# การปรับปรุงสมบัติเชิงกลของวัสดุเชิงประกอบพอลิโพรพิลีน / เยื่อกระดาษหนังสือพิมพ์ที่ผ่านการดัดแปรพื้นผิว

นางสาว ทัศนีย์ พุทธนา

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิทยาศาสตรมหาบัณฑิต
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# MECHANICAL PROPERTIES IMPROVEMENT OF POLYPROPYLENE / SURFACE – MODIFIED NEWSPAPER PULP COMPOSITES

Miss Tassanee Puttana

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for the Degree of Master of Science in Applied Polymer Science and Textile Technology
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Accepted by the Faculty of Science, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master’ s Degree

……………………………………………. Dean of Faculty of Science
(Associate Professor Wanchai Phothiphichitr, Ph.D.)

THESIS COMMITTEE

……………………………………………. Chairman
(Associate Professor Saowaroj Chuayjuljit)

……………………………………………. Thesis Advisor
(Duangdao Aht – Ong, Ph.D.)

…………………………………………….. Member
(Associate Professor Paiparn Santisuk)

…………………………………………….. Member
(Associate Professor Werasak Udomkichdecha, Ph.D.)

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แนวทางในการลดปัญหาขยะจำพวกกระดาษ เช่น กระดาษถ่ายเอกสาร กระดาษหนังสือพิมพ์ นอกจากการนำกระดาษเหล่านี้มาผลิตเป็นกระดาษรีไซเคิลแล้ว การนำกระดาษที่ใช้แล้วมาแปรสภาพเป็นตัวเสริมแรงในวัสดุเชิงประกอบเพื่อทดแทนการใช้เส้นใยสังเคราะห์ซึ่งมีราคาแพง นับเป็นอีกวิธีการหนึ่งที่ช่วยเพิ่มมูลค่าของวัสดุเหลือใช้ ในงานวิจัยนี้จึงศึกษาการเตรียมวัสดุเชิงประกอบระหว่างพอลิโพรพิลีนและเยื่อเซลลูโลสจากกระดาษหนังสือพิมพ์เก่า อย่างไรก็ตามเนื่องจากปัญหาความไม่เข้ากันและขาดการยึดติดระหว่างเนื้อพลาสติกและเยื่อเซลลูโลส ทำให้สมบัติเชิงกลของวัสดุเชิงประกอบที่เตรียมได้ไม่ดีเท่าที่ควร ในงานวิจัยนี้จึงใช้สารช่วยผสมคือ พอลิโพรพิลีนกราฟต์มาเลอิกแอนไฮไดรด์ (MAPP) เพื่อปรับปรุงการยึดติดระหว่างองค์ประกอบทั้งสองเปรียบเทียบกับการปรับปรุงพื้นผิวของเยื่อเซลลูโลสโดยการทำปฏิกิริยาเอสเทอริฟิเคชันด้วยแอซิดคลอไรด์ชนิดหนึ่งคือ โดเดคคาโนอิล คลอไรด์ (dodecanoyl chloride) ผลการทดสอบของวัสดุเชิงประกอบพบว่า MAPP เป็นสารช่วยผสมที่ดีและเหมาะสมสำหรับการเตรียมวัสดุเชิงประกอบชนิดนี้ นั่นคือ ทำให้สมบัติเชิงกลของวัสดุเชิงประกอบที่เตรียมได้มีค่าสูงกว่าวัสดุเชิงประกอบที่ไม่มี MAPP เป็นสารช่วยผสม ในทำนองเดียวกัน การปรับปรุงพื้นผิวของเยื่อเซลลูโลสด้วยปฏิกิริยาเอสเทอริฟิเคชันนั้นพบว่า สามารถส่งเสริมความเข้ากันระหว่างเยื่อเซลลูโลสจากกระดาษหนังสือพิมพ์เก่า และพอลิโพรพิลีน อีกทั้งยังช่วยเพิ่มความสามารถในการยืดตัว (elongation) และช่วยเพิ่มเสถียรภาพทางความร้อนของวัสดุเชิงประกอบ แต่ในด้านความแข็งแรงจะต่ำกว่าวัสดุเชิงประกอบที่ใช้ MAPP เป็นสารช่วยผสม และเมื่อเปรียบเทียบสมบัติเชิงกลของวัสดุเชิงประกอบทั้งหมดพบว่า วัสดุเชิงประกอบระหว่างพอลิโพรพิลีนและเยื่อกระดาษหนังสือพิมพ์ปริมาณ 20 เปอร์เซ็นต์โดยน้ำหนัก ซึ่งมี MAPP เป็นสารช่วยผสมที่ปริมาณ 10 เปอร์เซ็นต์โดยน้ำหนักของเยื่อกระดาษหนังสือพิมพ์มีสมบัติเชิงกลที่สูงที่สุด

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| ภาควิชา วัสดุศาสตร์ | ลายมือชื่อนิสิต ........................................ |
| สาขาวิชา วิทยาศาสตร์พอลิเมอร์ประยุกต์ฯ | ลายมือชื่ออาจารย์ที่ปรึกษา........................... |
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# # 4272286323 : MAJOR APPLIED POLYMER SCIENCE AND TEXTILE TECHNOLOGY
KEY WORD : polypropylene / surface modification / composite / newspaper

