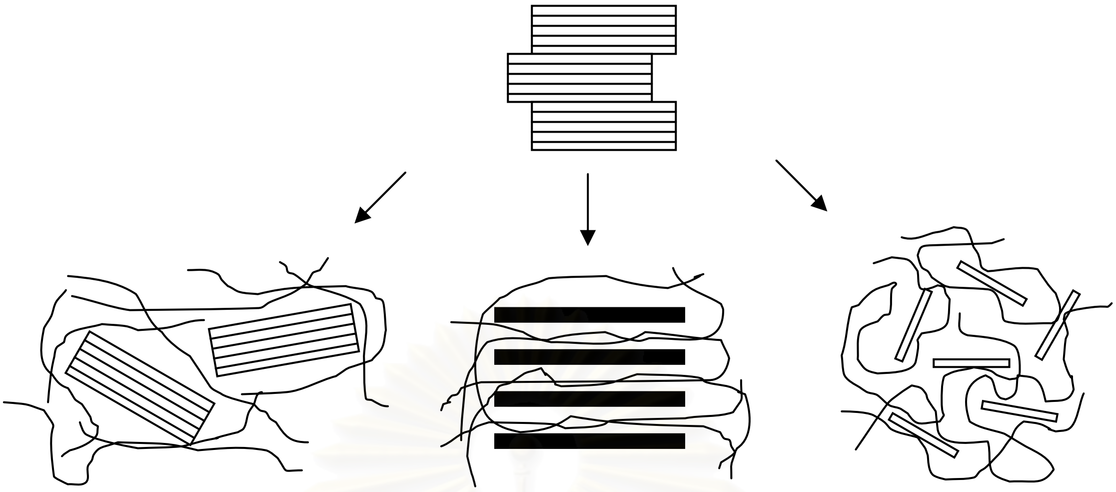


Figure 2.6 A conceptual picture of polymerization in the presence of montmorillonite (layered clay mineral) (15)

2.5.3 Type of Polymer/Clay Nanocomposites Structure

Polymer/clay composites can be generally classified into conventional or micro-composites and nanocomposites. For conventional composite, stack of clay nanolayers is retained when mixed with polymer and there is no polymer chain intercalated into clay structure as can be seen in figure 2.7. If polymer chains intercalate between layered clay, two main types of nanocomposites can be obtained. Intercalated structures are self-assembled, well-ordered multilayered structure where extended polymer chains are inserted into a gallery space between parallel individual layered silicates separated by 2-3 nm. The delaminated (or exfoliated) structure is obtained when the individual layered silicates are no longer close enough to interact with the adjacent layer clay.

Exfoliated nanocomposites show greater phase homogeneity than intercalated nanocomposites. More importantly, each nanolayer in exfoliated nanocomposites contributes fully to interfacial interactions with the matrix. This structural distinction is the primary reason why the exfoliated clay state is especially effective in improving mechanical and other properties of clay composite materials.



(a) Conventional (b) Intercalated (c) Exfoliated

Figure 2.7 Illustration of three types of polymer/clay nanocomposites.

2.6 Processing Techniques

There are several methods to prepare polymer clay nanocomposites, i.e., in-situ polymerization, solution induced intercalation and direct polymer melt intercalation. Melt mixing method is the most common one because of energy efficiency, operability environmental containment, low cost, high productivity and compatibility with current polymer processing techniques. The processing of polymeric materials such as plastics, elastomers and composites are characterized by various distinct techniques. Techniques involving the continuous manufacturing of product have basically uniform cross section, which include extrusion, extrusion based processes, film blowing and calendering.

2.6.1 Extrusion

Extrusion process produces the uniform cross-sectional product which can be designed by the die. There are two types of extruder; i.e., single screw and twin screw extruders which are shown in figure 2.8. Extrusion process is used to produce sheet, profiles or pellets of thermoplastic composite.

In recent years there has been a steady increase in the use of extruders which have two screws rotating clockwise or counter clockwise in a heated barrel as can be seen in figure 2.9. A twin screw extruder allows various possibilities in terms of output rates, mixing efficiency and heat generation compared with a single screw extruder. The output of a twin screw extruder can be typically three times higher than that of a single screw extruder of the same diameter and speed (16).

Typical single-screw extruder has four sequential segments, i.e., solid conveying, melting, melt pumping and extruder dies. *Solid conveying*, where the polymer pellets, flake, powder or granules are conveyed from the extruder hopper to the conveying flights of the extruder. The particulates are compacted and heated by shearing between the metal screw and barrel. After that, polymer is passed to *plasticating or melting* step, where the gap between the barrel and screw’s core is reduced, which polymer melts and compressed solid cake break up. The degree of compression usually depends on the morphological nature of the neat polymer. Crystalline polymers need greater compression ratios than amorphous polymers. Polymers with particulate added need a lower compression ratio than neat polymers. The polymer melt is then arrived *melt pumping* segment, where polymer is fully fluid. Pressure and temperature condition is ready for the extruding. Polymer melt passes *extruder dies*, where the polymer melt is shaped and presented to the take-up equipment. The extruder die shape varies due to an application of product.

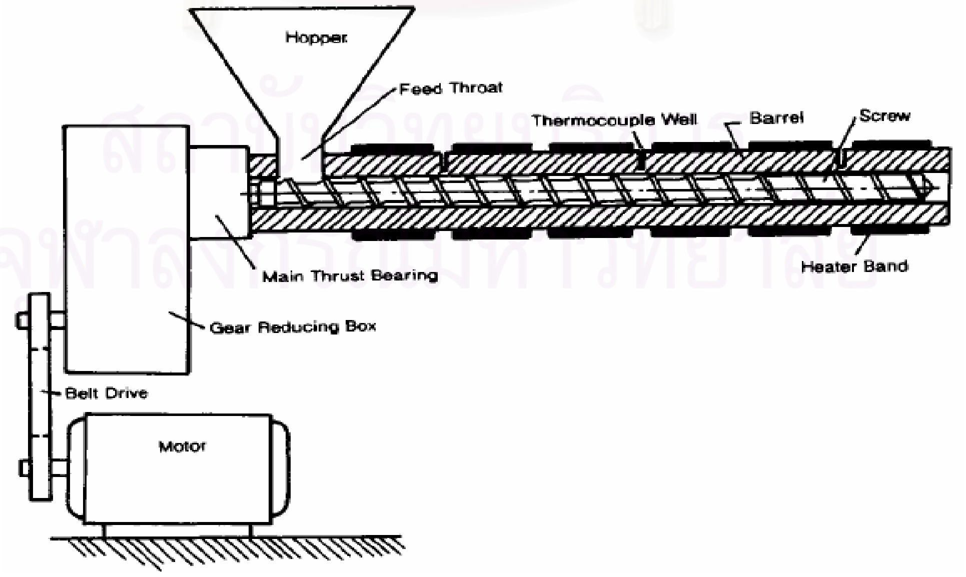


Figure 2.8 Schematic of conventional single screw extruder without extrusion die(8)

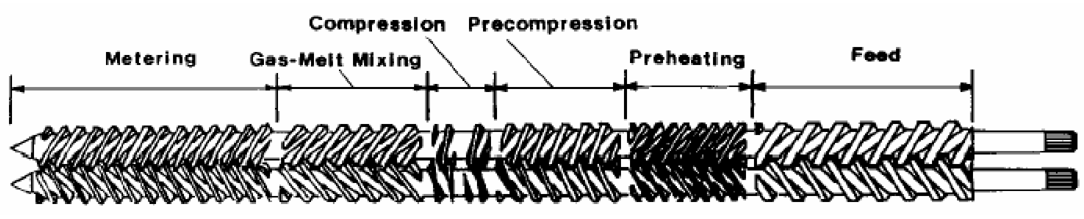


Figure 2.9 Schematic of standard configuration of cylindrical twin screws(8)

2.6.2 Injection Molding

Another polymer processing we used in this study is an injection molding process. An injection molding process involves the rapid pressure filling of a specific mold cavity with fluid material, followed by the solidification of the material to form a product. This process can be used with thermoplastic, thermosetting resins, and rubbers. All thermoplastic materials are, in principle, suitable for injection molding process. Injection molding machine is shown in figure 2.10. Since fast flow rates are needed, polymer grades with low viscosity or high melt index are normally preferable. The major problem occurred with this process is shrinkage of solidified polymer.

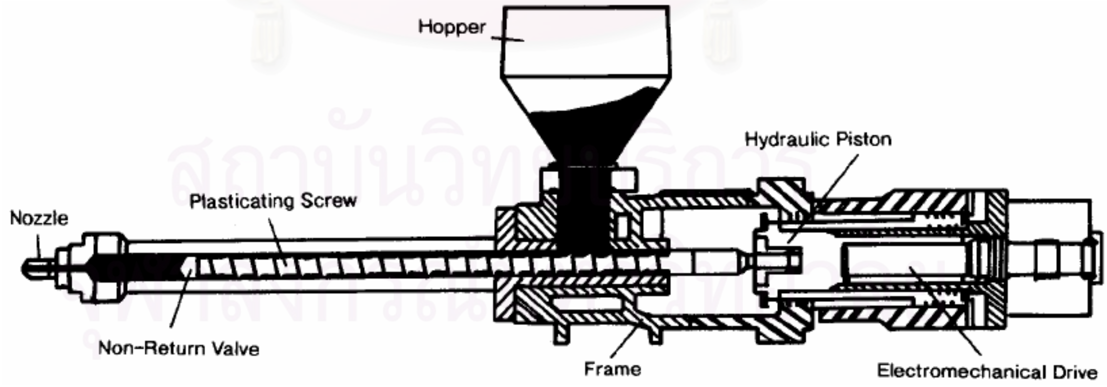


Figure 2.10 Schematic of plasticating and injection portion of conventional reciprocating screw injection molding machine(8)

Most plastic materials are used because they have desirable mechanical properties at an economical cost. Therefore, the mechanical properties of materials need to be characterized to obtain the right choice. In stress-strain tests, the build up force (or stress) is measured as a specimen is being deformed at a constant rate such as, tensile, flexural and impact testing. Occasionally, stress-strain tests are modified to measure the deformation of a specimen as the force is applied at a constant rate, and such tests are becoming common with the advent of commercially available load controlled test machines.

2.7 Mechanical Property Testing

2.7.1 Tensile Properties

Tensile properties refer to a behavior of a material when it is subjected to force, which tends to pull it apart. According to ASTM standard for testing tensile properties, a standard dumbbell-shape specimen is used. ASTM D-638 is the standard used to test plastic sheet. In this standard, the sample is pulled at a constant rate of crosshead movement (50 mm/min). The specimens are tested in a machine giving a straight tensile pull without twisting or bending. The universal testing machine is used for this work.

Two properties are measured while the sample is being pulled apart, i.e., tensile stress and tensile strain. Tensile stress is strength of the pull within the area between the gauge marks. Tensile strain is a measure of how much the sample has been stretched by the pull. The definition of tensile modulus is the ratio of tensile stress to tensile strain in the beginning of a test which it is still in linear region. Some materials, such as methacrylates, will break when they is stretched, even though they still show essentially elastic behavior. Other materials, such as nylons and polycarbonates, can be stretched many times longer than their original length before they break because they have a yield point, and a corresponding yield stress.

The yield point is reached when the material continues to elongate (strain) with no increase in the stress. When it takes place, the material yields, in which a material is permanently deformed by elongation. The tensile stress which yield takes place is called yield stress.

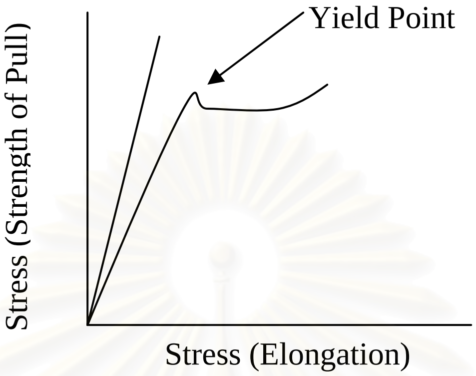


Figure 2.11 Diagram of stress/strain of sample under tension.

2.7.2 Flexural Properties

Flexural modulus and flexural strength are related to stiffness or resistance to bending, and the force required to break a sample by blending or flexing, respectively. Flexural properties are determined by grabbing specimens and put the load in the middle of a specimen, as illustrated in figure 2.13. When the sample is bent in this test, force of resistance (stress) is set up within the plastic, which tries to retain its shape to its original flat condition.

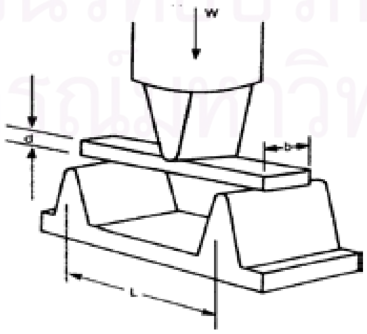


Figure 2.12 Sketch of flexural properties test(17).

2.7.3 Impact Resistance

The resistance to impact is one of the key properties of materials. Impact resistance is an ability of material to withstand such mechanical abuse as being struck by a dropped weight or hammer. For practical purposes, plastic parts are tested by striking them with hammers or dropping them from a distance. The standard test methods used are the Izod and Charpy tests which specimens are illustrated in figure 2.13(a) and (b). The specimens are notched by a standard notch machine and the impact energy absorbed while breaking the specimen is recorded (17)

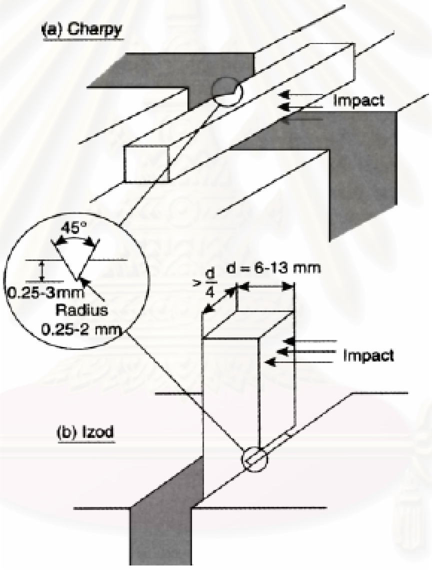


Figure 2.13 Pendulum impact tests

One of the primary reasons for adding fillers to polymers is to improve their mechanical performance. For example, the addition of high-modulus fillers increases the modulus and the strength of a polymer. In conventional composites, unfortunately, this often comes at the cost of a substantial reduction in ductility, and sometimes in impact strength, because of stress concentrations caused by fillers. This section highlights the potential effect of nanofillers on the modulus, failure stress/strain, and toughness.

The modulus of conventional composites can be predicted, within bounds, and the mechanism that leads to a change in modulus is load transfer. If high modulus filler is added to low modulus polymer, then load transfers from the matrix to filler, leads to an increase in modulus. Plate-like filler also increase the modulus of polymer significantly. When the interaction between polymer matrix and filler increases, mechanical property such as tensile modulus increases. Polypropylene nanocomposites in which maleic anhydride (MA) was added to the matrix indicated the change in the degree of filler dispersion (18). Despite the plasticizing effect of PP-MA, the improvement in tensile modulus is due to the enhancement in clay dispersion. As the polymer chain intercalates between clay platelets and swells layered silicates, interfacial interaction between the polymer and filler increase. Hence, tensile modulus increases significantly. The addition of rigid fillers to a polymer often increases its strength, but decreases its toughness. A tradeoff is a significant technical problem for commercial applications of filled polymers. The reason for the decrease in ductility is straightforward, i.e., the fillers or agglomerates act as stress concentrators, and the defects initiated at the filler quickly become larger than the critical crack size; therefore, mechanical failure occurs.

2.8 Differential Scanning Calorimetry

The DSC measures the power (heat energy per unit time) differential between a small weighed sample of polymer (ea. 5 mg) in a sealed aluminum pan and an empty pan in order to maintain a zero temperature differential between them during programmed heating and cooling temperature scans. The technique is used in our work for characterizing melting temperature, T_m of nanocomposites materials (19). The difference in temperature between sample and reference must be capable calibration, such that(20)

$$\Delta T \;=\; K\Delta(mC_p)R \tag{2.3}$$

Where ΔT = Temperature difference between a sample and a reference

$\Delta(mC_p)$ = Difference in total heat capacity between sample and reference

R = Heating rate

(PPPPPPPPPPPPPPPPPPPPPPPPPPPPPPPPPPPPPPPP°C/min)

2.9 Interlayer Spacing

X-ray diffraction, XRD is used to identify intercalated structures and interlayer spacing of clay. The sample is characterized at ambient temperature. The spacing was calculated by Bragg's equation:

$$2d\sin\theta = n\lambda \tag{2.4}$$

Where λ = the wavelength of the X-Ray radiation used in the diffraction experiment, which is 1.542 $\overset{o}{\mathrm{A}}$

d = the spacing between diffractional lattice planes

θ = The measured diffraction angle

n = peaks correspond to the {001} basal reflection (n=1)

2.10 Dynamic Mechanical Measurements

Dynamic mechanical measurements describe viscoelastic behavior of polymer in solid state. A freely oscillating torsion pendulum can be used to provide shear moduli data of solid specimens versus temperature or time. Dynamic measurement is very important in the case of polymeric material due to its well-known sensitivity to the speed of loading. The dynamic measurement is often applied when a polymeric test specimen is subjected to repeated (cyclic) load that is not designed to cause failure. For dynamic mechanical measurements, the polymer specimen is deformed cyclically under small amplitude sinusoidal loads while the temperature is raised simultaneously. The deformation induced by the small amplitude sinusoidal load allows the determination of two basic quantities through the theory of linear viscoelasticity, i.e., storage and loss moduli. Storage modulus exhibits the elastic response of the material, and the loss modulus or tan δ is related to the viscous response. Dynamic methods lead to an identification of a glass transition temperature (Tg), an important parameter characterizing all polymers and estimate properties at different temperatures. The glass transition is the most important solid-solid transition in plastic materials. Any change in the mobility of polymer structure will appear as a peak in the loss modulus and tan delta curves and a step reduction in the storage modulus. These secondary relaxations are typically due to the onset of rotational motion in the polymer and many of them occur at temperatures below the range of practical interest. In addition, the magnitude of these transitions is much smaller than that of the glass transition. Nevertheless, some of this observations support the change in impact performanc (21).