TASSANEE PUTTANA : MECHANICAL PROPERTIES IMPROVEMENT OF POLYPROPYLENE / SURFACE – MODIFIED NEWSPAPER PULP COMPOSITES. THESIS ADVISOR : DR. DUANGDAO AHT – ONG. 138 pp.
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Besides reuse or recycling which are the direct methods to reduce the amount of waste papers such as magazines or newspapers, attempt has been made to use these papers as the reinforcing filler in composite materials. This approach is not only to replace the use of expensive synthetic fibers, but also to increase the value added of these materials. In this work, a newspaper pulp reinforced polypropylene (PP) composite was made. However, the main problem in preparation of this type of composite is the incompatibility and poor interfacial adhesion between the newspaper pulp and PP matrix, resulting in poor mechanical properties. Thus, maleic anhydride grafted polypropylene (MAPP) was used as coupling agent to improve the interfacial bond strength between the two phases. For comparison, the esterification reaction using dodecanoyl chloride was adopted to modify surface of the newspaper pulp prior to mix with the PP matrix. Experimental results revealed that the MAPP was a good coupling for newspaper pulp / PP composites. The mechanical properties of the composites with MAPP were better than the ones without MAPP. Likewise, the surface modification by esterification reaction helped promoting the compatibility between the newspaper pulp and PP. Although, comparing to the MAPP – newspaper pulp / PP composites, the strength of esterified – newspaper pulp / PP composites was lowered; it was found that this surface treatment increased the flexibility, elongation at break and thermal stability of the composites. In conclusion, the polypropylene / 20% newspaper pulp with 10% MAPP by weight of newspaper pulp composite showed the highest mechanical properties.

Department Materials Science Student's signature………………..
Field of study Applied Polymer Science and Textile Technology Advisor's signature………………..
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## CHAPTER I

# INTRODUCTION

The utilization of thermoplastics and composites has increased tremendously in recent years. Considerable efforts have also been made to find suitable reinforcing fillers. Using reinforcing fillers can reduce costs and, at the same time, improve certain properties of materials. Inorganic reinforcing fillers such as glass fibers, carbon fibers and organic reinforcing fillers such as aramid fibers are very expensive. Moreover, it can cause some damages to the equipments during processing. On the other hand, organic reinforcing fillers, in particular cellulose fibers, show low cost per unit volume and flexibility during processing with less abrasive to the equipments. Other benefits of composite materials based on cellulose fibers include high specific stiffness and strength, desirable fiber aspect ratio, low density, and biodegradability. Also, they are readily available. Thus, cellulose fibers are attractive alternatives for reinforcing thermoplastics. Some examples are cotton, flax, jute, ramie, sisal, abaca, pineapple, kanaf, bamboo, etc. Of these fibers, jute, ramie, flax, and sisal are the most commonly used fibers for polymer composites. Nevertheless, cellulose fibers seem to have little resistance towards environmental influences. This drawback can, in turn, be advantageously utilized for the development of biological degradable composites.

Paper is made from cellulose fibers usually from wood or cotton waste. The demanding and consumption of paper in daily life are still very high and increasing every year, leading to waste problem. In view of the amount of wastepaper, such as from newspaper, magazines, and packaging, it is imperative to find ways to reuse these wastepapers. A great deal of interest has been generated in the use of the wastepapers as reinforcing fillers in thermoplastic composites such as in polypropylene. Polypropylene, one of the widely used thermoplastics, can be used in many applications such as in packaging, owing to its low cost, ease of processing, to name but a few.

Inspite of the advantages stated above, use of cellulose fibers or newspaper fibers in thermoplastics has not been extensive. Possible reasons, all of which contribute to unsatisfactory final properties of the composites, include limited thermal stability during processing, poor dispersion in the thermoplastic melt, and limited compatibility with the matrix. However, the main problem in preparation of this composite is the incompatibility between the hydrophilic newspaper fibers and the hydrophobic thermoplastic matrix. Without any modifications of these raw materials, the fiber will disperse within the matrix without sufficient interaction between the two components; hence, the properties of the composites are poor.

In general, to achieve compatibility between fiber – matrix interface, physical and chemical surface modifications of fiber can be employed. In other words, modification of cellulose fibers has been attempted to make the fibers hydrophobic and to enhance interfacial adhesion between the fiber and the matrix. Stretching, calendering, thermotreatment, and electric discharge (corona, cold plasma) are defined as physical methods. They do not change the chemical composition of the fibers, but structural and surface properties and thereby influence the mechanical bonding to polymer matrix. Chemical treatments such as dewaxing, delignification, bleaching, acetylation, chemical grafting, and so on provide a bridge of chemical bonds between fiber and matrix.

In addition to the surface treatment of fibers, such problem has often been overcome with the addition of a proper compatibilizer or a coupling agent. The effect is to lower the interfacial tension and to promote the adhesion, dispersion, and compatibility between the components. These agents are usually tetrafunctional organometallic compounds based on silicon, titanium, and zirconium, and are commonly known as silane, titanate, and zirconate coupling agents, respectively. At present, another well - known compatibilizer is olefin – maleic anhydride which can from covalent and hydrogen bonds across the interface.

In this study, a composite made of old newspaper and polypropylene has been developed. The blending of newspaper pulp and polypropylene matrix was done by a two – roll mill. After compounding, the composite sheet was removed from the two – roll mill and ground by a grinder. The premix was then proceeded in a twin screw extruder. The extrudate was subsequently cooled in water and pelletized by a granuator. Finally, the compound pellets were moulded by an injection moulding. In this work, fiber content was varied from 5% to 20%. In order to enhance the compatibility between newspaper pulp and polypropylene, two approches for modifying interfacial adhesion of newspaper pulp were adopted. The first method was an esterification reaction by dodecanoyl chloride. Maleic anhydride grafted polypropylene (MAPP) was used as a coupling agent in the second method to improve the interfacial adhesion of the composite. The effects of fiber contents, compatibilizer, and surface modification were evaluated in terms of mechanical properties, thermal properties, morphological properties, and water absorption.