CHAPTER III

LITERATURE REVIEWS

The blending of two polymers has become an increasingly important industrial technique, because blends meet performance demands that cannot be satisfied by currently available commodity polymers. In addition polymer blend is an alternative for high growing demand for polymeric materials which having a desirable combination of properties at lower cost and improving the performance of commodity and engineering plastic in order to find wider applications. In general, the combination of polymers is insoluble between each other due to their different polarities. Therefore, they have high interfacial tension and consequently, poor adhesion. Polypropylene and Nylon6 (Ny6) are an example for pairs of polymer which have different polarities. This couple is not compatible if no compatibilizer is added to reduce interfacial adhesion between phases. Roeder et al.(22) studied an influence of compatibilizing agent at interface of immiscible PP/Ny6 (70/30 wt%) blends with various compositions. PP was matrix, Ny6 was dispersed phase and polypropylene grafted maleic anhydride (PP-MA) was used as a compatibilizer. The experiment indicated that addition of small quantities (10 wt %) of compatibilizer into an incompatible blend of PP/Ny6 increase the homogeneity of Ny6 phase dispersed in the PP matrix as can be seen in figure 3.1. Size of domain phase was reduced and copolymer formation was occurred at an interface(22, 23) PP-MA was used as a reactive compatibilizer in PP/Ny6 blend, due to the fact that PP-MA showed better improvement in physical properties such as the morphological(22, 24, 25), mechanical (22, 26, 27) and thermal properties (22, 27) properties than other substances. The main reason for property improvement is good adhesion between two phases, in which all of the compatibilizer became adhesive between phases of polymer by copolymerizing process. PP-MA formed interfacial layer around Ny6 particles and enhanced compatibilization induced by copolymers as can be seen in figure 3.2. This copolymer is presumably developed from the hydrophobic interaction with PP and the hydrophilic hydrogen bonding with Ny6. In addition, the unreacted MA groups in PP- MA react with Ny6 amine terminal group competitively to form a

PP-MA-co-Ny6 copolymer which results in breaking up Ny6 domains into smaller droplets and dispersing them in PP matrix. Both strength and toughness of materials were improved when compatibilizers were added(28). Wilkinson et. al.(29) showed the increase in tensile modulus and stress at break of the 70/30(PP/Ny6) blend (containing 30% w/w of Ny6) compared to neat PP. Higher modulus (~ 2.75 GPa) and higher yield stress (~70 MPa) was observed as a reinforcing effect of Ny6 on the blend.

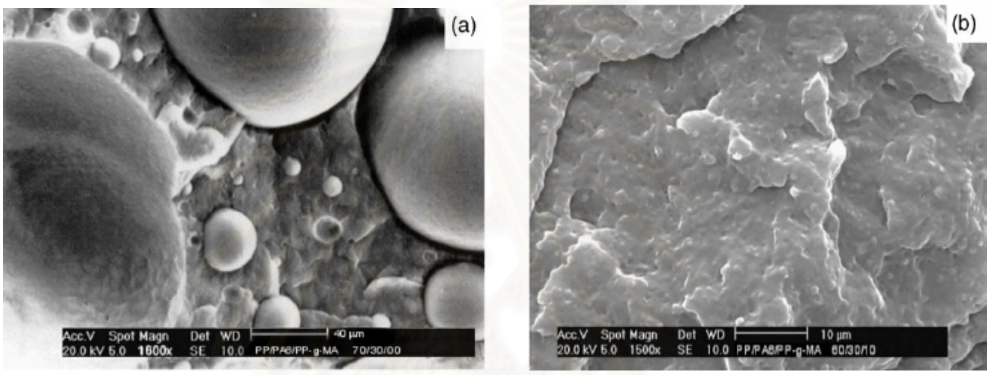


Figure3.1 SEM micrographs of PP/ Ny6/PP-MA (a) 70/30/00 (b) 60/30/10(22)

Not only PP-MA, polypropylene functinalized glycidyl methacrylate (PP-GMA) were also used as compatibilizer in PP/Ny6 blend. Tedesco et al.(28) compared the use of PP-MA and PP-GMA on PP/Ny6 blends. Blends of PP/Ny6/PP-MA or PP-GMA were prepared using 30% wt of Ny6. The mixture of PP/Ny6/PP-MA presented an improvement in properties when compared with PP/Ny6/PP-GMA, which attributed to the improvement in compatibility of the system. The elongation value of the blend using PP-MA was higher than the blend using PP-GMA. Tseng et. al.(30) studied the use of product from reacting poly (oxypropylene)-amide grafted polypropylene (POP) with PP-MA, as novel compatibilizer for PP and Ny6 blends with various MA contents. The blends were carried out by extrusion and injection molding process. Melt reaction in extruder carried out copolymer POP functionalized PP (PP-MA-co-POP) that was confirmed by FTIR analysis. This copolymer has different properties depending on the amine structure and MA content. High cross link in copolymer was obtained when PP-MA with high MA content was used. Finer dispersion of polymer blend was observed upon the addition of PP-MA-co-POP. As a result, the mechanical properties in PP/ Ny6 (70/30) blend were significantly improved. In spite of blending PP and Ny6, superior thermal or mechanical properties of Ny6, and advantageous characteristics of PP such as insensitivity to moisture, high chemical resistance, low density, and low cost can be combined.

Furthermore the compatibilizer have an impact on mechanical and morphological, the case study of Mehdi et. al.(24) They showed rheological properties of blends of two polymers PP and Ny6 (80/20 %wt) with compatibilizer at low and high shear rates. The difference depends on the amount of Ny6 dispersed phase. Co-continuous morphology was observed for the blend containing 50% of Ny6. These blends exhibited higher viscosity at low shear rate and lower viscosity at high shear rates than the value calculated by the simple rule of mixture. At higher shear rates, viscosity was lower than that given by the rule of mixture for all blend ratios. An increase in viscosity was observed in the 80/20(%wt) PP/Ny6 blends after the concentration of the interfacial agent (PP-MA) was increased. Moreover the compatibilizer was used decreasing surface tension between pairs of polymers; it can be more compatible and dispersed with fillers when added in polymer nanocomposites.

The development of new polymeric materials has various techniques not only polymer blending, but also adding of reinforcing filler. Addition of filler to form composite material can reduce compound cost and extents the resin with minimal sacrificing in physical properties(31). Recently, one of the widely used interesting fillers for thermoplastic is *nano-particle* because the general idea of the nanocomposites is based on the concept of creating a very large interface between the nanosized building block and the polymer matrix. Polymer nanocomposites also created much interest since researcher from Toyota laboratory published their work. Polymer nanocomposites consisting of a polymer matrix and organoclays have attracted great interest because of improvement in physical and mechanical properties when compared with unmodified polymer. Xiaohui et al.(14) investigated mechanical and dynamic mechanical properties, morphology and water absorption of Ny6-clay nanocomposites with PP-MA. Addition of PP-MA results in decreasing tensile and flexural modulus but increasing elongation at break and impact strength. The PP-MA phase was finely dispersed at a scale smaller than 1μm at concentrations of 10 and 20wt%. In addition water absorption of nanocomposite was reduced by 25% with 5wt% montmorillonite loading when compare with pure Ny6.

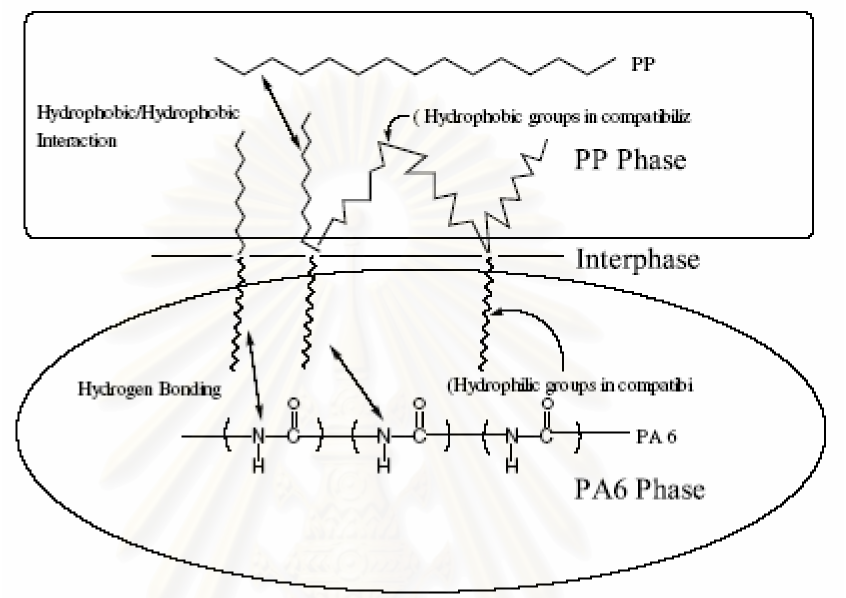


Figure 3.2 Conceptual structure of compatibilization of PP/ Ny6 blend(30)

Nearly all of the work have been done on homopolymer such as polyolefin, polystyrene (3) and polyurethane(2). However, Chow et al.(26) were interested in studying thermoplastic nanocomposites based on blends of PP and Ny6 and compatibilized by maleic anhydride-grafted ethylene–propylene rubber (EPR-MA). Adding EPR-MA to PP/Ny6 (30/70 wt %) blends resulted in the finer dispersion of PP, dispersed phase, caused from the formation of an interphase between Ny6 and PP. The presence of compatibilizer affects a structure of nanocomposites on intercalating or exfoliating layered clay as shown by Transmission electron microscope (TEM) microgroup in figure3.3. Not only TEM micrograph displayed structure of nanocomposites materials, but X-ray diffraction (XRD) also showed the interlayer spacing of clay galleries by the Bragg’s relation. Reflections in the low angle region indicated the d-spacing (basal spacing) of clay which is intercalated or ordered exfoliated in nanocomposites. If layered clays in nanocomposite material have an exfoliated structure, no more diffraction peak is observed in the XRD diffractograms because too large d spacing between the layered clay presented(32).

Osman et al. studied weld line properties and morphology of a ternary blend composite which composed of two immiscible organic phases, i.e., PP and Ny6, and talc as inorganic filler. The effect of different filler loading and compatibilizer loading on weld line strength under tensile loading condition of each polymeric phase were investigated. When the amount of 30% talc added to PP/ Ny6 blend results in 69.7% increase in weld line strength. Therefore the addition of talc filler seems to have positive effect on the weld line strength. However, this system exhibited nearly constant tensile strength compared to uncompatibilized ones. Extra strong interaction between carboxyl groups of PP-MA and amine end group of Ny6 and the special interaction between talc and amine group of Ny6 lead to higher tensile properties compared to uncompatibilized composites for all level of talc. PP/ Ny6 blend is not the only blend system which interests researchers. There are studies of PC/ABS/montmorillonite nanocomposites(33) and PEO/PMMA/clay nanocomposite (34). PC/ABS/clay nanocomposites were prepared by melt mixing to improve thermal stability and lower flammability(33). Poly(ethylene oxide) and poly(methyl methacrylate)/organoclay nanocomposites were prepared by solution intercalated method (34). Reinforcing fillers such as montmorillonite, talc(31) and glass fiber (35) were used in composites. Not only type of fillers but orientation of filler(36), blend sequence(37) also affect on mechanical and rheological properties. In this study we investigated the relationship between morphology of polymer blend nanocomposites and their mechanical properties. The effect of compatibilizer and clay content on their mechanical and thermal properties was also studied.

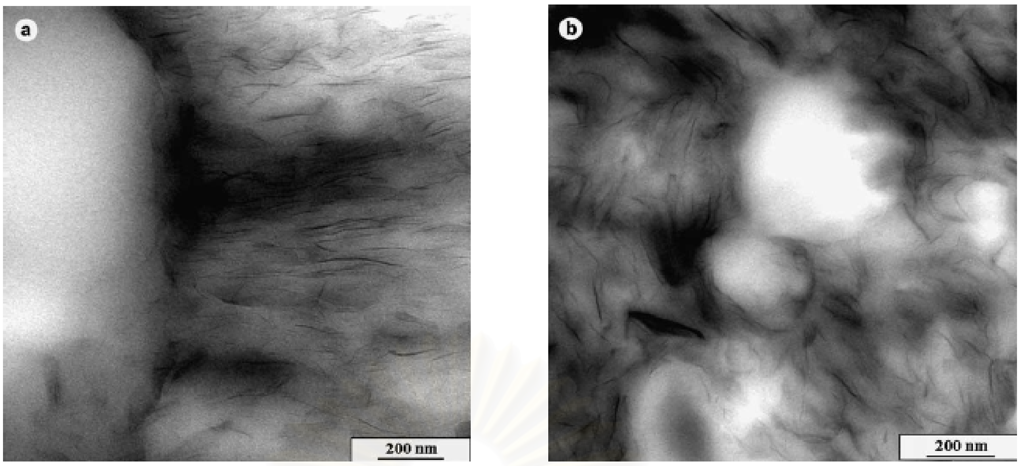


Figure 3.3 TEM micrograph of PP/Ny6/organoclay(26)

Several studies showed that by adding small amounts of filler caused substantial change in size and degree of crystallinity (38). Tensile strength increased with degree of crystallinity increased. In some composite systems, although degree of crystallinity decreased as a result of the presence of filler, tensile strength still increased and the elongation decreased. This indicates that fillers affected the formation of crystalline structure of polymer and reinforced the composite which is capable of producing reinforcement.

Campoy et al. investigated the crystallization kinetics of PP/Ny6 compatibilized blends(39) Blends were prepared in Brabender plasticorder at 230^{o}C and 60 rpm. The effect of the compatibilizer concentration was studied using different percentages of modified PP, i.e., 1, 3, 5 and 10% in PP/Ny6 blend composition. The concentration of compatibilizing agent caused reduction in the associated crystallization enthalpy of the Ny6 observed by WAXS analysis, and the existence of interactions between the amide groups of the Ny6 and the functional groups of modified polypropylene, raised the crystallization temperature of PP in blends, compares with that of neat PP.

CHAPTER IV

EXPERIMENTS

4.1. Materials

The matrix of polymer blends in this study was isotactic polypropylene (27), HP648N, of which was obtained from HMC, Thailand. It had melt flow index (MFI) 12g/10 min, according to ASTM D-1238 and specific gravity of 0.9. A dispersed phase, polyamide 6 or nylon 6 (Ny6), 1015B, was obtained from UBE NYLON, Thailand. Nylon-6 had molecular weight (MW) of 15000 g/mol and specific gravity of 1.14. A compatibilizer, Polypropylene grafted maleic anhydride (PP-MA), known as MZ109D, was obtained from Polymer Innovative., Thailand. PP-MA had melt flow index (MFI) of 120g/min, according to ASTM D-1238 and 0.55 wt% of maleic anhydride. Organophilic montmorillonite (Bentone SD-2) was supplied by Connell Bros., Thailand. It has been used as received.

4.2 Polymer Blends and Nanocomposites Preparation

Preliminary blend components were manually premixed before melt mixing process. In this study polymer blends and polymer/clay nanocomposites have been obtained by melt mixing method. Because PP-MA, Ny6 and organoclay could absorb moisture in the air, they were dried in a vacuum oven at 80 °C overnight to eliminate the hydrolyzing effect of absorb water until constant weight. All the components were manually premixed and melt compounding all components (PP/Ny6/PP-MA/Organoclay) were carried out by twin screw extruder. The screw rotation speed was set to 230 rpm at 230°C. The sample was listed in table 4.1 to 4.3 for study the effect of compatibilizer in PP/Ny6 blends, the effect of compatibilizer in nanocomposites by increasing PP-MA content. Another was investigated the effect of filler as organoclay loading. All of variation compositions were prepared by the same method.

Table 4.1 Composition of polypropylene, nylon 6 and compatibilizer

Sample code	Polypropylene (%by weight)	Nylon6 (% by weight)	Compatibilizer (% by weight)
S/0	68	32	0
S/2	62	29	9

Table 4.2 Composition of nanocomposites at different compatibilizer loading

Sample code	Polypropylene (%by weight)	Nylon6 (%by weight)	Compatibilizer (%by weight)	Organoclay (%by weight)
S/0.5/0.5	65	30	2.5	2.5
S/1/0.5	63.4	29.3	4.9	2.4
S/2/0.5	60.5	27.9	9.3	2.3
S/3/0.5	57.7	26.7	13.3	2.2

Table 4.3 Composition of nanocomposites at different organoclay loading

Sample code	Polypropylene (%by weight)	Nylon6 (%by weight)	Compatibilizer (%by weight)	Organoclay (%by weight)
S/2/0	62	29	9	0
S/2/0.5	60.5	27.9	9.3	2.3
S/2/1	59.1	27.3	9.1	4.5
S/2/1.5	57.7	26.7	8.9	6.7

4.3 Mechanical Characterization

4.3.1 Tension Property Measurement

Tensile testing (ASTM 638) required dumbbell (dog bone) test specimens. The test specimens were measured by a Universal Testing Machine (model 5567, from Instron Instrument). Test specimens had a uniform thickness and the tabs were pinched in grips attached to the testing machine with crosshead speed 50 mm/min. The tensile modulus were defined as the ratio of stress to strain, and determined from the initial slope of the stress-strain curve. Tensile strength is ultimate stress and elongation at break indicated how the material fails in tension. The specimens were tested in a machine giving a straight tensile force without twisting or bending.

4.3.2 Flexural Property Measurement

Flexural modulus and flexural strength of composite specimens were measured by a Universal Testing Machine (model 5567, from Instron Instrument) according to ASTM 790. Three-point bending mode with a support span of 85 mm at the crosshead speed of 4.01 mm/min until 10% strain has been used. The dimension of the specimens was 115mm x 3 mm x 3 mm.

4.3.3 Impact Resistance

The test bars, whose dimension was 63.5mm x 12.5mm x 3.2mm according to ASTM 256, were used to measured impact resistance. They were notched across one edge. The notch was milled into it with in a special milling cutter at a specified angle, to the depth of 0.1 in. The specimens were clamped into impact testing machine and they were hit at rate 30 kgf/cm.

4.4 Interlayer Spacing of Clay

XRD was used to identify whether an intercalated structure of polymer/clay nanocomposites has been occurred and how large the interlayer spacing of clay was. The samples were characterized at ambient temperature using D8 advance BRUKER German with CuKα radiation of wavelength 1.542 Å. The acceleration voltage was 40 kV and 30 mA. The scanning speed of 0.01 °/min in the range of 1° to 30° was used.

4.5 Thermal Behaviors

The thermal behaviors of polymer blends and polymer/clay nanocomposites were examined using a differential scanning calorimeter, DSC (model 2910, TA instruments). The samples, weighed 5-10 mg, were encapsulated in an aluminum pan. The experiment was done using a heating rate of 10^oC/min from 50^oC to 300^oC.

Crystallinity was calculated using an extrapolated value of enthalpy corresponding to the melting of 100% crystalline sample: ΔH_{PP} = 137.9 J/g and ΔH_{Ny6} = 190 J/g (2).

4.6 Nylon 6 Extraction

The dispersed phase, nylon 6 was extracted with formic acid from compatible and incompatible polymer blend and nanocomposites. The samples were immersed formic acid at room temperature for 24 h.

4.7 Interfacial Interaction between Phases

The interfacial interaction can be determined qualitatively from the size and size distribution of dispersed phases, nylon 6. They can be obtained by using ISM-5400 Scanning Electron Microscope (SEM) at an acceleration voltage of 10 kV.

Nylon 6 was removed from the samples by immersed the samples in formic acid at room temperature for 24 h. After washing them with fresh solvent, the samples were dried at 40°C until constant weight was attained. The samples were them cryo-fractured after immersed in liquid nitrogen. The sample with resulting fractured surface was sputtered with gold ready for imaging.

4.8 Rheological Properties

Rheological properties of each composition were examined using a rheometer (MCR300, Physica Parr) with parallel plate geometry in shear rate mode. The diameter of the upper plate was 20 mm. And the gap was set to 0.5 mm. The pre-heated upper plate was then lowered to a set gap of 0.5 mm. All measurements were carried out at 230 °C in nitrogen environment. The temperature was immediately equilibrated at the set point for 1 min and 30 min for sample relaxation. The complex viscosity and dynamic moduli were measured by shear rate ranging from 0.01- 1 s^{-1}.

4.9 Dynamic Mechanical Measurement

Dynamic mechanical analysis was characterized by using dynamic mechanical analysis (NETZSCH, DMA 242C). The dimensions of the specimen were ca. 55 mm × 10 mm × 2.5 mm and were tested in temperature sweep mode. The strain was applied sinusoidally with a frequency of 1 Hz. The data were collected at -80^{o}C to 150 ^{o}C. The storage modulus (G′), loss modulus (G″), and damping curve (tanδ) were determined. The glass transition temperature was taken as the maximum point on the loss modulus curve in the temperature sweep tests.

4.10 Transmisssion Electron Microscopy (TEM)

Transmission electron microscopy (TEM) analysis was used to confirmation of the morphological information obtained on the platelet dispersion and distribution from the XRD data. Ultra-thin sections measuring approximately 55 nm were ultra cryo microtomed at -110°C with an accelerating voltage of 100 kV (JEOL 200CX).

CHAPTER V

RESULTS AND DISCUSSION

Polypropylene and nylon6 (Ny6) blended with organoclay were prepared by twin-screw extruder at rotational speed 230 rpm, 230 ^{o}C to study the effect of compatibilizer, maleic anhydride grafted polypropylene and organoclay on nanocomposites structure and mechanical properties ,i.e., tensile, flexural and impact properties. Thermal and rheological properties of the nanocomposites were also investigated.

5.1 The Effect of Compatibilizer Loading

5.1.1 Tensile Properties and Izod Impact Properties

The mechanical properties of the materials can be classified into two categories: strength and toughness. Tensile strength and modulus can be considered as material's strength while tensile toughness and izod impact strength can be considered as material toughness. Tensile properties are measurement of material by pulling without twisting and blending at constant rate (50 mm/min) and izod impact properties are measured by striking with hammer at rate 30 kgf/cm.

The extent of maleation added to PP/Ny6 blends and nanocomposites was expected to have an important effect on the morphology and mechanical properties of these materials, and this issue was examined here. The incorporation of the PP-MA (9.3 wt %) increased the tensile strength of the PP/Ny6 blends significantly (Table 5.1). When PP-MA was added to the PP/Ny6 blend, a PP-co-Ny6 copolymer formed which strongly improved the interfacial adhesion between PP and Ny6 and most likely affected the morphology of the blends. However in presence of PP-MA content was varied from 2.5 to 13.3 wt% in nanocomposites, the tensile modulus and tensile strength was slightly decreased. In figure 5.1 showed the effect of compatibilizer loading in the nanocomposites on the tensile properties. By adding, PP-MA from 2.5 to 13.3 wt %), tensile modulus decreased by 10.83% and tensile strength reduced by 4.18%. Tensile modulus and tensile strength decreased with increasing of PP-MA. These results indicated that the effect of the plasticization, effect of low molecular weight of PP-MA(7) and chain scission by MA. So addition of compatibilizer was continuity increasing, both tensile modulus and tensile strength was likely to decrease.

Table 5.1 Mechanical properties of PP/Ny6 blend with and without compatibilizer

Properties	Compatibilized	Uncompatibilized	Percent of improvement (%)
Tensile modulus (GPa)	1.46±0.03	1.21±0.04	20.5%
Tensile strenght (MPa)	34.03±0.38	33.77±1.03	0.78%
Elongation at break (%)	16.13±0.95	8.22±1.20	96.2%
Flexural modulus (GPa)	2.54±0.07	1.93±0.05	31.6%
Flexural strenght (MPa)	38.59±0.77	30.35±0.69	27.1%
Impact energy(J/m)	10.27±0.67	9.85±0.23	4.3%

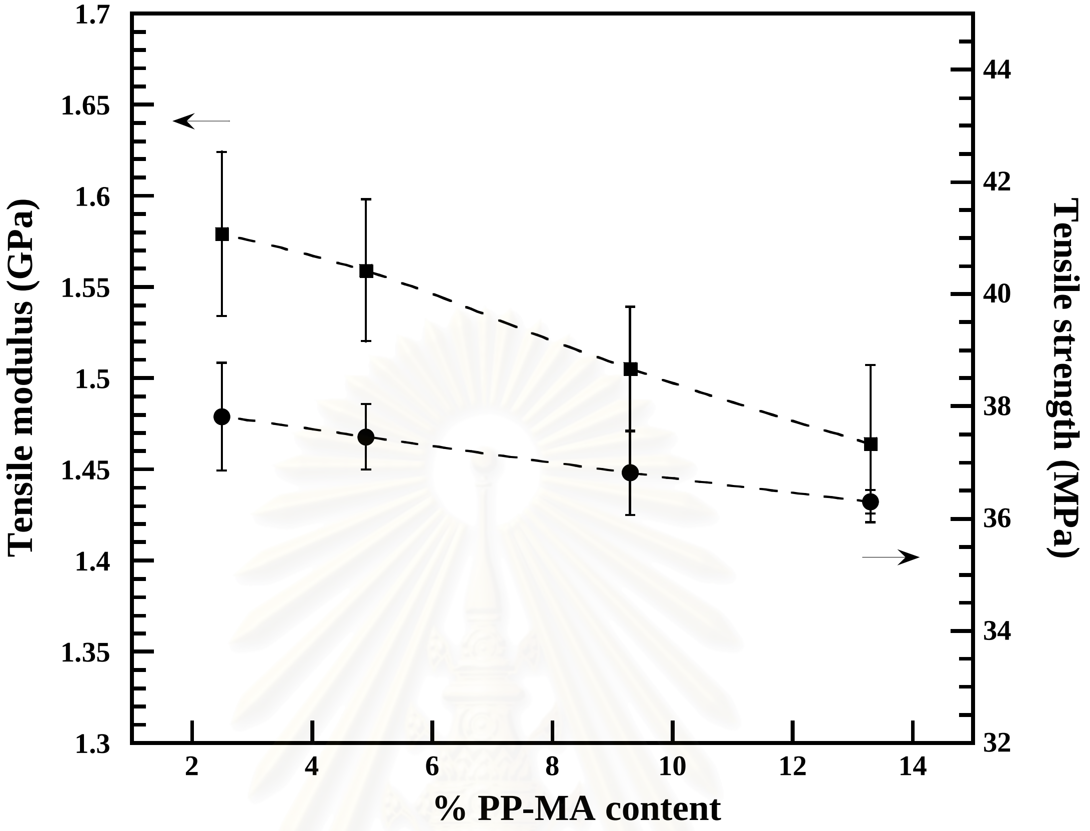


Figure 5.1 Tensile modulus and tensile strength of nanocomposites at different compatibilizer content.

The elongation at break of the PP/Ny6 blends increased with addition of PP-MA (Table 5.1). This indicated the formation of copolymer, which improved the interfacial between the PP and Ny6 phases(7). However, adding more PP-MA in the systems did not significantly changed elongation at break as can be seen in figure 5.2. Ductility or toughness was also referred to an area of stress-strain curves or impact strength, which tended to slightly increase with increasing PP-MA content as shown in figure 5.3.

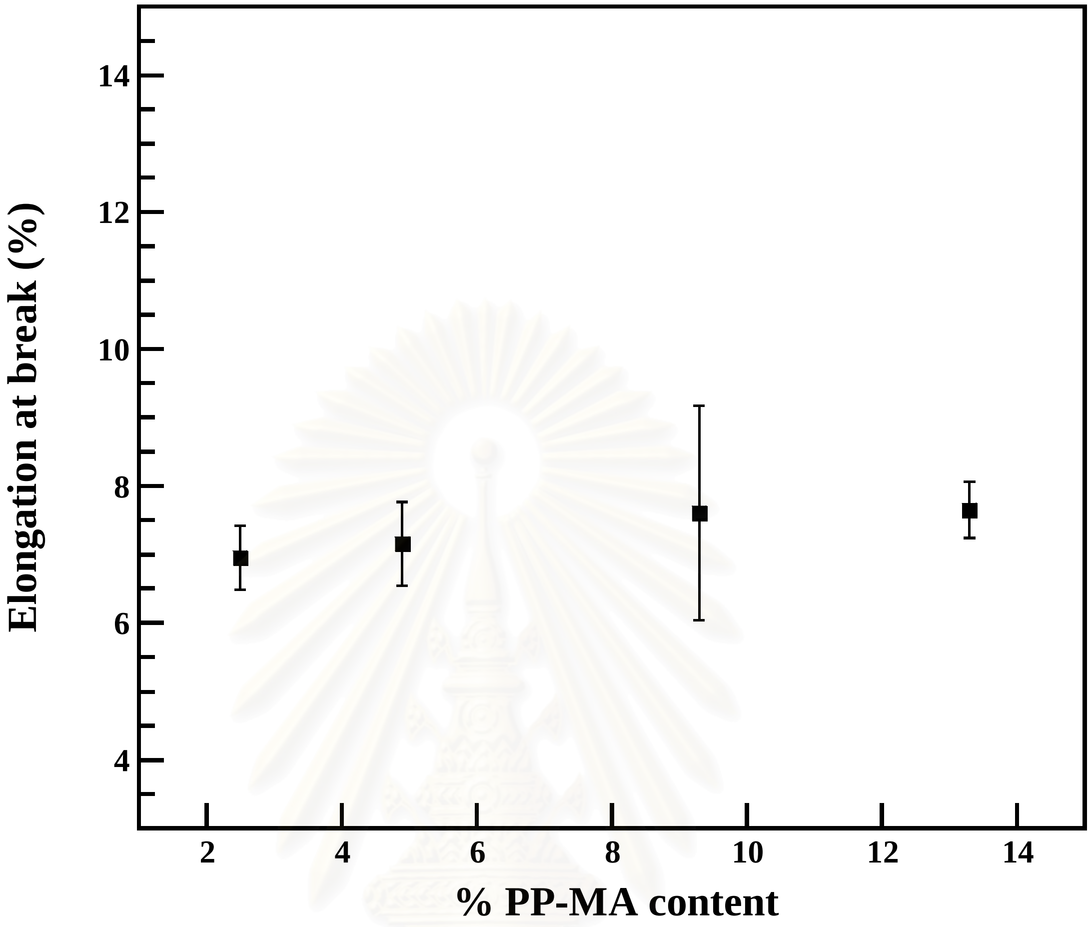


Figure 5.2 Elongation at break of nanocomposites at different compatibilizer content.

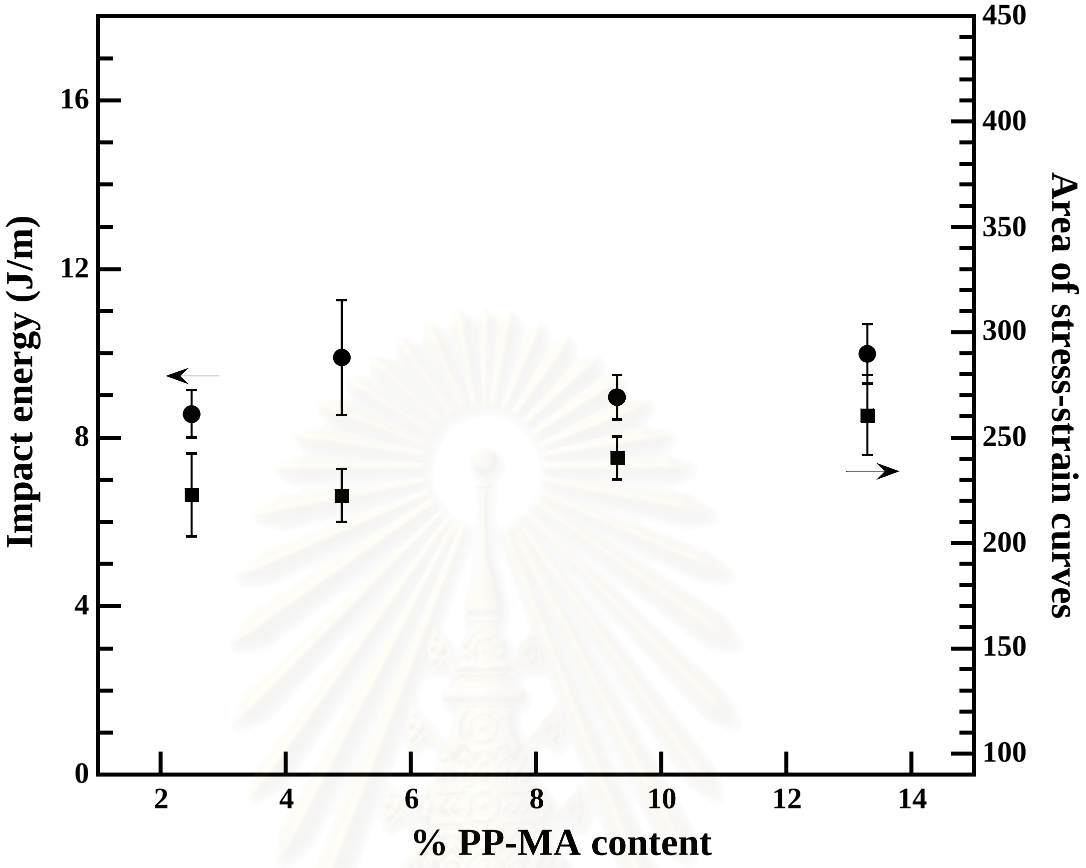


Figure 5.3 Impact energy of nanocomposites at different compatibilizer content.

5.1.2 Flexural Properties

From previous session, tensile and impact properties were enhanced in the presence of compatibilizer, PP-MA, because PP-MA improved the interfacial interaction between phases. However, adding more PP-MA did not affect the tensile and impact properties. The effect of compatibilizer PP-MA on flexural properties was then studied. Flexural testing was carried out by Universal testing machine according to ASTM 790 at rate 4.01 mm/min with various compositions of PP-MA and samples testing can not be broken by 3-point bending.

The amount of PP-MA affected on the flexural modulus and strength of the PP/Ny6 blends and nanocomposites by adding compatibilizer from 2.5, 4.9, 9.3 and 13.3 wt % as shown table 5.1 and figure 5.4. Flexural strength and modulus of S/0 were 30.35 MPa and 1933 MPa, respectively which were lower than S/2 by 27% and

32% respectively. That flexural strength and modulus increased, which improved both flexural modulus and strength of PP/Ny6 blends caused compatibilizer lead to increase the adhesive bond and degree of dispersion PP/Ny6 blend, resulting in improvement of the mechanical properties.

The addition of PP-MA in nanocomposites increased the flexural modulus and yield strength slightly until S/2/0.5. The enhancement in flexural properties was due to the presence of PP-MA, which formed interfacial interaction between PP and Ny6 and adhered strongly to both phases. The interphase improvement caused by reaction between PP-MA molecules and amide group of Ny6 at the interface that formed PP-Ny6 copolymer. When PP-MA was added to PP and Ny6 blends, the anhydride group of MA reacted with the terminal amino group of Ny6 during melt mixing and resulted in a formation of grafted copolymer at the interface between component phases which could be verify by Infrared spectroscopy (FTIR)(7, 34). The flexural property of nanocomposites increased until an optimum loading of PP-MA contents was attained at 9.3 wt%. Further incorporation of PP-MA reduced the strength of nanocomposites. It was believed that the flexural modulus and flexural strength with increasing PP-MA content depend on its low molecular weight and PP-MA acted as a plasticizer.