# CHAPTER II
# LITERATURE SURVEY

## 2.1 Composite Materials

Composite materials can be defined as a complex solid material consisting of two or more separated materials, combined in a macroscopic structure unit [1]. Composites are generally used because they have desirable properties which could not be achieved by either of the constituent materials acting alone. Many composite materials comprise just two phases, the matrix, which is continuous and surrounds the second phase, the reinforcement.

The matrix generally performs the function of binder to transfer stress to the reinforcements and ensure their cooperative interaction. The matrix may be metals, ceramics, and polymers. Both thermosets and thermoplastics can be used as the matrix for polymer – based composites.

Reinforcements give strength and stiffness to the composites and can be either fibers, whiskers, or particles. Fibers are the most important and have the largest effect on the composite properties. Fiber – reinforced composite materials consist of fibers of high strength and modulus embedded in a matrix with distinct interfaces between them. In general, the fibers are the principle load – carrying members, whereas the surrounding matrix keeps them in the desired location and orientation, acts as a load transfer medium between them, and protects them from environmental damages due to elevated temperature or humidity. The principle fibers in commercial use are various types of glass and carbon, as well as, aramid fibers. All these fibers can be incorporated in to a matrix either in continuous or in discontinuous (chopped) lengths. A numbers of commercially available fibers and their properties are listed in Table 2.1. Details of each fibers were briefly highlighted. More details can be found elsewhere [2].

Table 2.1 Properties of Some Commercial Reinforcing Fibers [2]

| Fiber | Typical Diameter (μm) | Specific Gravity | Tensile Modulus (GPa) | Tensile Strength (GPa) | Strain to Failure (%) | Poisson's Ratio |
|---|---|---|---|---|---|---|
| *Glass* | | | | | | |
| E – glass | 10 | 2.54 | 72.4 | 3.45 | 4.8 | 0.2 |
| S – glass | 10 | 2.49 | 86.9 | 4.30 | 5.0 | 0.22 |
| *PAN carbon* | | | | | | |
| T – 300 | 7 | 1.76 | 231 | 3.65 | 1.4 | 0.2 |
| AS – 1 | 8 | 1.80 | 228 | 3.10 | 1.32 | |
| IM – 7 | 5 | 1.78 | 301 | 5.31 | 1.81 | |
| GY – 70 | 8.4 | 1.96 | 483 | 1.52 | 0.38 | |
| *Pitch carbon* | | | | | | |
| P – 55 | 10 | 2.0 | 380 | 1.90 | 0.5 | |
| P – 100 | 10 | 2.15 | 758 | 2.41 | 0.32 | |
| *Aramid* | | | | | | |
| Kevlar 49 | 11.9 | 1.45 | 131 | 3.62 | 2.8 | 0.35 |
| Kevlar 149 | | 1.47 | 179 | 3.45 | 1.9 | |
| Technora | | 1.39 | 70 | 3.0 | 4.4 | |
| *Extended chain Polyethylene* | | | | | | |
| Spectra900 | 38 | 0.97 | 117 | 2.59 | 3.5 | |
| *Boron* | 140 | 2.7 | 393 | 3.1 | 0.79 | 0.2 |
| *SiC* | | | | | | |
| Nicalon | 14.5 | 2.55 | 196 | 2.75 | 1.4 | |
| $Al_2O_3$ | 20 | 3.95 | 379 | 1.90 | 0.4 | |

### 2.1.1 <u>Glass Fibers</u>

Glass fibers are the most widely used of all reinforcements for plastic materials. Glass fibers are produced by drawing monofilament of glass from a furnace containing molten glass, coating the monofilament with a polymer to “ dull “ any surface craking, and gathering a large number of this filament to from a strand of glass fibers [3]. Advantages of glass fibers over other reinforcements include a favorable cost/performance ratio with respect to dimensional stability, corrosion resistance, heat resistance, and ease of processing. The major types of glass fibers are E-glass, S-glass, and C-glass. Fiber strength decreases greatly with surface defects and with moisture absorption. The surface of glass fiber can be treated with a size finish or coupling agent to improve the mechanical properties. Glass fibers are mainly used for non-critical applications.

### 2.1.2 Carbon Fibers

Carbon fibers have a combination of very high strength, low density, and high elastic modulus. These properties make the using of carbon fibers for critical uses such as in advance composites and aerospace applications. Carbon fibers are produced mainly by two sources, polyacrylonitrile (PAN) and pitch, which usually called precursors [3]. In general, carbon fibers are produced from PAN precursor by three processing stages. The first stage is stabilization, the PAN fibers are stretched to align the fibrillar network within each fiber paralled to the fiber axis, then they are oxidized in air about 200 - 220$^{\circ}$C while held in tension in order to provide crosslinking between the fibers to avoid melting at the next stage. In the second stage, carbonization, the crosslinked fibrils are pyrolyzed untill they become transformed into carbon fibers by the elimination of O, H, and N from the PAN fibers. The third stage, graphitization, involves complete conversion of the fiber to oriented graphite crystal form by heating to 2000$^{\circ}$C while under tension. A surface treatment is important in improving the fiber mechanical properties. Carbon fibers have very high specific strengths and moduli.