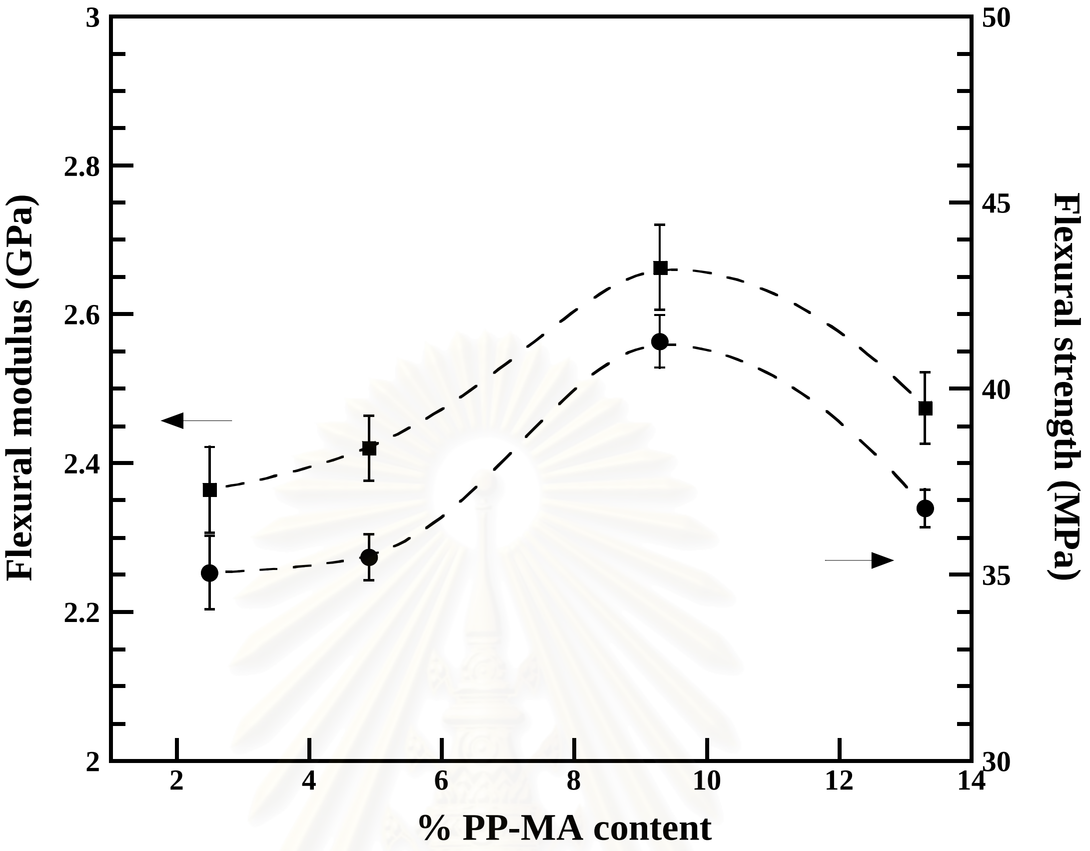


Figure 5.4 Flexural modulus and flexural strength of nanocomposite at different compatibilizer content.

5.1.3 Dynamic Mechanical Properties

Dynamic mechanical analysis (DMA) has emerged as one of the most powerful tools available for the study of behavior of plastic materials. Simply stated, DMA measures the viscoelastic properties of materials. Since all polymers are viscoelastic in nature, this analytical method is perfectly suited to the task of evaluating the complex array of phenomena that polymeric materials present to us. Viscoelastic behavior can be readily measured and interpreted using dynamic mechanical analysis.The DMA experiment was performed between -80°C and 160°C. The changes in storage modulus (E′) of nanocomposites as a function of temperature with vibration frequency of 10 Hz was shown in figure 5.5. All curves could be divided in three main zones, i.e., glassy, glass-rubber transition and rubbery zone. In the first two zones, the storage modulus of nanocomposites increased with the addition of compatibilizers. Figure 5.5 exhibited the E′ modulus of nanocomposites with PP-MA contents ranging from 2.5 to 13.3 wt%. The addition of 9.3 wt% PP-MA content increased the maximum E′ modulus in nanocomposites at all temperature range which indicated this material is more stable than neat PP. These results were consistent with flexural test at room temperature.

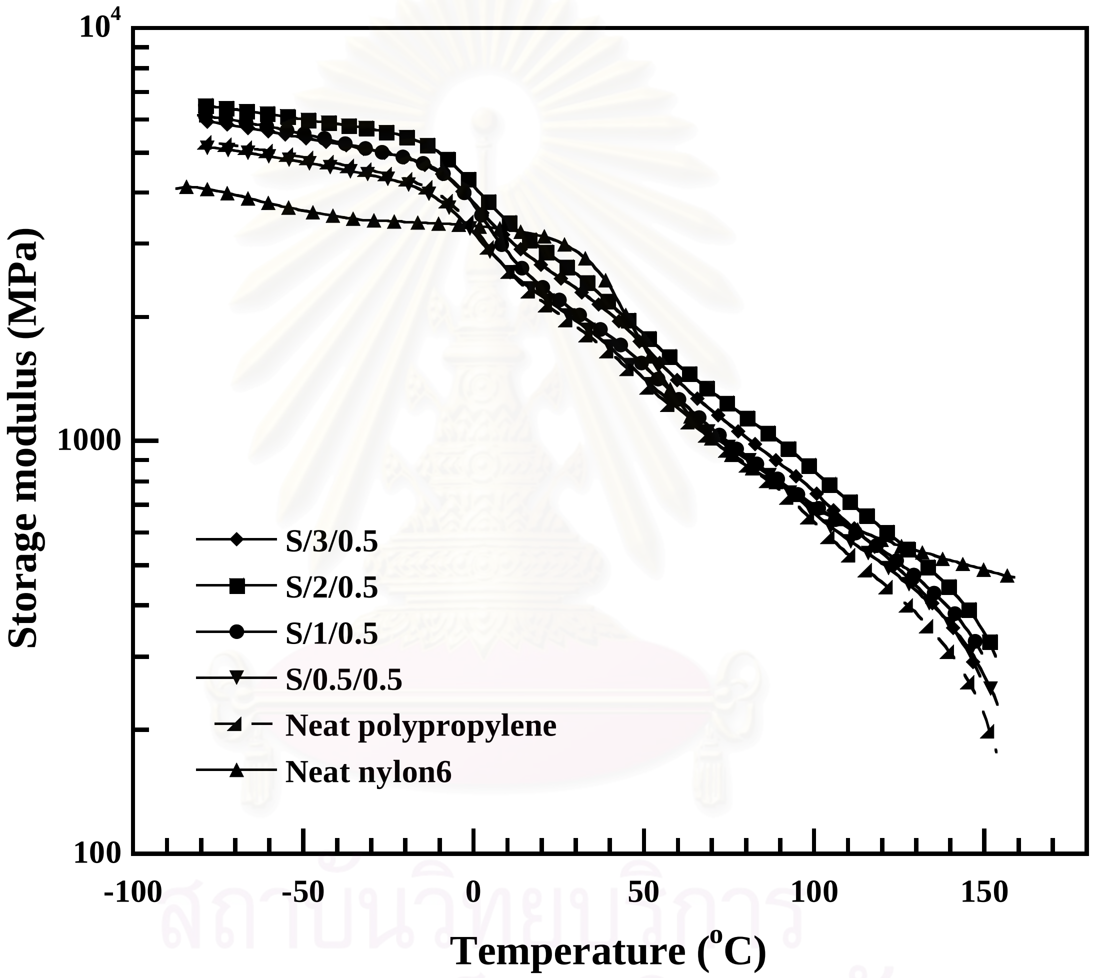


Figure 5.5 Storage modulus of nanocomposites at different compatibilizer content

The rapid rise in the tanδ indicated an increase in a structure mobility of polymer, a relaxation process. The magnitude of the tanδ peaks varied with the severity of the decline in storage modulus. The effect of PP-MA on the tanδ for nanocomposites with various PP-MA contents as a function of temperature was shown in figure 5.6. Three dynamic relaxation peaks were shown in the plot.

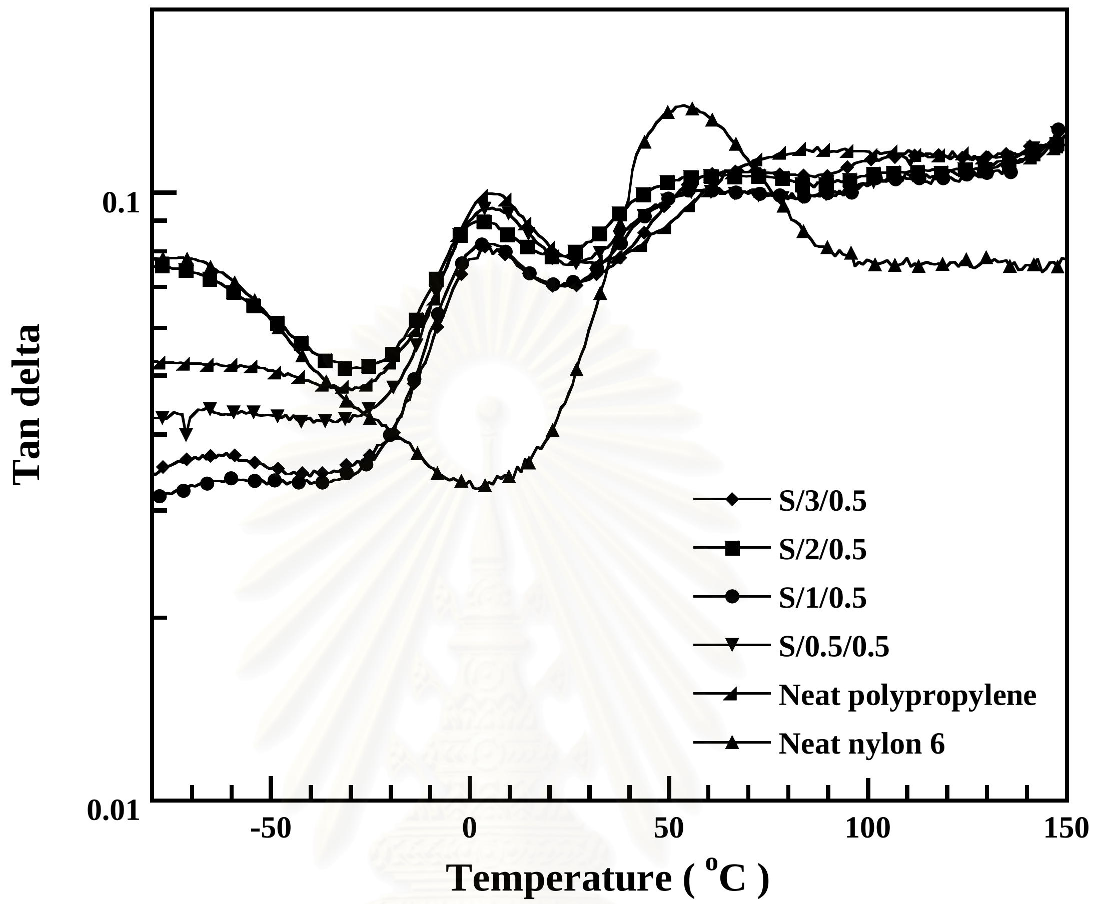


Figure 5.6 Tan δ of nanocomposite at different compatibilizer content.

Two relaxation peaks were observed at around 0°C and 85 °C, which referred to relaxation peaks of PP. While the dominant relaxation appearing at 0°C was the glass transition of the PP, which caused by the movement of large-chain segments, the weak peak appearing as a shoulder at about 85°C was associated with the crystalline region of PP. Another peak at around 55°C was indicated the glass transition of Ny6. PP-MA affected Ny6 phase more than the PP phase and reduced the magnitude of Ny6 glass transition as a consequence of the lower crystallinity detected by X-Ray Diffractometer (XRD). Moreover, the glass transition peak of PP in nanocomposites was slightly shifted toward lower temperature and glass transition peak of Ny6 increased, when increasing of PP-MA contents. It was observed that they established a possible chemical-physical influence on the crystalline properties of the PP and Ny6 phases(39).

5.1.4 Morphology

Adhesion at the interface of inorganic fillers and polymers is one of the main factors determining the properties of polymer nanocomposites. The principal feature here is a contribution of organic molecules grafted to the filler surface; therefore polymer properties at the boundary layer have been changed. Since the modified filler surface promotes polymer plasticization at the phase boundary under an influence of modifier molecules, resulting in improvement of the physical-mechanical properties of nanocomposites such as Young’s modulus. Hence young’s modulus increased when adhesion bond between the binder and a filler is strong sufficiently(47). Moreover, adhesion between polymer matrix and fillers and adhesion between polymer blend (PP/Ny6) are necessary. The interfacial adhesion between phases has been examined by Scanning Electron Microscope (SEM) after formic acid extraction. SEM micrographs of fracture surface of S/0 and S/2 were shown in figure 5.7(a) and 5.7(b) respectively. It can be seen in figure 5.7 (a) that Ny6 phases were in irregular shape and had large sizes. This was due to high interfacial tension between PP and Ny6 because of their dissimilar polarity. When compatibilizer, PP-MA was added to polymer blend, S/0, polymer blend with PP-MA, S1 has more homogeneous texture than S/0, as shown in figure 5.7(b). Since adding compatibilizer leded to chemical linkage between PP and Ny6 phase, uniform morphology occurred (7, 8, 34). Therefore, when materials were under tension, its character altered from brittle to ductile.

Figure 5.8 showed the SEM micrographs illustrating the effect of the amount of PP-MA on the morphology of the PP/Ny6 nanocomposites.

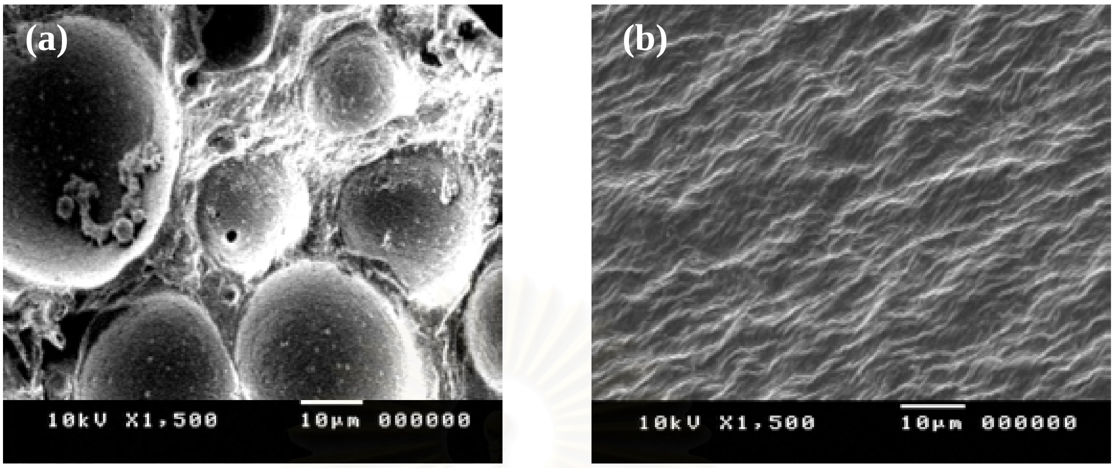


Figure 5.7 SEM micrographs of S/0 and S/2.

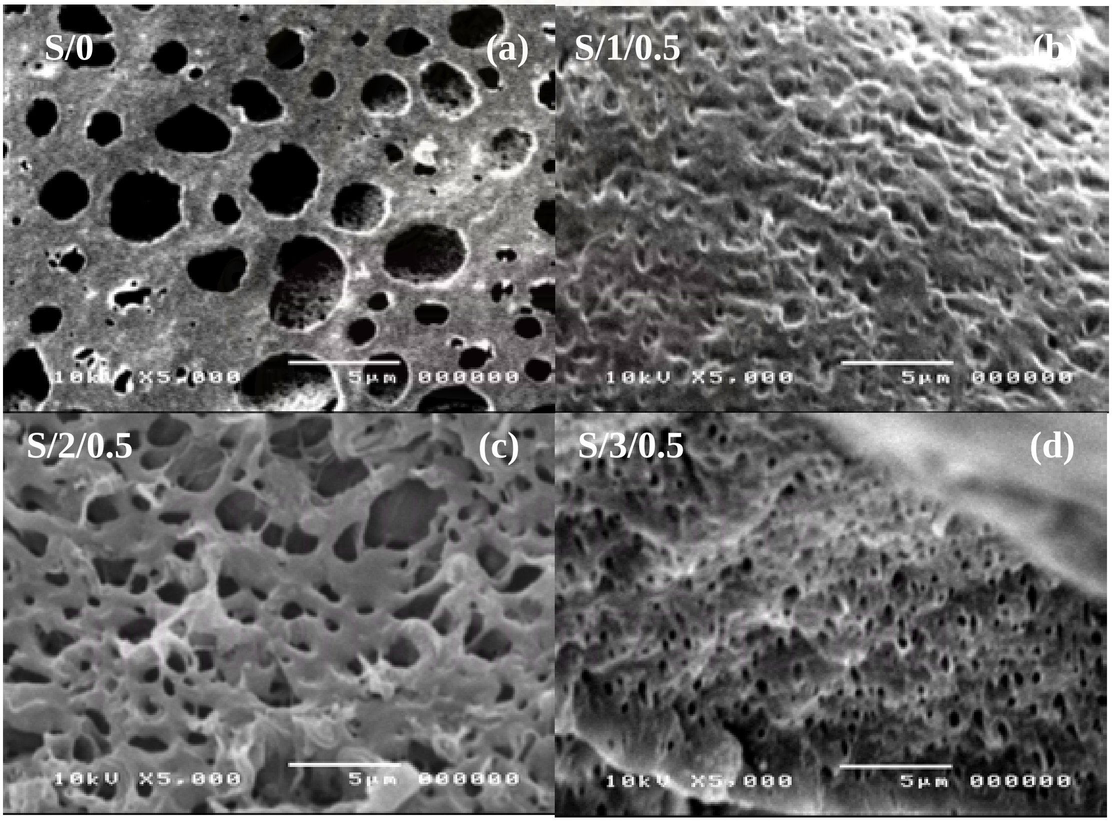


Figure 5.8 SEM micrographs of nanocomposites at different compatibilizer content.

All samples shown in figure 5.8 were etched by formic acid to remove Ny6 from nanocomposites. Figure 5.8 showed the holes of the dispersed phase Ny6 phase. S/0 showed in figure 5.8(a) exhibited coarse dispersion of Ny6 phase in PP matrix. Figure (b), (c) and (d) showed the morphology of etched surface of the nanocomposites with increasing PP-MA content. The small holes in figure 5.8 indicated that the mean particle size of Ny6 was substantially reduced owing to the presence of the PP-MA compatibilizer. Addition 5 wt% up to 13.3 wt % PP-MA content, size of the dispersed phase became uniform size, indicating a strong interaction and adhesion between the PP and Ny6 phase due to the reactive compatbilisation with the PP-MA. According to Sathe et. al.(37, 38), PP-MA molecules were located in the interphase between the matrix and the dispersed phase. Recall that the major function of a compatibilizer is to reduce the interfacial tension between the components in melt and create a finer dispersion in the blend.