### 2.1.3 Aramid Fibers

### 2.1.3 Aramid Fibers

The most common organic fibers for composite reinforcements are the aramids and the most common brand name is Kevlar by the DuPont Corporation. Aramid fibers are tougher than glass or carbon fibers and are often used in ballistic applications and damage control. The chemical repeating unit of the Kevlar polymer chain is that of an aromatic polyamide in Figure 2.1.

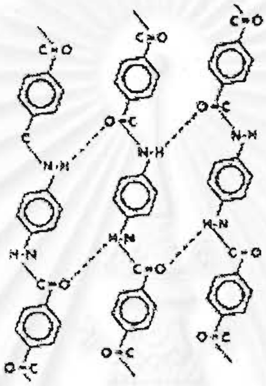


Figure 2.1 Chemical structure of Kevlar.

Kevlar aramid is used for high performance composite applications where light weight, high strength, stiffness, impact, and fatigue resistance are important.

### 2.1.4 Polyethylene Extended-chain Fibers

Polyethylene (PE) fibers, known as Spectra, are produced by solution spinning a high molecular weight PE. Two outstanding features of these fibers are low moisture absorption (1% compare to 5-6% for Kevlar 49) and high abrasion resistance, which make them very useful in marine composites, such as boat hulls and water skis. However, their use in high temperature is limited (about 120°C) beyond this temperature the fibers lose their strength.

### 2.1.5 Mineral Fibers

Mineral fibers such as asbestos although has an excellent high strength and is a low cost reinforcement, it has been the subject of much legislation, regulation, and litigation in view of the potentially adverse health effects resulting from excess inhalation of free fibers. As a result, material supplier and fabricator no longer utilize asbestos in composites [4].

### 2.1.6 Ceramic Fibers

Ceramic fibers (other than glass fibers) include alumina, boron, silicon carbide, alumina-silica, and other metal oxide-silica fibers. Boron and silicon carbide continuous fibers are made by chemical vapor deposition using other high modulus fiber, such as tungsten and carbon, as the substrates. The high cost of these fibers limited their uses even though they have very high modulus and strength. The other physical properties of these reinforcements in matrices compare with glass fibers and other fibers are high compressive strength and retention of properties at elevated temperatures.

### 2.1.7 Metal Fibers

Metal fibers include stainless steel, aluminium, and nickle – plated glass or carbon fibers. These fibers are typically used in composites intended for applications requiring electrostatic charge dissipation or electromagnatic frequency shielding. They are not optimal for reinforcing since they tend to curl up during processing, but the low concentration of fiber, 5 – 10% required to achieve satisfactory shielding performance usually does not degrade the mechanical properties of composites based on them to unaccepTable levels. Stainless steel fibers are the most widely used at present.

### 2.1.8 Natural Fibers

Natural fibers are used almost exclusively in low-severity applications for thermoset composites. Some examples are cotton, ramie, jute, flax, sisal, and abaca fibers. Of these fibers, jute, ramie, flax, and sisal are the most commonly used fibers for polymer composites.

Natural fibers themselves are cellulose fiber reinforced materials as they consist of microfibrills in an amorphous matrix of lignin and hemicellulose. The chemical composition of natural fibers varies depend upon the type of fiber. Primarily, fibers contain cellulose, hemicellulose, pectin, and lignin. Hemicellulose is responsible for the biodegradation, moisture absorption, and thermal degradation of the fibers as it shows least resistance whereas lignin is thermally sTable but is responsible for ultraviolet degradation. Genarally, the fibers contain 60-80% cellulose, 5-20% lignin, and up to 20% moisture. The hydrogen bonds and other lingkages provide the strength and stiffness to the fibers. The properties of natural fibers are shown in Table 2.2.

Table 2.2 Mechanical Properties of Natural Fibers [2]

| Fiber | Specific Gravity | Tensile Strength ( MPa ) | Modulus ( GPa ) | Specific Modulus (Gpa) |
|---|---|---|---|---|
| Jute | 1.3 | 393 | 55 | 38 |
| Sisal | 1.3 | 510 | 28 | 22 |
| Flax | 1.5 | 344 | 27 | 50 |
| Sunhemp | 1.07 | 389 | 35 | 32 |
| Pineapple | 1.56 | 170 | 62 | 40 |
| E – glass | 2.5 | 3400 | 72 | 28 |

As can be seen from Table 2.2, the tensile strength and modulus of glass fibers are substantially higher than natural fibers. But when the specific modulus of natural fibers (modulus/specific gravity) is considered, the natural fibers show properties that are comparable to or better than glass fibers. The higher specific properties are one of the major benefits of using natural fiber composites for applications wherein the desired properties also include weight reduction. Other advantages of using natural fibers are low cost, biodegradable, and nonabrasive, unlike other reinforcing fibers. However, they have undesirable properties such as dimensional instability as a result of moisture absorption and low heat resistance, i.e, strength loss sets in around 124°C and thermal degradation commences around 163°C.

## 2.2 Natural Fibers Polymer Composites

In view of the amount of natural fibers, natural fibers polymer composites are attractive ways to improve the properties of polymer over other conventional materials. Natural fibers have recently attracted the attention of scientist because of the following reasons.

1. These fibers, despite their low strength, can lead to composites with high specific strength because of their low density.
2. These fibers are biodegradable, nontoxic, and nonabrasive, unlike other reinforcing fibers.
3. They are readily available.