5.1.5 Microstructures of Nanocomposites

As layered silicates are highly organized materials, wide angle X-ray scattering gives valuable information on changes of their structure, especially concerning intercalation, exfoliation that affected on mechanical properties and rheology of materials. XRD is the most powerful and reliable technique to study the dispersion of organoclay inside the polymer matrix. The X-ray diffraction pattern was shown in the range of 2 theta 1-10^o. From figure 5.9, organoclay showed strong diffraction peak at $2\theta = 4.39°$. According to Bragg's equation, $2d\sin\theta = n\lambda$, the interlayer spacing is equal to 1.99 nm. The large broadening of peak that has been shifted towards a bit higher interlayer spacing than that the pure organoclay by the main peak decreasing to 2.19 nm. The XRD exhibited large profile broadening, which indicates strong structural disorder and inhomogeneity in the interlayer composition of samples. The broad peak indicated that partial exfoliation has occurred(27). By adding, PP-MA (2.5 wt% to 13.3 wt %), d-spacing increased from 2.19 nm to 2.25 nm. The slightly increment of d-spacing observed the organoclay galleries may be swelling.

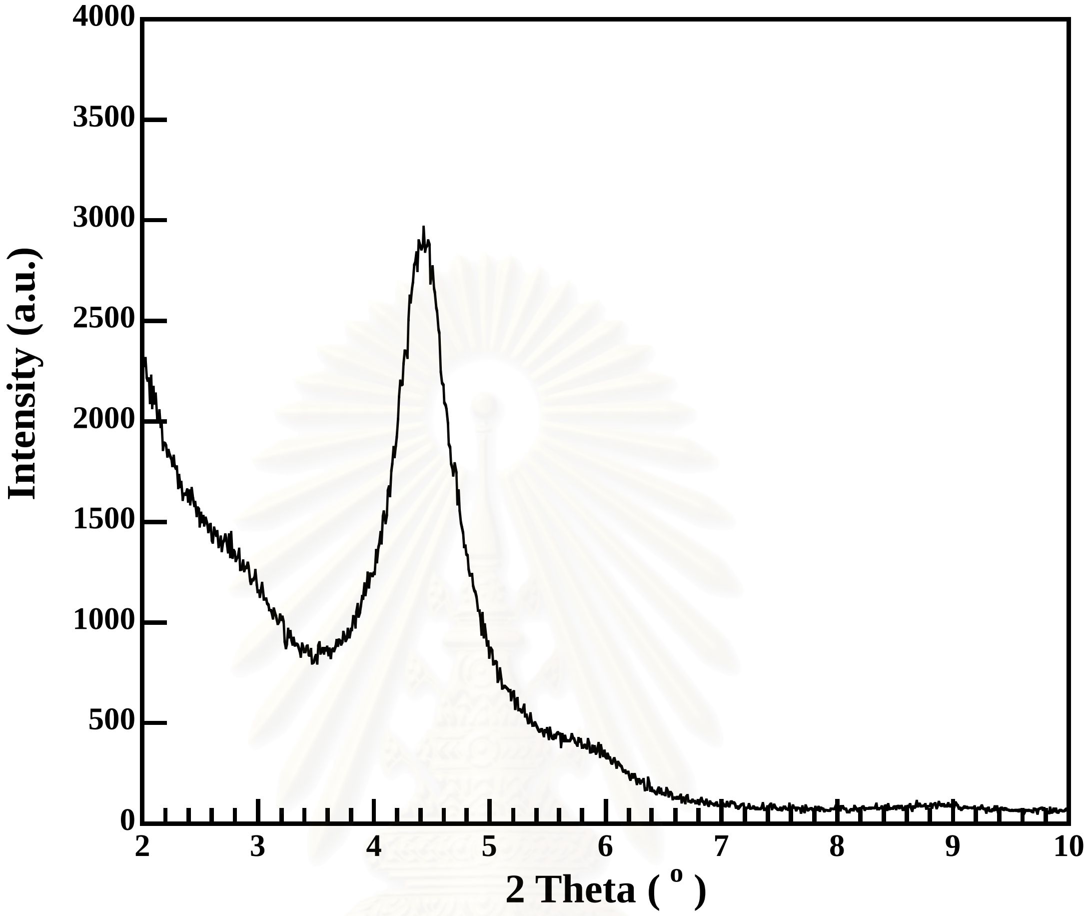


Figure 5.9 XRD patterns organoclay.

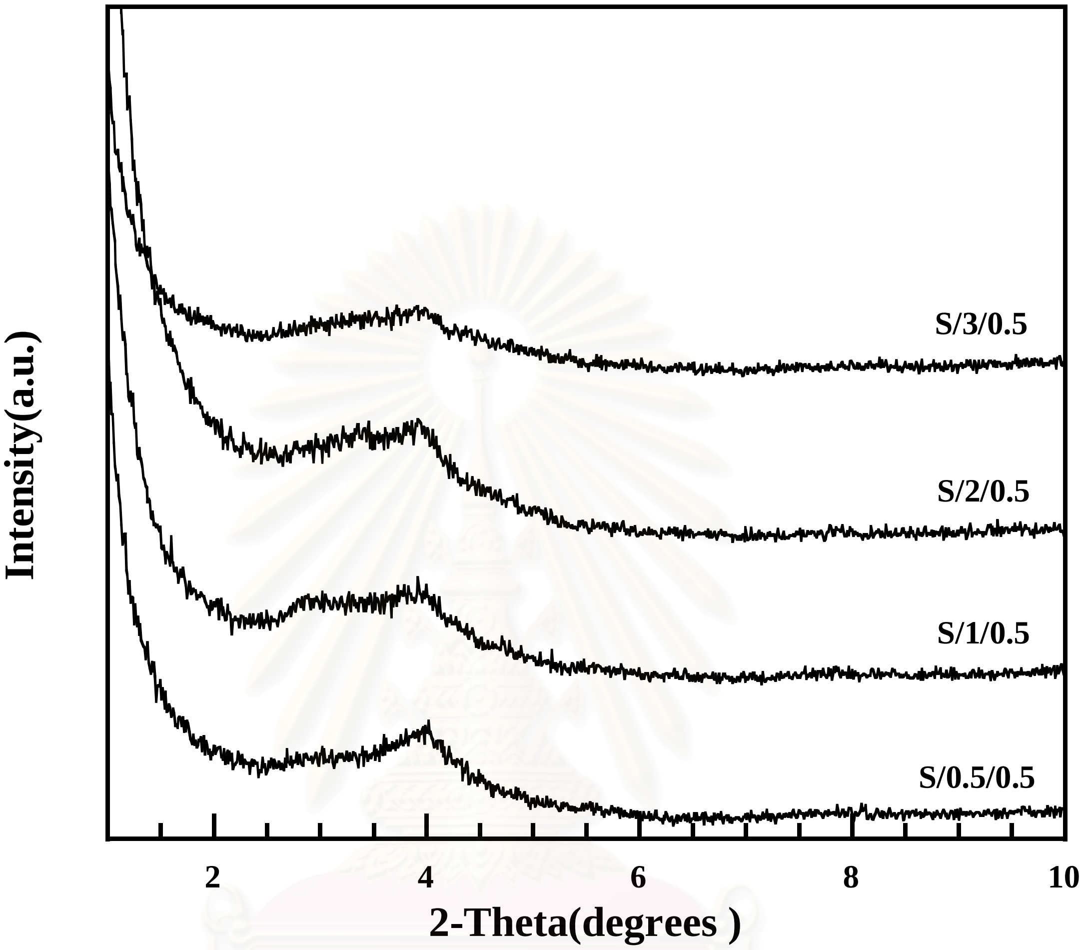


Figure 5.10 XRD patterns of nanocomposites at different compatibilizer content.

Moreover in wide angle X-ray diffraction (2θ in range 10-30°) can be determined the crystallinity of nanocomposites. The reflection α-crystalline form of PP phase at 2θ = 14, 16.8, 18.6, 21, 21.8, corresponding to the (110), (040), (130), (111) and (131) plane of α-PP(11). Another reflection at 2θ = 21.3°, correspond to the γ-form of Ny6 component as shown in figure 5.11. The intensity of the α-PP form and the γ-form of Ny6 decreased with increasing PP-MA content in nanocomposites, which indicated that the crystallinity was decreased. It was observed that they established a possible chemical-physical influence on the crystalline properties of the PP and Ny6 phases(3). These results confirmed that the presence in PP-MA did not disturb the crytalline phase structure of the components.

Compatibilization reduced the relative intensity of PP and Ny6 reflections and increased the amorphous, indicating a good dispersability of the components in the amorphous phase(3).

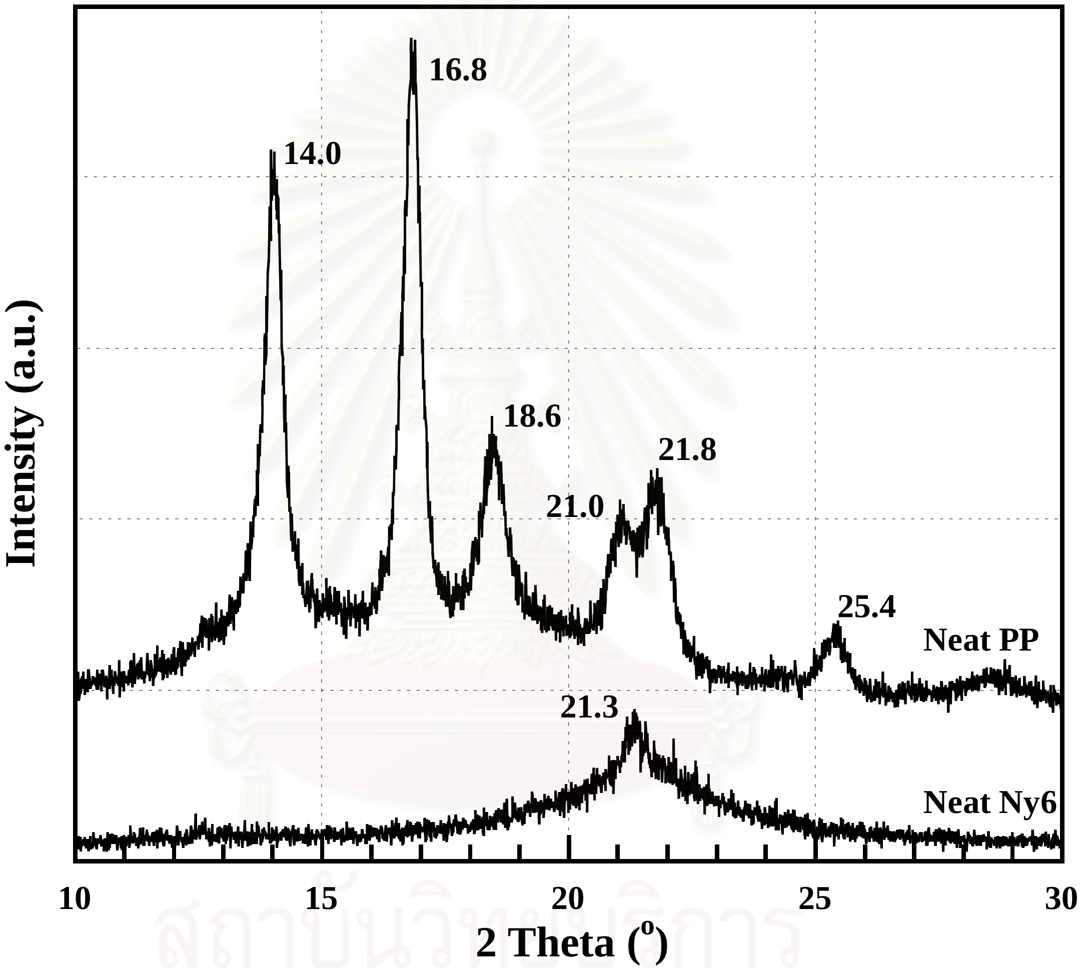


Figure 5.11 : XRD patterns of Polypropylene and Nylon6.

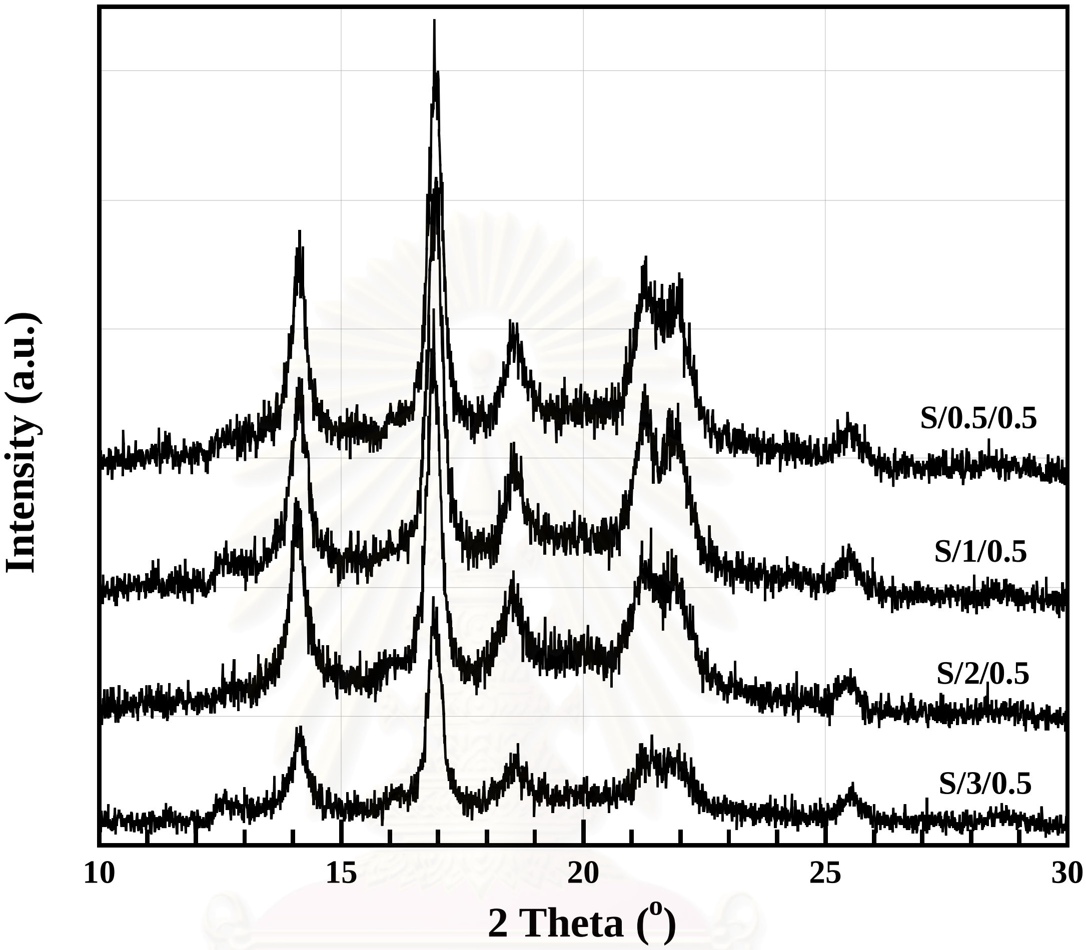


Figure 5.12 XRD patterns of nanocomposites at different compatibilizer contents.

5.1.6 Thermal Properties

Differential Scanning Calorimetry (DSC) showed the thermal characteristics of PP, Ny6 and nanocomposites. Polypropylene gave a melting temperature(T_m) at 168.9 °C and Ny6 has a T_m at 223.7°C while a PP-MA has a T_m 164.7°C. The DSC curves of the incompatible exhibited two separate melting around 165 °C and 221 °C. The heating scanning melting temperature of the Ny6 component in these nanocomposites were about 2-3 °C lower than that of the neat Ny6 as shown in figure 5.13. These presences of the in situ formed PP-co-Ny6 copolymer, which tended to be more compatible. Furthermore, the results obtained by DSC thermogram confirmed that the crystallinity of PP and Ny6 with addition of PP-MA. The addition of PP-MA in nanocomposites did not change crystalline structure (as shown in XRD

results) but it decreased the crystallinity both of PP and Ny6 phases (see in Table 5.3). The increasing an amount of PP-MA, which results in the decrease of segmental movement of the polymer chains caused a decrease in the enthalpy associated with the crystallinity of PP and Ny6.

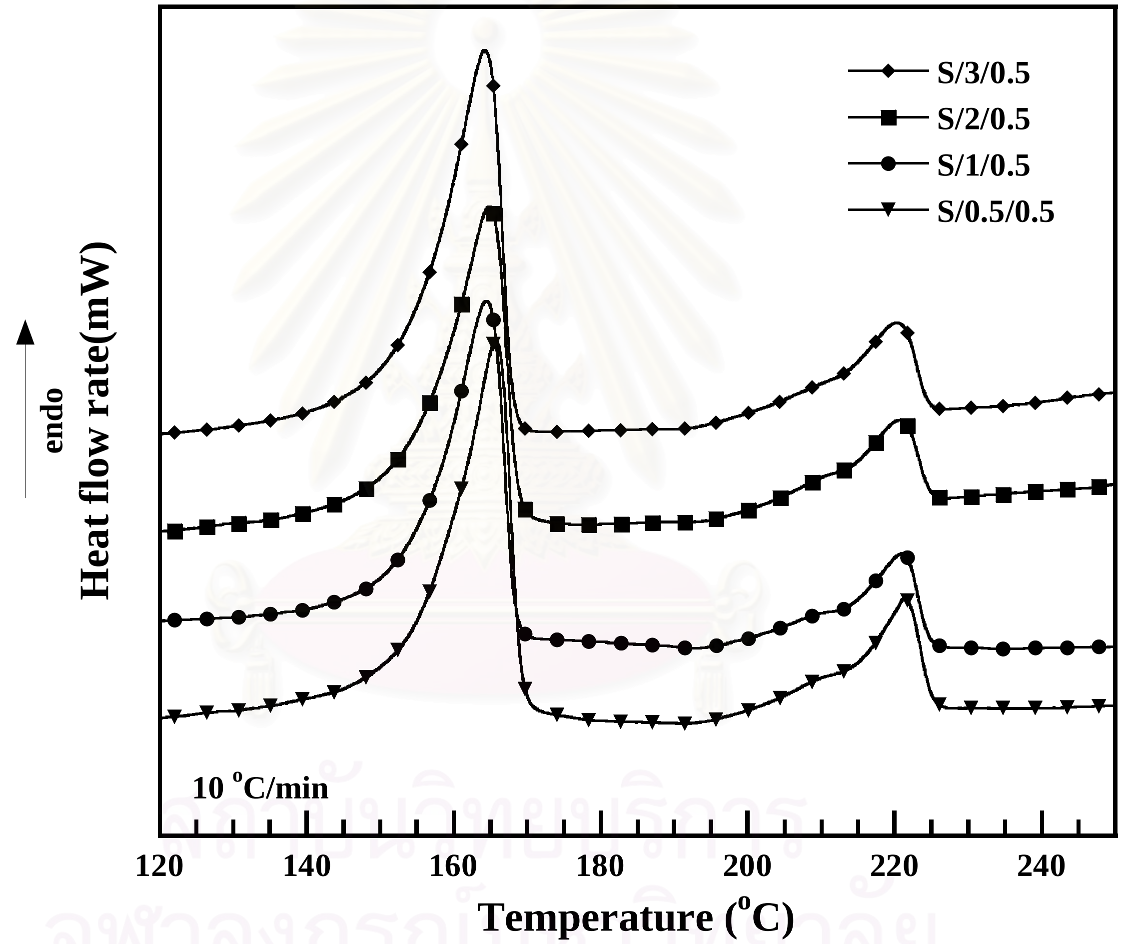


Figure 5.13 DSC thermograms of nanocomposites at different compatibilizer content.