Both thermosets and thermoplastics are attractive as matrix materials for natural fiber composites. Using thermoplastics offer many advantages over thermosets. For example, molding temperatures of thermoplastics are lower than thermosets, leading to low processing costs. In addition, simple method such as extrusion and injection molding can be used for processing of thermoplastic composites. Another advantage is design flexibility and ease of molding complex parts. Thermoplastics such as PE, PP, PS, and PVC are mostly used as a matrix because the processing temperature is limited to below 200°C to avoid thermal degradation of natural fibers.

However, the main problem of these composites is incompatibility between the hydrophilic natural fibers and the hydrophobic polymer matrix. Thus, they have a tendency to form aggregates. Without any modifications of these raw materials, the fibers will disperse within the matrix without sufficient interaction between the two components. As a result, the properties of the composites are poor.

## 2.3 Modification of Natural Fibers

The incorporation of the hydrophilic natural fiber in polymer leading to heterogeneous systems whose properties are inferior owing to lack of adhesion and compatibility between the fiber and the matrix. To achieve compatibility between the two components, physical and chemical surface modifications of the fibers can be applied.

### 2.3.1 Physical Methods for Surface Modification of Natural Fibers

Reinforcing fibers can be modified by physical methods, such as stretching, calendering, thermotreatment, and electric discharge (corona, cold plasma), which do not change the chemical composition of the fibers. Physical treatments change structure and surface properties of the fiber and thereby influence the mechanical bonding in the matrix.

Corona treatment is one of the most interesting techniques for surface oxidation activation. This process changes the surface energy of the fibers. Electrical discharge methods are known to be very effective for nonactive polymer substrates such as PS, PE, and PP.

The field of material surface modification by "cold" low pressure plasma and corona has undergone enormous expansion, particularly in the surface modification of polymeric materials for improving adhesion. This is because undesirable physical characteristic of polymer is low surface energy and their resulting intrinsically poor adhesion. Generally, adhesion is defined as the mechanical resistance to separation of a system of bonded materials.

### 2.3.1.1 Cold and Low Pressure Plasma Process

A plasma may be briefly defined as a partially ionized gas with equal number densities of electron and positives ions, in which the charged particles are "free" and possess collective behavior [5]. Cold plasma occurs at low pressure, 13 to 133 Pa (0.2 to 1 Torr), high frequency, the heavy particles (gas molecules and ions) are essentially at room temperature, while the electrons have enough kinetic energy to break covalent bonds of materials and even to cause further ionization. Chemically reactive species thus created can partake in homogeneous (gas - phase) , or heterogeneous reactions with solid surface in contact with plasma. Since this type of plasma chemistry take place at near ambient tempareture, it is well – suited for processing thermally sensitive materials such as semiconductors and polymers

In the case of polymer matrix composite, the plasma treatment of the filler can be very effective in promoting adhesion because of the large treated surface area. The modification of interfaces not only enhance the bond strength between the components, but it can also improve the electrical and ageing characteristics of the composite by reducing the penetration of water vapour and other contaminants.

### 2.3.1.2 Corona Discharges

Corona occurs at atmosphere pressure, usually under highly nonuniform electric fields. A typical corona discharge, as it was first implemented, occurs on electrode with sharp edges or small radii of curvature. Later, the term was extended to describe discharge between flat electrodes coated with a dielectric material. In this latter situation, an arc cannot develop since the dielectric interrupts the conductive path, and allows only an incomplete breakdown of the gas. Instead of a hot, localized arc, a cooler, diffuse glow develops between the electrode. Beside a continuous corona current, there also exist avanlanches and plasma channels (arcs, streamers) with a random character. Streamers represent much higher current pulses then avalanches, and they play an important rule in surface modification. The so – called corona inception voltage decrease with the frequency of the applied high voltage.

Regarding the chemistry of corona discharges, the best known and largest use for many years has been ozone generation either from dry air or flowing oxygen. Corona has long been known as a convenient, relatively inexpensive tools for improving the adhesion of coating and inks to plastic or paper.

### 2.3.2 Chemical Methods for Surface Modification of Natural Fibers

Chemical treatments such as dewaxing (defatting), delignification, bleaching, acetylation, and chemical grafting are used for modifying the surface properties of the fibers and for enhance its properties.

Delignification is generally carried out by extracting with alcohol or benzene, treating with NaOH, and drying at room temperature. Bleaching process results in loss of weight and tensile strength by using many oxidative bleaching agents such as hydrogen peroxide, alkaline calcium, or sodium hypochlorite. These losses are mainly attributed to the action of the bleaching agent on the noncellulosic constituents of fiber such as hemicellulose and lignin.

Acetylation of jute is reported to impart resistance to fungal attack and hydrophobicity. The change in properties is attributed to the decrease in moisture absorption in the cell wall and blocking of the hydroxyl group of the wall components in such a way that enzymes of the wood – degrading microorganism cannot recognize them as attachable substrates. Acetylated jute is considerably more hydrophobic than unmodified jute [18].