Table 5.2 Crystallinity of nanocomposite at different compatibilizer content

The amount of compatibilizer (PP-MA)	Crystallinity of Polypropylene (%)	Crystallinity of Nylon 6 (%)
Pure	59.31	38.79
S/0.5/0.5	42.10	9.12
S/1/0.5	45.19	8.75
S/2/0.5	42.07	8.17
S/3/0.5	41.07	8.35

5.1.7 Flow Behavior

In many applications, it is important to know how apparent viscosity changes when shear rate (and shear stress) are changing in varied range. The relationship between apparent shear viscosity and apparent shear rate of nanocomposites with various compatibilizers, PP-MA, loads were shown in figure 5.14. The flow curves of the nanocomposites possess two distinct regions: a Newtonian region and shear-thining region. The Newtonian region was observed at very low shear rates, where the apparent viscosity was dependent of shear rate. In the shear thinning region, the viscosity decreased linearly with increasing shear rates on log-log plots. Therefore, all sets of polymer melts exhibited shear-thinning behavior (i.e. pseudoplasticity). At a given apparent shear rate, the apparent viscosity have shown the increasing loading of PP-MA until 2.5 wt % PP-MA content. This may be attributed to the compatibilizer was forced to locate at the interface between PP and Ny6 phases. The polar functional group in PP-MA interacted with polar functional groups of Ny6 while the backbone was capable of compatibilizing with the PP in the nanocomposites. This gave rise to increase interaction at the interface, improved interfacial tension and leaded to decreasing size of dispersed phase, that have shown in table 5.2. However, a decreasing trend of apperent viscosity was observed after the compatibilizer loading of 2.5 wt% because of a low molecular weight and a low viscosity of PP-MA.

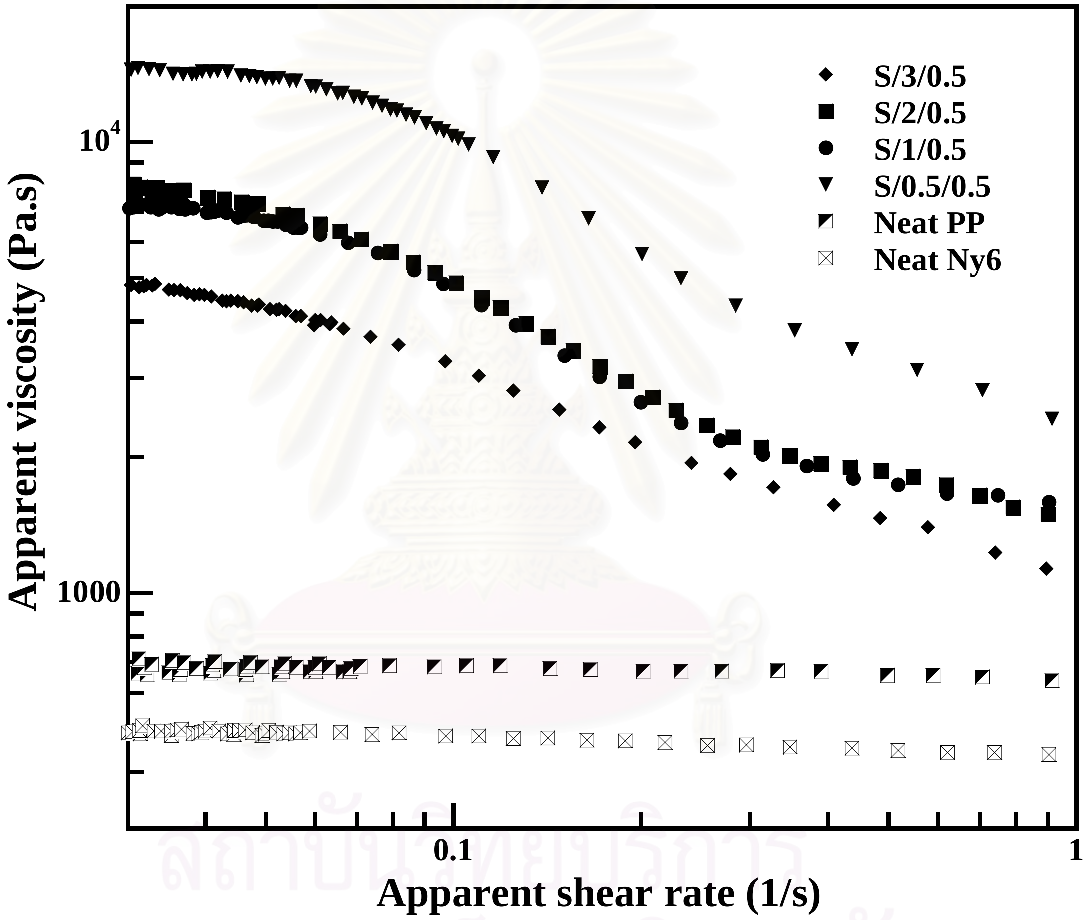


Figure 5.14 Flow behavior of nanocomposites at different compatibilizer content.

5.2 The Effect of Filler Loading

This section investigated the effect of filler on mechanical properties, such as tensile, flexural and impact resistance, microstructure, dynamic mechanical properties, thermal properties and rheological properties of at different filler contents from 0, 2.3, 4.5 and 6.7 wt % Org-MMT content.

5.2.1 Tensile Properties and Izod Impact Properties

The effect of organoclay (Org-MMT) contents on the tensile mechanical properties of nanocomposites was shown in figure 5.15. The addition of Org-MMT significantly leaded to substantial improvement in stiffness of polymer blends (PP/Ny6). By adding 6.7 wt% Org-MMT content, tensile modulus increased by 32 %. The increasing of organoclay loading content enhanced tensile modulus of nanocomposites. The increment of tensile modulus indicated a decrease in molecular mobility that could be a consequence of the interaction of the polymer chain with Org-MMT. The large number of interacting molecules resulted of the large interphase area between molecules(16).

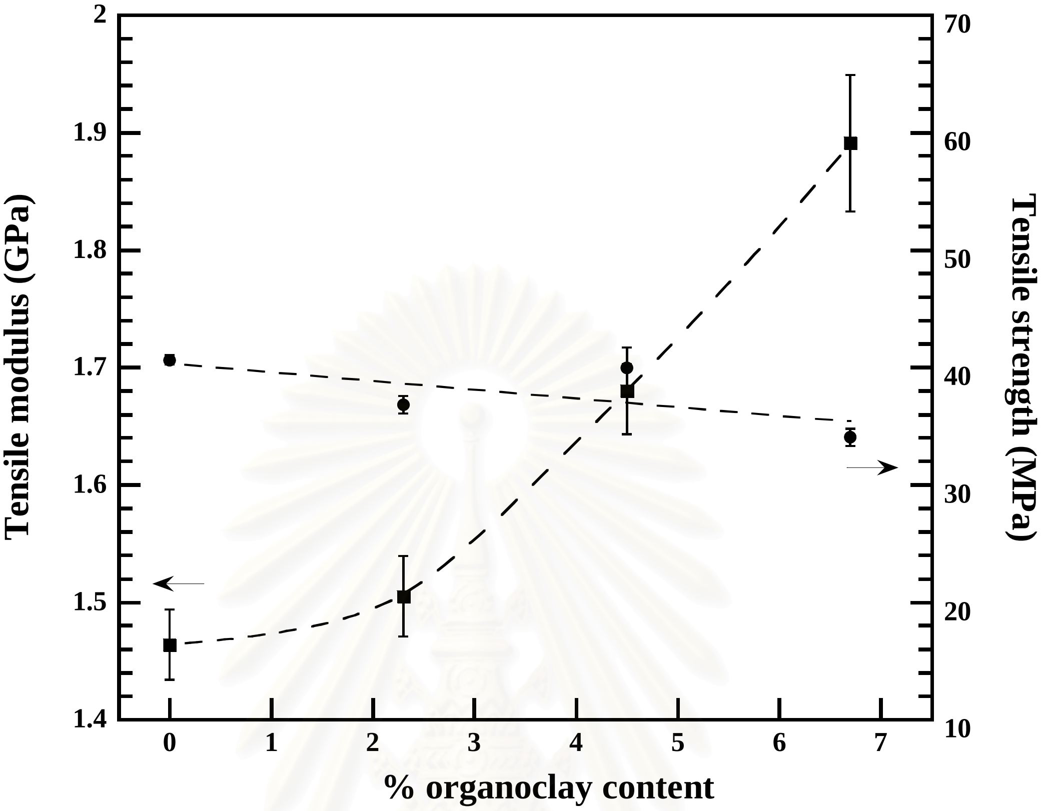


Figure 5.15 Tensile modulus and tensile strength of nanocomposites at different filler content.

Although tensile modulus increased with increasing Org-MMT contents, the addition of the organoclay resulted from a drop in elongation at break without necking formation. From the XRD curves could be verified that the nanocomposites structure had agglomerate layered silicate(un-exfoliated organoclay) and exfoliated/intercalated organoclay layers and particle in matrix (6) at higher filler contents as a result of nanocomposites had more brittle. In figure 5.16 showed the impact energy and area of stress-strain curves, which referred to ability of energy absorbed or toughness. It can be seen the addition of Org-MMT, which diminished the ductility due to inhomogeneous nanocomposites structure.

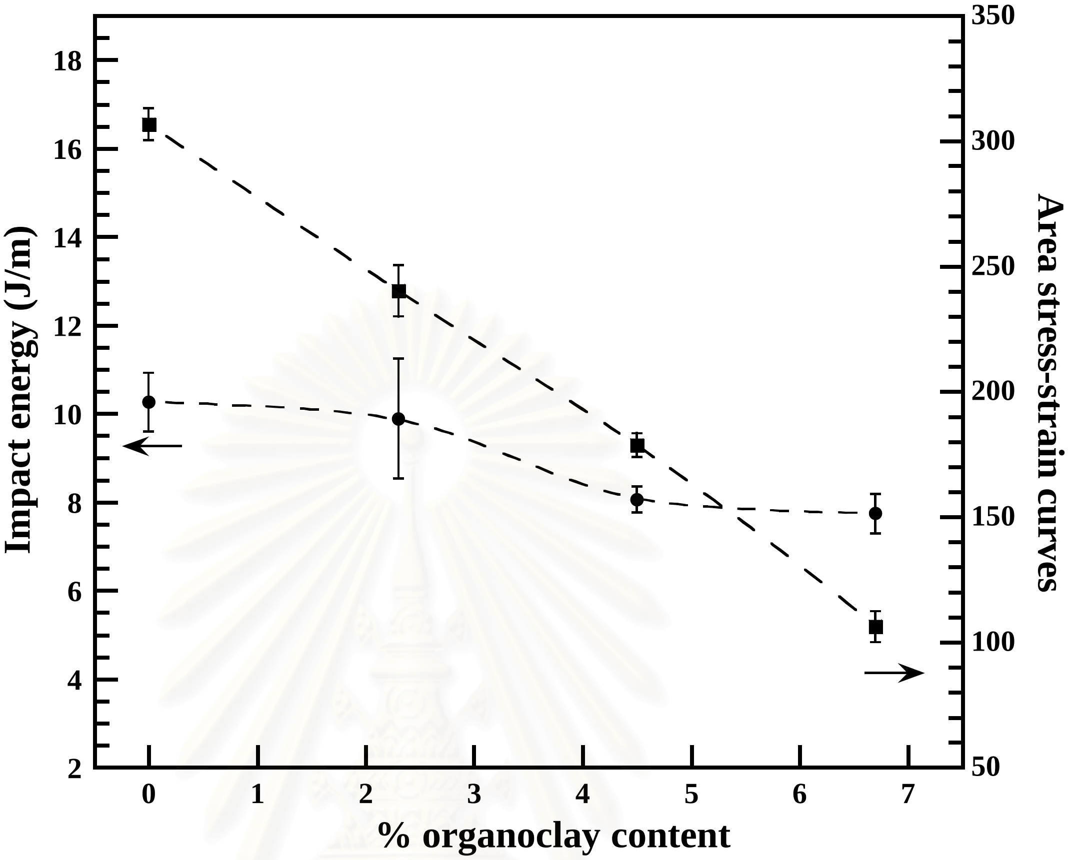


Figure 5.16 Impact energy and area stress-strain curve of nanocomposites at different filler content.

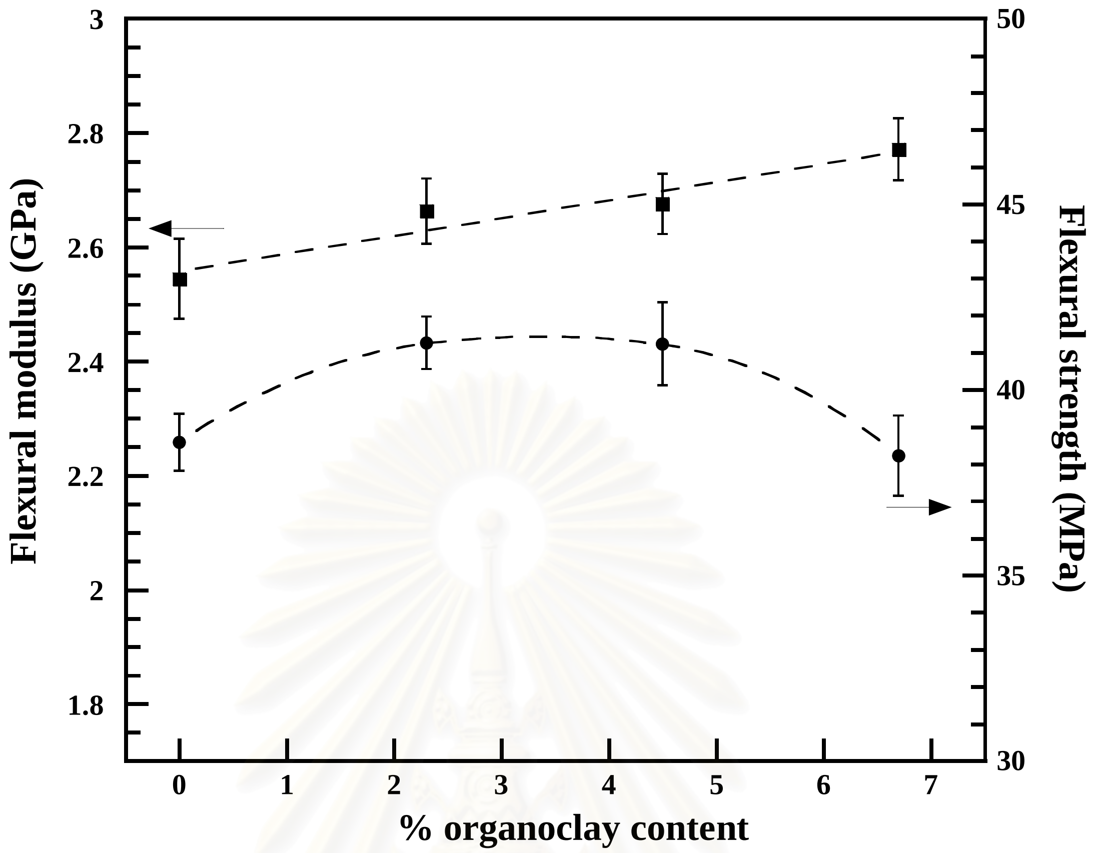


Figure 5.17 Flexural modulus and flexural strength of nanocomposites at different filler content.

5.2.2 Flexural Properties

The effect of nanocomposites on flexural modulus and strength at different of organoclay contents were showed in Figure 5.17. By adding from 2.3 wt% - 6.7 wt % Org-MMT content, flexural modulus increased by as similar trend in tensile modulus results. The flexural modulus increased with increasing of Org-MMT, which indicated that the effect of the increment in surface area between Org-MMT and polymer matrix. For example, S/2/1.5, nanocomposites had a flexural modulus of 2.77 GPa, which was larger than polymer blends. The addition of Org-MMT in nanocomposites improved the flexural modulus when they compared to S/2. While the flexural modulus of nanocomposites was improving, the flexural strength decreased. For example, S/2/0.5, the flexural strength of nanocomposites increased by 7 % of nanocomposites and decreased the flexural strength by 7.3%.

As the Org-MMT content increased, the increase in interaction between Org-MMT, i.e., by touching or bridging, resisted the uniform distribution of the Org-MMT filler, resulting in the lower flexural strength of the nanocomposites.