Chemical grafting involves attaching to the surface of a fiber/filler a suiTable polymer with a solubility parameter similar to the polymer matrix. It acts as an interfacial agent and improves the bonding between the fiber and the matrix. Moreover, it can alter the physical and mechanical properties of the composites. Graft copolymerization of vinyl monomers such as methyl methacrylate, acrylamide, and acrylonitrile on to cellulose, cellulose derivatives, and lignocellulosic fibers has been extensively studied [18]. Impregnation with monomer followed by its polymerization has also been the common method used for treatment of fibers. Another method that graft copolymerization onto cellulose takes place through an initiation reaction involving attack by macrocellulosic radicals on the monomer to be grafted. The generation of the macrocellulosic radicals is accomplished by many methods such as diazotization, chain transfer reaction, redox reaction, photochemical initiation, and radiation-induced synthesis. The chemical treatment by using sodium alginate and sodium hydroxide have been reported for coir, banana, and sisal fibers. The treatment resulted in an increase in debonding stress and thus improved the ultimate tensile strength. Table 2.3 listed some example of chemical treatment used for modification of natural fibers.

Table 2.3 Chemical Treatments Used for Modification of Natural Fibers [18]

| Fiber | Chemical Treatment | Coupling Agent |
|---|---|---|
| Wood flour | Succinic acid, styrene, urea–formaldehyde,<br>m–phynylene bismalemide, acetic anhydride,<br>maleic anhydride, itaconic anhydride,<br>polyisocyanate, linoleic acid, oxalic acid,<br>rosin | Maleated PP,<br>Acrylic acid<br>Graft PP, Silane,<br>Zirconate,<br>Titanate |
| Jute | Phenol-formaldehyde, malamine-formaldehyde,<br>cardonol-formaldehyde | |
| Sisal | NaOH, isocyanate, sodium alginate,<br>n-substituted mathacrylamide | |

| Fiber | Chemical Treatment | Coupling Agent |
|---|---|---|
| Pineaple | P-phenylene duamine | |
| Banana | Sodium alginate | |
| Coir | Sodium alginate, sodium carbonate | |

Strongly polarized cellulose fibers inherently are little compatible with hydrophobic polymer. When two materials are incompatible, it is often possible to bring intermediate between the two components. The addition of proper compatibilizer or a coupling agent was an another method of the surface treatment that can be used for lowering the interfacial tension and stress transfer across the interface, and promoting the adhesion, dispersion, and compatibilization between the components. Coupling agents are usually (but not limited) used in system of an inorganic filler and organic polymer.

The coupling agents are tetrafunctional organometallic compound based on silicon, titanium, and zirconium and are commonly known as silane, titanate, and zirconate coupling agent.

Silanes

Semi – organic silanes is established for use in fiber reinforced plastics and with special organofunctional groups. They are also important for all types of polymer composites. One important function of filler treatments by silanes is to reduce the inhibitory action of filler on cure of thermosetting resins and to promote alignment of molecular segments of thermoplastic polymers. Some examples of silanes coupling agents structure : $CH_2 = CHSiCl_3$, $CH_2 = CHSi(OC_2H_5)_3$, $ClCH_2CH_2CH_2Si(OCH_3)_3$, $C_6H_5Si(OCH_3)_3$

Titanates

Titanium – derived coupling agents are unique in that their reaction with the free photons at the inorganic interface results in formation of monomolecular layers on the inorganic surface. Absence of polymolecular layers at the interface, together with the chemical structure of the titanates, creates novel substrate surface energy modifications, and polymer phase interactions which often result in reduction in viscosity in unfilled as well as in filled polymer composites. Some examples of titanate coupling agents are [6] :

*Monoalkoxy* : originally designed to take advantage of the universality of stearic acid functionally in composites, its first applications testing was for dispersion of mineral fillers in polyolefins and now it is used very widely.

*Chelate* : offering better stability in wet environments.

*Quat* : designed to offer a water - soluble system.

*Coordinate* : showing significant viscosity reduction in epoxy formulations without producing cure acceleration typical of some monoalkoxy and chelate types.

*Neoalkoxy* : It is developed as coupling agents for high temperature thermoplastics and urethane composites.

Cycloheteroatom : developed for high thermal and speciality applications.

Many reports have studied on natural fiber polymer composites [19 – 27]. In 1991 Felix et al. have stuided the nature of adhesion in composite of modified cellulose fibers and polypropylene [19]. Cellulose fibers were surface modified with polypropylene – maleic anhydride copolymer before compounded with polypropylene. ESCA showed that the modifying agent was localized at the surface of the fibers. FTIR result confirmed that the surface modifying agent is covalently bonded to the fiber through esterification. All mechanical properties were improved when treated fibers were used. Later on, in 1994 Sain et al. have reported that the mechanical properties of wood fiber – filled polypropylene are very poor due to the absence of suiTable interface modifier [20]. However, it was found that use of a suiTable interface modifier such as maleated polypropylene, itaconic anhydride, or bismaleimide – modified polypropylene improved tensile strength and thermal resistance because of the development of a sTable interface.

Two years later, Bledzki et al. have demonstrated the properties and modification methods for vegateble fibers for natural fiber composites [21]. By using a coupling agent, like silanes or stearic acid, the young's modulus and tensile strength increase, dependent on the resin, until 50% of fiber. In the same year, Thiebaud et al. have studied properties of fatty – acid esters of starch and their blend with LDPE [22]. Starch octanoate and starch dodecanoate were prepared by esterification of native starch with fatty acid chlorides and these starch esters were mixed with LDPE. The starch dodecanoate/LDPE blends showed, in general, better thermal stability and higher elongation, but lower tensile strength and water absorption.

After that, in 1997 Fernanda et al. have found that the use of vinyl – tris (2 – methoxy ethoxy) silane with or without maleated polypropylene coating is the best surface treatment for polypropylene – wood fiber composites [23]. The mechanical properties of polypropylene/wood flour composite with ethylene/propylene/diene/ terpolymer (EPDM) and maleated styrene – ethylene/ butylene – styrene triblock copolymer (SEBS – MA) as impact modifiers and maleated polypropylene (MAPP) as a compatibilizer have also reported by Oksman et al.with the same year [24]. All impact modifiers increased the impact strength of the composites and addition of MAPP did not affect the impact properties of the composites but improved tensile strength. Moreover, MAPP had a negative effect on the elongation at break.

Also in 1997, Liao et al. have reported that the wood fibers were treated with titanated coupling agent or grafted by acrylonitrile for wood fibers – reinforced polyethylene [25]. Both treatments resulted in an improvement in the mechanical properties of the composites. Moreover, the grafting method displays a more benefit than titanate method to the mechanical properties improvement. Devi et al. have studied the mechanical properties of pineapple leaf fiber – polyester composites and have found that composites with good strength were obtained by using vinyltri (2–ethoxy methoxy) silane treated pineapple leaf fiber [26]. Recently, the effects of fiber surface pretreatment on the interfacial strength and mechanical properties of wood fiber/polypropylene composites were investigated by Jingshen et al. in 2000 [27]. The WF/PP composite containing fibers pretreated with an acid – silane aqueous solution exhibits the highest tensile properties among the material studied. This observation is a result of the strong interfacial bond caused by the acid/water condition used in the fiber pretreatment.

All of these reports were mostly studied the natural fiber polymer composites and showed that the mechanical properties of the composites were improved by the surface modification of fiber such as using coupling agent. Now attempt to make use of wastepaper as the reinforcing filler in composite materials has drawn an intention of many researchers. Replacing the expensive synthetic fibers with these natural fibers is not only reducing the amount of wastepaper, but also increasing the value – added of these waste materials. In this research, the mechanical properties of the composites made from old newspaper and polypropylene has been investigated.

## 2.4 Wastepaper

Paper is made from cellulose fibers usually from wood or cotton waste. Cellulose is a linear polymer, the molecule of which is composed of glucose units. Because the average degree of polymerization (DP) of cellulose will be several hundred or several thousand glucose units, and since each glucose unit contains three free hydroxyl groups; as a result, the average molecule will contain thousands of hydroxyl groups. Figure 2.2 represents the chemical structure of cellulose.

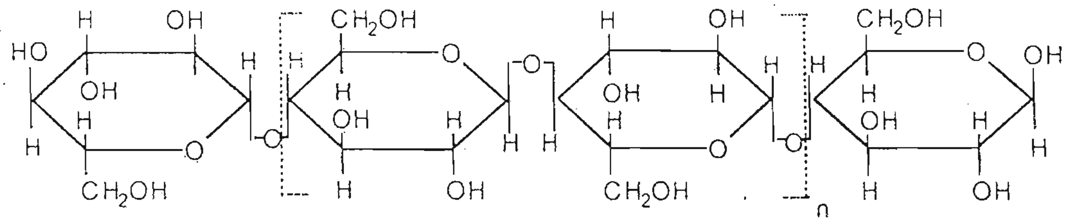


Figure 2.2 Chemical structure of cellulose.

The property of the hydroxyl group which is of the most important to the papermaking is the ability to form hydrogen bonds to oxygen. Such hydrogen bonds contribute to the rigidity and strength of the cellulose fibrillar structure, are a major factor in the formation of the fiber to fiber bonds in paper, and are the cause of the remarkable affinity of cellulose for water. On the other hand, the hydroxyl group is a reactive group. In oxidative degradation of cellulose, the hydroxyl is the first point of attack. It also contributes to thermal degradation, elimination of water being one of the reactions which occur in this process.

### 2.4.1 Use of Wastepaper or Recycled Paper

About 80% of all wastepaper comes from three sources : corrugated boxes, newspaper, and office papers [9]. Less than 20% of wastepaper is deinked to be used in newsprint, tissue, or other bright grades. Most of wastepaper is used in paperboards, clipboards, and roofing materials where color is not important. A great deal of interest has been generated in the use of the wastepaper as reinforcing fillers in thermoplastic composites such as in polypropylene.

### 2.4.2 Recycled Fiber Preparation

The source of recycled fiber is recycled paper. One of the biggest obstacles to using recycled or secondary fiber is effective contaminant removal. Recycling of paper is a process of removing contaminants from the useful fiber including solids such as paper clips, adhesives, and ink. Contaminants can be classified according to their source as follows :

1. *Stickies* are complex chemicals which have their origin in adhesives applied during paper conversion and use. The common sources of stickies are labels and boxes to which hot melt adhesives have been applied. They may enter the process through the polymeric contaminants of secondary fiber including hot melt adhesives (typically consisting of ethylene vinyl acetate – wax – hydrogenated resin acid combinations), wax and polyethylene from coated boxes, contact adhesives (polybutylene, natural rubber, etc), pressure sensitive adhesives (styrene butadiene rubber, carboxylated polybutadiene, and vinyl acetate), polystyrene, and so forth.

2. *Fillers* include calcium carbonate, which can interfere with rosin/alum sizing, clays, and titanium dioxide.

3. *Films and laminates* include polyethylene, aluminium foil, etc.

4. *High density materials* include materials such as glass, grit, sand, etc.