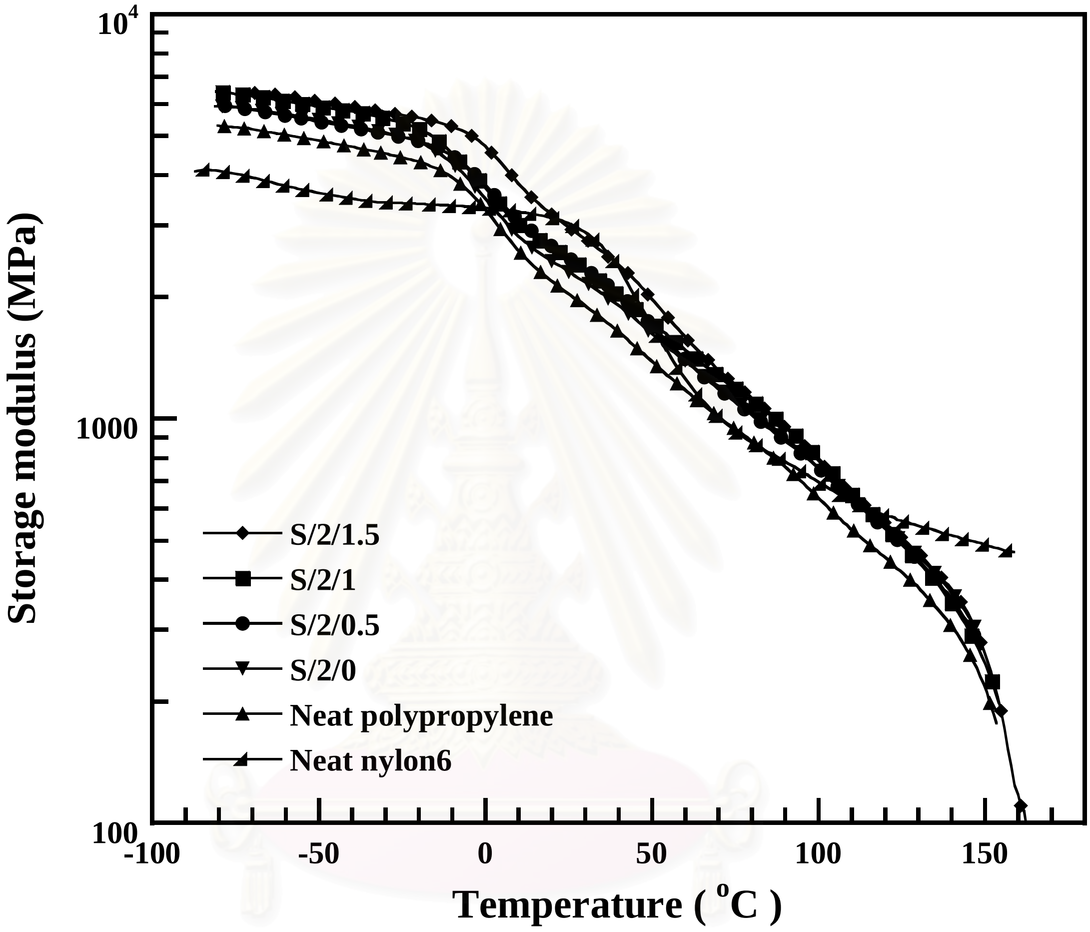


Figure 5.18 Storage modulus of nanocomposite at different filler content.

5.2.3 Dynamic Mechanical Properties

The storage modulus as a function of temperature (E′ modulus) and tanδ of nanocomposites were shown in figure 5.18 and 5.19. By adding 2.3wt%-6.7wt% Org-MMT content, the storage modulus increased by 12.7%, 20.5% and 21.6%, respectively as compared to that of neat PP. Furthermore, the temperature in range 0 to 70 °C involves room temperature, S/2/1.5 had the hardest deformed by an applied load because of its highest modulus. These were consistent with the flexural modulus from short-term property test as discussed earlier. The rubbery transition, the entire nanocomposites were indifferent in storage modulus pattern in the region of rubbery transition were almost the same for all test mixtures. They were indicated that these composite has the same in thermal stability, while the weakest has appeared for PP.

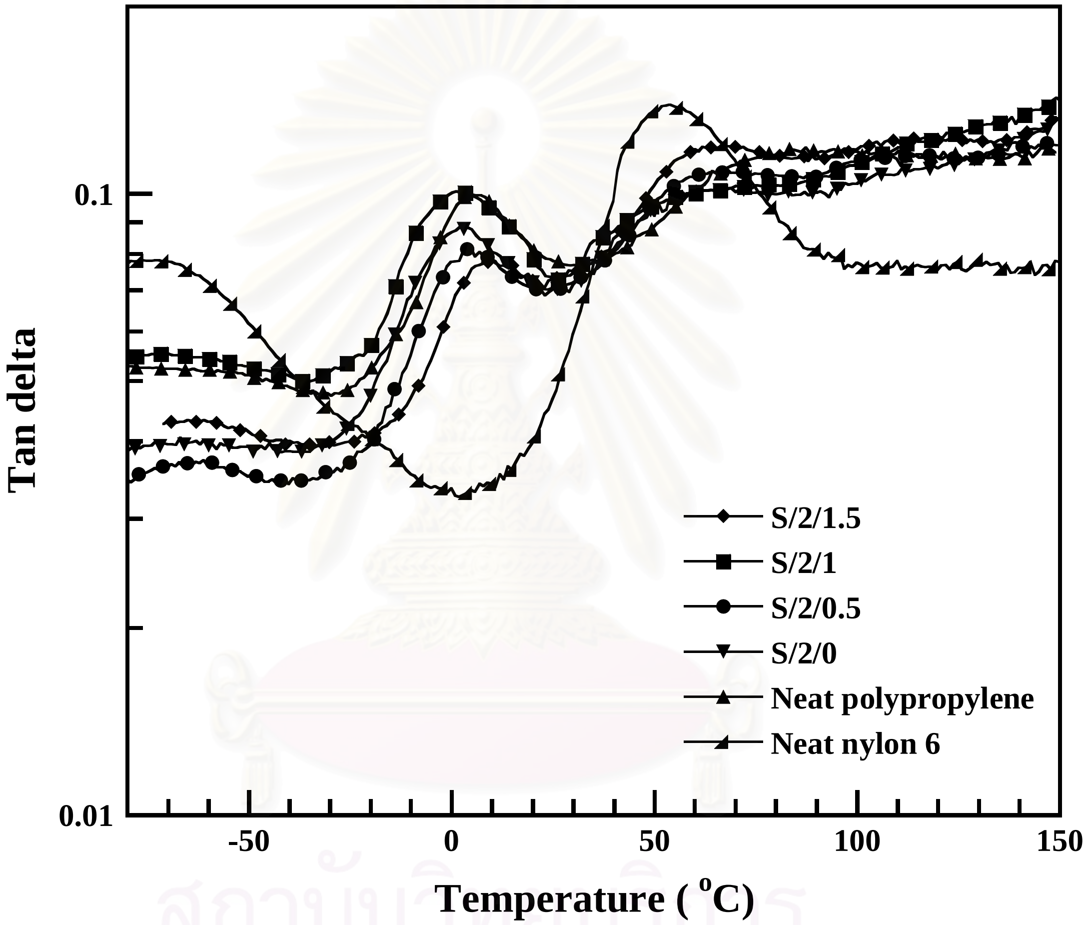


Figure 5.19 Tan δ of nanocomposites at different filler content.

It is known that the glass transition temperature, Tg, corresponded to the temperature at which mobility of segments of polymer begin to occur. Consequently, the adsorption and adhesion are to be reflected in Tg (47). The effect of Org-MMT contents on the glass transition temperature of nanocomposites showed in figure5.19. The three relaxation peaks observed at 0 ^{o}C and weak peak appearing as a shoulder at about 50-70 ^{o}C and 110 ^{o}, respectively. The weak peak corresponded to the glass relaxation peak of matrix polymer as a PP, and the latter to glass transition of dispersed phase of polymer as a Ny6. From figure, it confirmed the major effect of Org-MMT on the enhancement of glass transition of the resulting nanocomposites. The implication of these phenomena was possibly due to the contribution of the good interfacial adhesion between the Org-MMT and the polymer matrix mentioned previously. Since the Org-MMT filler was known as a high stiffness material, the mobility of the matrix can be highly restricted with this filler when adhering on the filler surface. This can also lead to the decrement in the glass transition temperature of their composites. For example, the predicted values of the glass-transition temperatures of the PP were extrapolated to be 5.3^{o}C. By adding.3 wt% to 6.7 wt % Org-MMT content, the relaxation peak of the neat PP took place around 2-3 ^{o}C compared to neat PP. The above observation may also the correlated with the intercalated/exfoliated formed in nanocomposites structure. The layer restricted the segmental motion of polymer molecules. As a consequence, the glass transition was lower.(4, 32). By adding 6.7 wt % Org-MMT content, glass transition temperature of PP increased. These results can be concluded that the strong polymer/filler interactions that caused of increment in modulus as a mechanical improvement previously

5.2.4 Microstructures of PP/Ny6 Nanocomposites

To investigate the mechanism of the morphological change of the nanocomposite with the Org-MMT content, we have to consider the clay dispersion and distribution in the blend. For figure 5.20 showed the XRD profiles of the nanocomposites. All nanocomposite varied Org-MMT content from 2.3 to 6.7wt %. The diffraction of pure organoclay was at 2θ = 4.43°, which corresponds to d-spacing of 1.99 nm. For S/2/0.5 and S/2/1, a small broad shoulder was observed around 2θ = 3.92° and a small shoulder peak at 2θ = 3.97°, respectively; correspond to the plane of silicate layer in the polymer matrix. In the highest of Org-MMT content, the strong diffraction peak was observed as a well-defined peak at 2θ = 3.98° (≅ 2.22 nm), implied that the ordered intercalated nanocomposite was formed. For case of 2.3wt%

and 4.5wt % Org-MMT content, we can also concluded that the polymer chain were intercalated in the silicate galleries and the homogeneous of the silicate layer was much higher than S/2/1.5. The XRD results can be verified by TEM micrograph. TEM micrograph, as shown in figure 5.21, can be seen the nanocomposites structure had partially exfoliated and intercated.

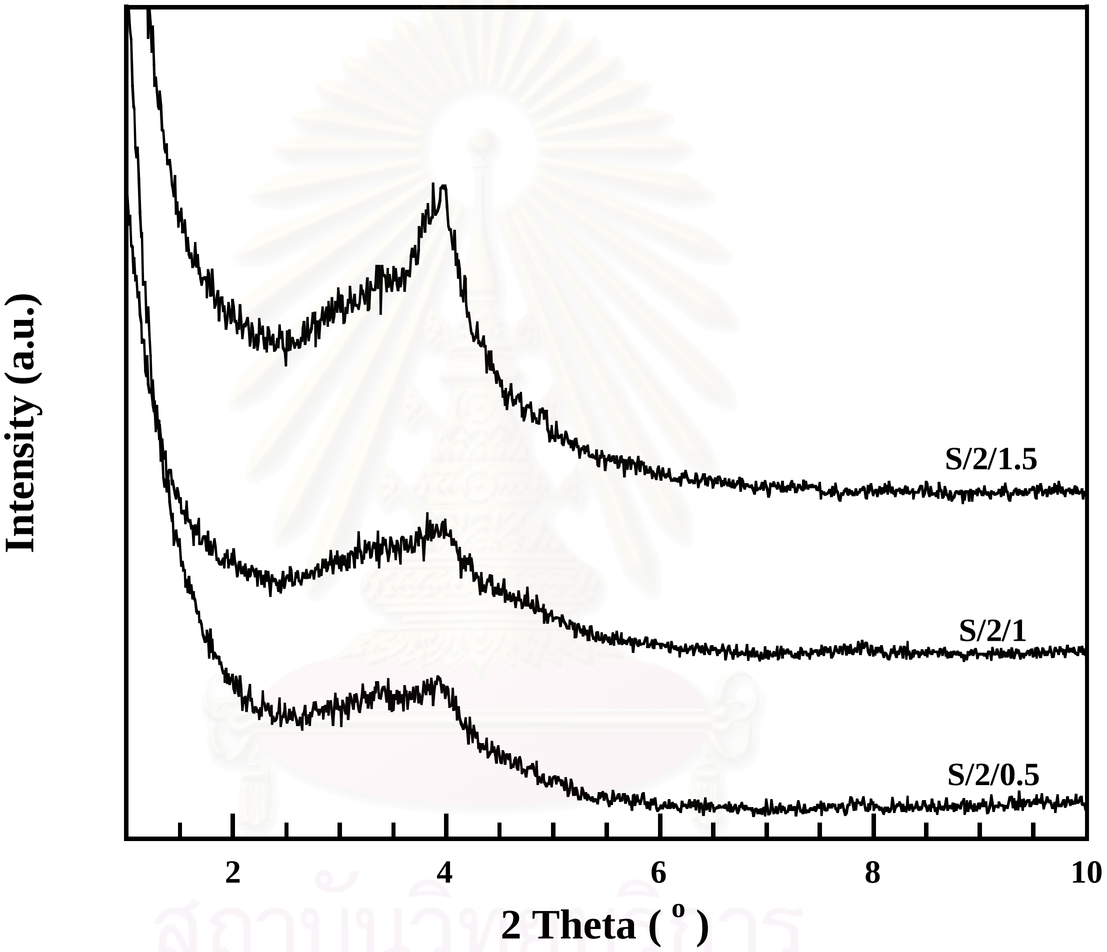


Figure 5.20 XRD patterns of nanocomposites at different filler content.

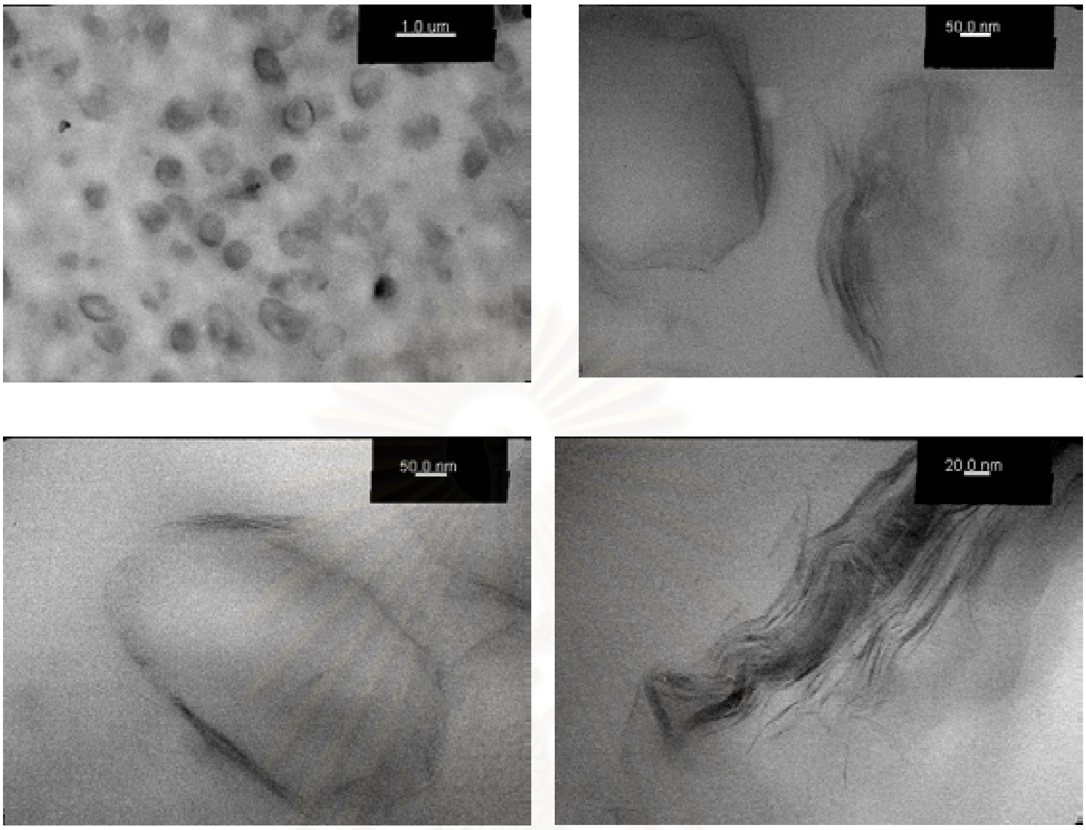


Figure 5.21 TEM micrographs of S/2/0.5

In figure 5.22 was illustrated the comparison of XRD patterns of nanocomposites containing 2.3wt% to 6.7wt % Org-MMT content. The following structure features can be seen. A peak detected location was held constant, while the peak heights were varied. The Org-MMT reduced the intensity of PP phase. The reduction of the PP chain's mobility might lead to smaller, less-ordered crystalline. As showed in table 5.4, this indicated the DSC thermogram with variation of PP and Ny6 crystallinity. These results indicated that the effect of Org-MMT decreased the crystallinity of PP, which could be associated due to good molecular mixing(39).

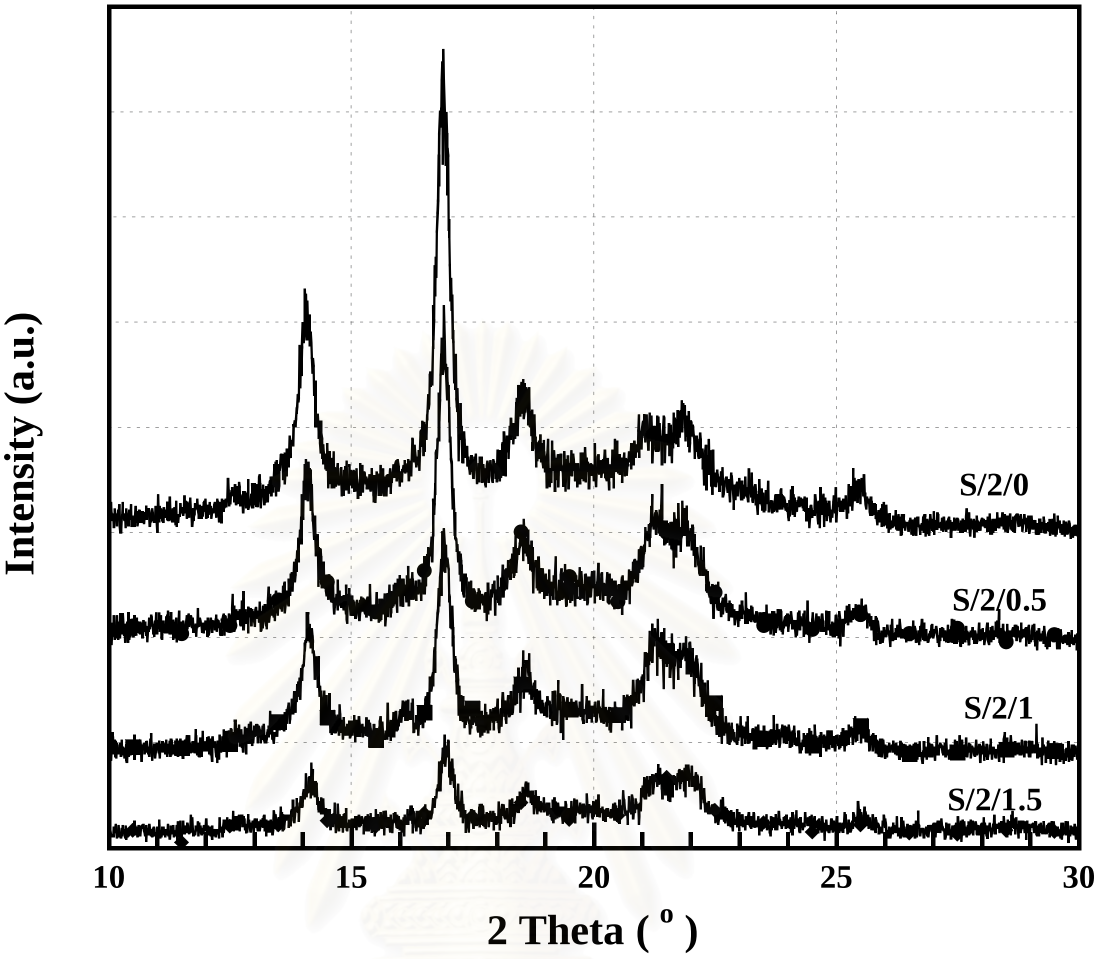


Figure 5.22 XRD patterns of nanocomposites at different filler contents.

5.2.5 Thermal Properties

The thermal characterized of nanocomposites at different Org-MMT content. The DSC curves were shown in figure 5.23. The heating scanning melting temperature of the PP component were 3-4°C lower than neat PP and Ny6 component in these nanocomposites were about 2-3°C lower than that of the neat Ny6. According to Chow et. al.(7) hydrogen bonding could form between the amide group of the PP-Ny6 copolymer and the surfactant of organoclay. The hydrogen bonding occurred between Ny6 and surfactant of organoclay. It tended to interference crystal structure and weak interchain attraction of the Ny6 structures. Furthermore, the Org-MMT had an influence on the crystallinity (%) as shown in table 5.4. Though the organoclay reduced the total crytallinity of the matrix but it did not change in cryslline phase, which increased the resistance to the movement of polymer chains under stress and improved tensile and flexural properties.

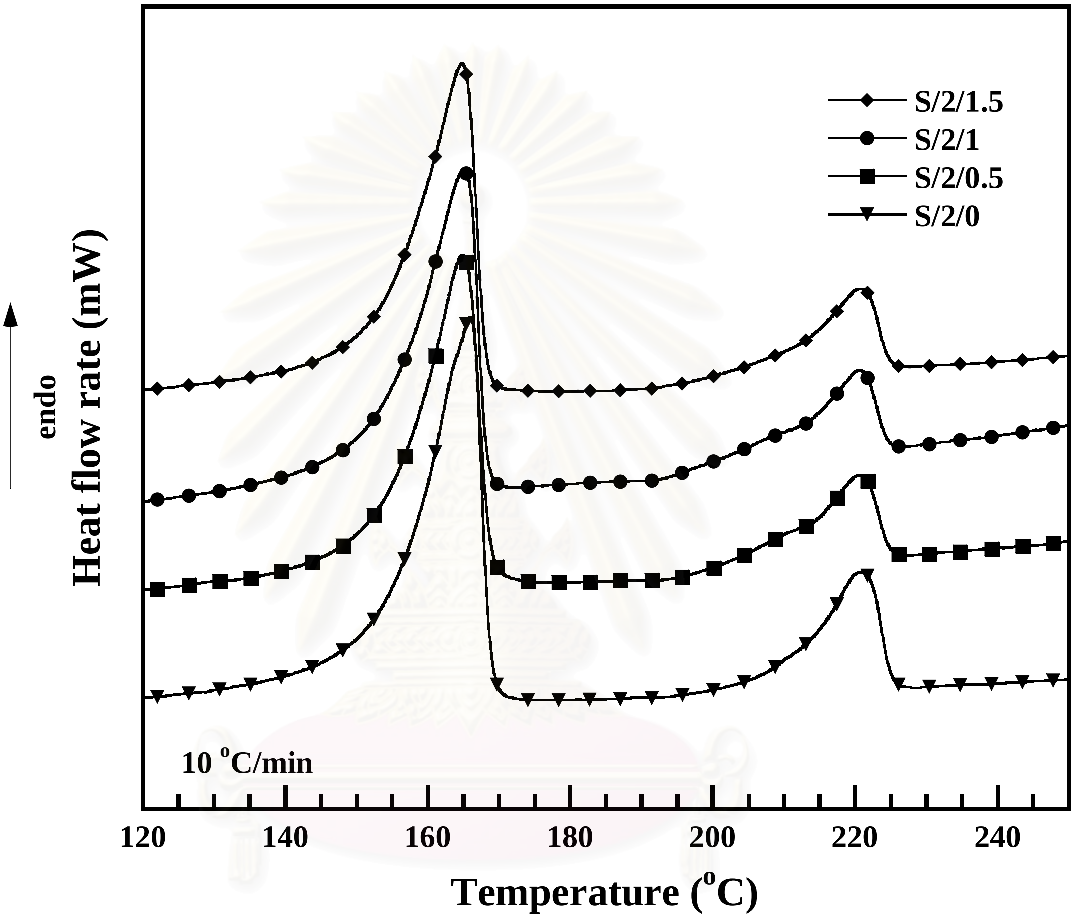


Figure 5.23 DSC thermogram of nanocomposites at different filler contents.

Table 5.3 Crystallinity of nanocomposites at different filler contents.

The amount of organoclay (Org-MMT)	Crystallinity of Polypropylene (%)	Crystallinity of Nylon 6 (%)
Pure	59.31	38.79
S/2/0	45.72	9.57
S/2/0.5	42.07	8.17
S/2/1	41.95	7.98
S/2/1.5	44.52	7.91

5.2.6 Flow Behavior

Many industrial processes are affected by the influence of filled-materials on the flow properties of material. Flow properties of materials can be adjusted by fillers to meet the requirements. Flow properties can also be adversely affected by numerous phenomena related to the presence of filler in formulations. One common example is related to the flow of industrial slurries which contain concentrated suspensions of small particles.(9). Such suspensions are usually non-Newtonian fluids with a stress which is formed through strong interactions between fillers. During flow, these interactions are continuously broken and rebuilt. These properties can be more precisely measured by rheometry. Figure 5.24 showed how various Org-MMT cause stress increase in range 0.01-1 $s^{-1}$of shear rate. Moreover, the increment of Org-MMT had an influence on steady shear viscosity (η) on shear rate (s^{-1}) at 230^{o}C for nanocomposites as figure 5.25. The shear viscosity of the nanocomposites with range from 2.3 wt% to 6.7 wt% Org-MMT loading showed significantly higher zero-shear viscosities and observed a decreasing trend of shear viscosity with an increase in shear rate. For example S/2/0.5, S/2/1, S/2/1.5 were added, the apparent viscosity at low shear rate were 3220, 4622 and 8251 Pa.s. Particularly, the interaction between clay layers becomes stronger at higher clay contents as the distance between layers become smaller. Controversy, high shear rates because a breakdown in network structure and layered silicate become oriented in the flow direction, contribute to shear thinning behavior observed in the nanocomposite. Therefore, all sets of polymer nanocomposite melts exhibited shear thinning behavior (i.e. pseudoplasticity). Shear thinning its self may be attributed to a disentanglement of chains, orientation in flow direction, and structure deformation-all resulting from increase or shear rate. The high zero-shear viscosities of nanocomposites indicated that at low shear rate the nanostructure of these materials consist of a strong interaction between dispersed clay layers and polymer chain. As observed in many filled systems, the steady shear viscosity of the layered silicate nanocomposites depends on the clay content and interactions between the clay particles(21).

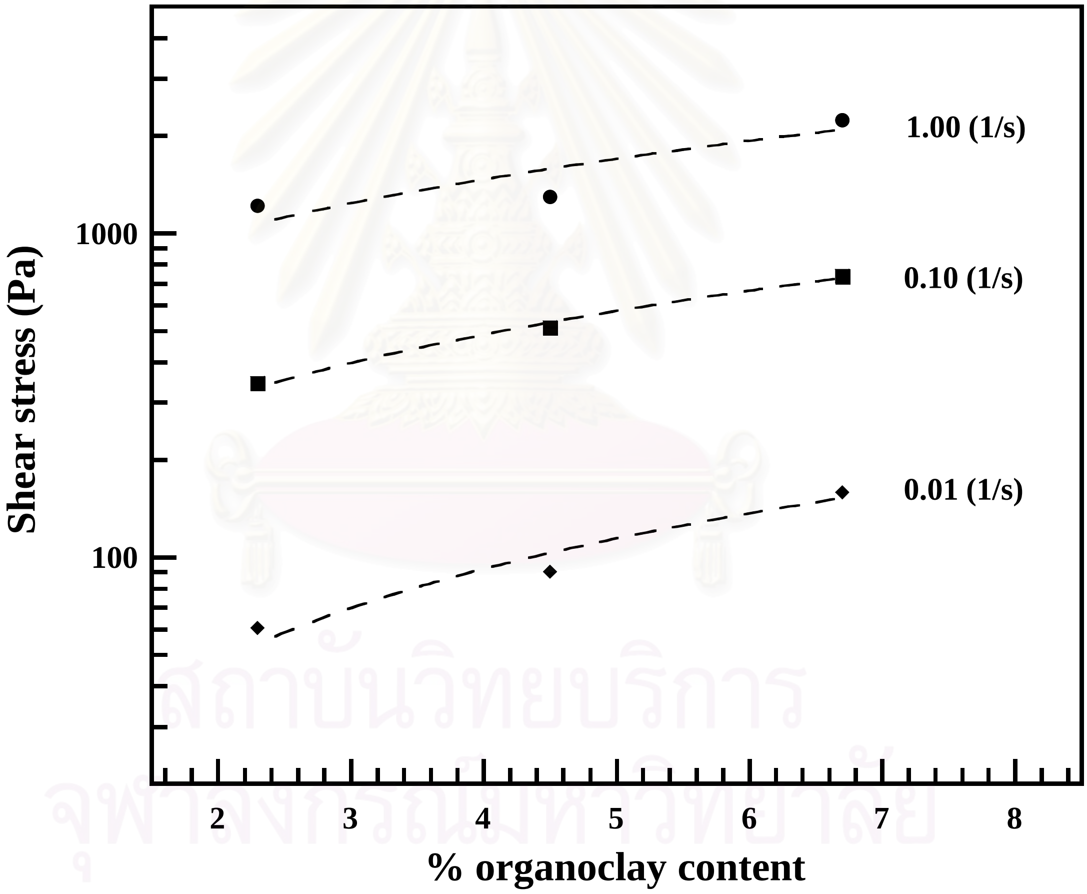


Figure 5.24 Shear stress of nanocomposites at different filler contents.

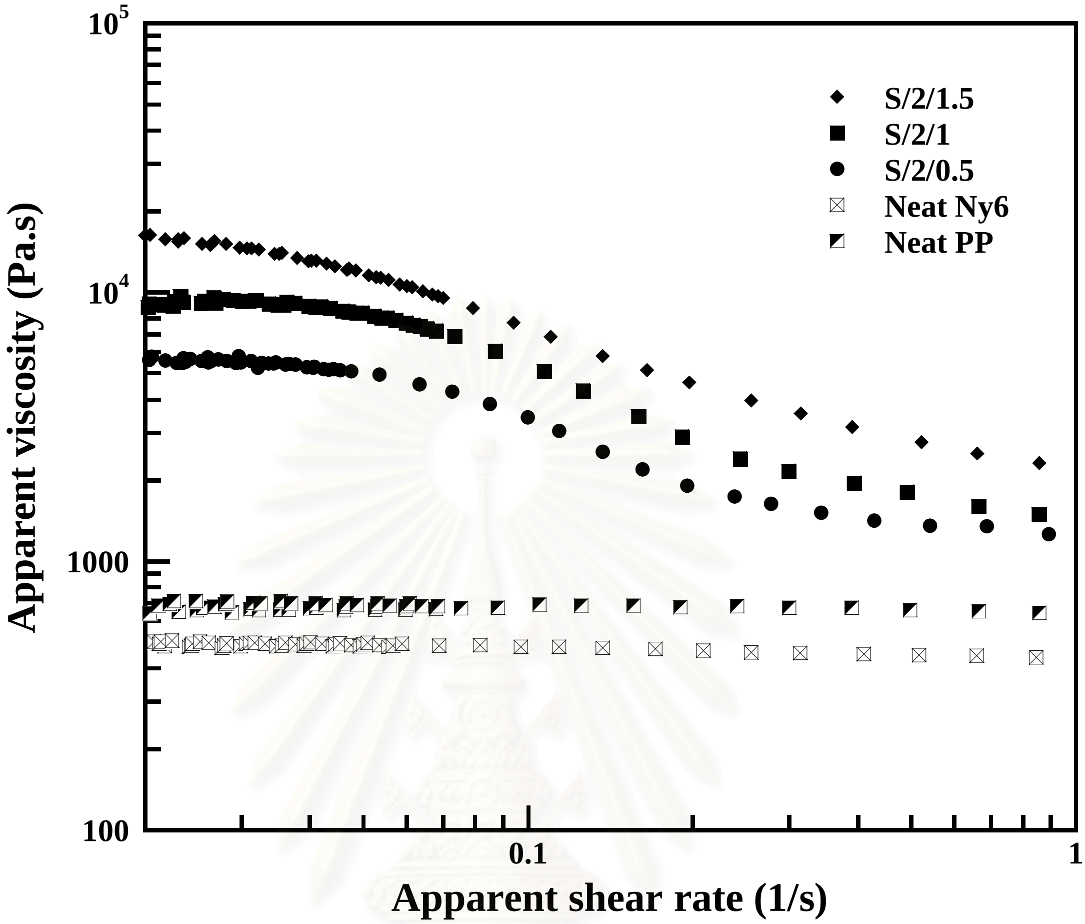


Figure 5.25 Flow behavior of nanocomposites at different filler contents.

CHAPTER VI

CONCLUSIONS

These results suggest that both of compatibilizer and organoclay have significant effects on mechanical properties and rheological properties of the composites. Additions of compatibilizer can effectively adhesion between phases by occurring co-polymer whereas organoclay helps improve mechanical properties. The results can be summarized as follows.

The compatibility and dispersion of organoclay increased when compatibilizer, PP-MA increased comparing at the same organoclay content. Increasing loading level of compatibilizer in range 2.5-13.3 wt% caused an increased intreraction at the interface, improved interfacial tension and leaded to decreasing size of dispersed phases (Ny6) in PP matrix, which were reason of rendering enhancing mechanical properties of our nanocomposite systems. The tensile properties were not noticeably affected by increasing the compatibilizer. Moreover, the flexural properties were relatively high at S/2/0.5. Moreover, adding of compatibilizer increased d-spacing of layered silicate in nanocomposites from 2.19-2.25 nm by lower angle (1-10 °C) XRD. Wide angle (10-30°C) XRD can be indicated that co-polymer between PP-MA and Ny6 reduced the degree of crystallinity both PP and Ny6 phase but did not change in crystalline structure. However, increasing levels of compatibilizers higher than 4.9wt% caused a decreasing trend of flow properties. This may be attributed to the chemical interaction between phases of the nanocomposites by compatibility, which consist of segments chemically reactive to their respective counterparts in the polymer pairs.This section indicated that there is route for improving tensile modulus and flexural modulus of nanocomposites by improving interfacial tension between phases.

Incorporation of organoclay improved the tensile modulus value by 30% and and slightly increased of flexural modulus as expected owing to its exfoliation/intercalation, which confirmed these results by XRD and TEM. The storage modulus of all nanocomposites, which was considered at lower than glass transition temperature, has more storage modulus value than matrix. The glass transition temperature increased with increasing Org-MMT loading due to the contribution of the strong interaction between the Org-MMT and the polymer matrix, and Org-MMT restricted the mobility of polymer matrix, which decreased the degree of crystallinity of PP and Ny6 phases. The interaction between layered silicate became stroger at a higher Org-MMT content as the distance between layers become smaller. S/2/1.5 had the highest viscosity at a low shear rate. This section indicated that the incorporation of Org-MMT improved the tensile and flexural modulus and reduced ductility owing to its exfoliated/intercalated structure.

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APPENDICES

APPENDIX A

D-spacing Calculation

The d-spacing of organoclays in polymer nanocomposites was calculated by Bragg’s law equation as shown below.

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

where n = integer

λ = wavelength, 1.542 ^{o}A

d = d-spacing of organoclay

θ = diffraction angle

Diffraction angle of organoclay powder was measured by XRD. The value of 2θ peak is 4.39° which we can calculate d-spacing of powder showing as follow.

$$(1)(1.542) = 2d \sin (4.39/2)$$

$$d = 19.9\ ^{o}\mathrm{A}$$

APPENDIX B

Crystallinity Calculation

The crystallinity was calculated using an extrapolated value of enthalpy corresponding to the melting of 100% crystalline sample:

$$\% \text{ Crystallinity} = \frac{\Delta H^*_f \times 100}{\Delta H^\circ_f}$$

where $\Delta H^\circ_f = 137.9$ J/g
ΔH°_f (Ny6) = 190 J/g

Heat of fusion was determined by DSC thermogram. The value of enthalpy of PP is 58.06 J/g which can be calculated percentage of crystallinity of PP in nanocomposites showing as follow.

$$\% \text{ Crystallinity} = \frac{58.06 \times 100}{137.9}$$

$$= 42.1 \%$$

VITAE

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