5. *Ink* consists of pigments, such as carbon black or titanium dioxide, to supply color and opacity and a vehicle to carry the pigment and bind it to the paper. The vehicle consists of solvent and resin to bind the pigment to the paper. Traditionally the vehicle was vegeTable oil. Inks may set on the paper by one of the following mechanisms.

- Absorption of the hydrocarbon vehicle into the paper substrate; this type of ink is used in newsprint and tends to smudge.
- Evaporation of the ink vehicle; this is used in magazine and catalog grades using letter press or offset printing with rosin esters and metal binder.
- Oxidation of a drying oil with multifunctional carboxylic acids and alcohols left on the paper surface after the vehicle is absorbed into paper.
- UV or electron beam radiation curing of monomer or prepolymer in the vehicle into polymer such as acrylics.

The size of ink particles is very important. Typically, newsprint ink has very small particle, on the order of 1 – 10 μm, ledger has large particles , on the order of 50 – 1000 μm, and mixed news/magazines grades have intermidiate particle sizes on the order of 1 – 50 μm.

### 2.4.3 Recycled Fiber Recovery

Recycling fiber is the process of separating useful fiber from the contaminants of wastepaper.

*1. Pulping*

Recycled fiber recovery begins at the pulper which is nothing more than a large blender to disperse pulp into an aqueous slurry. Pulping may be done at high or low consistencies using different rotors. During pulping, some of the gross contaminants are removed.

*2. Screening*

Screening is widely employed in wastepaper preparation systems and usually take two forms.

- High consistency coarse screening, at the beginning of stock, preparation to remove large impurities.
- Low consistency fine screening further downstream to remove smaller contaminants such as stickies, fiber bundles, ink flakes, etc.

*3. Centrifugal Cleaning*

Centrifugal cleaning is used to separate contaminants with a significant density difference from fiber and water. Usually contaminants which are heavier than the fiber are removed.

*4. Deinking*

Deinking is the process of removing ink from wastepaper. In addition of high wood costs, recent legislation will change this picture as many states will require recycled fiber in new newsprint as a means of reducing the large quantities of material sent to landfills, of which about 40% is paper. The ink is about 0.5 – 2 % of the mass of the waste paper to be deinked. Figure 2.3 shows the deinking process.

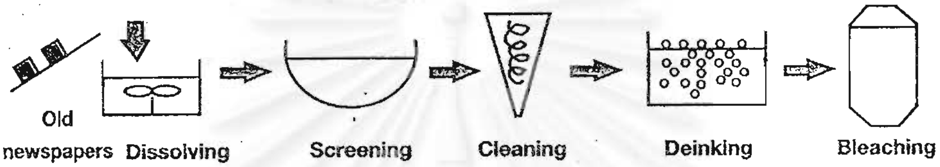


Figure 2.3 Deinking process

The overall deinking process from the point of view of the fiber can be broken down into four steps.

1) Repulping with concomitant ink removal from the fibers.
2) Cleaning and screening operations to remove the bulk of the ink from the stock.
3) Separation of the residual ink contaminants from the fiber stock.
4) Bleaching, if necessary.

A variety of chemicals are used in ink removal including the sodium salts of hydroxide (for fiber swelling, saponification of ester – containing resins, and ink dispersion), carbonate (as a buffer agent), silicate (peroxide stabilizea via metal ion sequestering, wetting agent, pH buffer, and ink dispersant), polyphosphate, peroxide or hydrosulfite, fatty acid soaps, nonionic surfactants. There are two commonly used methods of deinking : washing and flotation. They commonly deal with ink particles in different size categories, as illustrated in Figure 2.4 . Washing is a purely mechanical process whereas flotation relies on both chemical and mechanical processes.

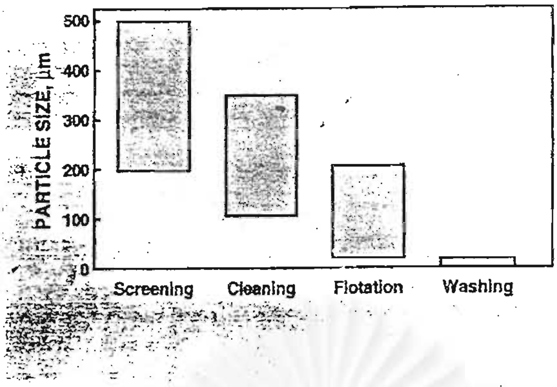


Figure 2.4 Efficient removal of contaminant by particle size and conventional stock preparation process steps.

- <u>Washing Process</u>

Ink washing involves ink removal by washing it from the fiber using sodium hydroxide, sodium silicate, and hydrogen peroxide, and stearic acid as a dispersant. Micelle formation occurs in the classic mechanism by which soap is able to make grease and oils water " soluble ". A water – ink emulsion system is formed with particle sizes averaging below 1 µm. The emulsion is washed from the pulp, and the ink is removed from the wash water by flocculation so the wash water may be reused. Hard water should not be used during ink washing since this will precipitate the soap and the complex will not be water soluble.

- <u>Flotation Process</u>

Flotation is a process that separate materials based on the property of wetability. Under appropriate condition, non – polar (hydrophobic) material are able to adhere to air bubbles and rise to surface. The process is carried out in ink flotation cells using sodium hydroxide, sodium silicate, and hydrogen peroxide with a collector system consisting of a surfactant. With ink flotation, large particle sizes are desired ( at least 5 µm, but 10 – 50 µm is ideal ).

5. *Bleaching*

Pulping quality obtained by a standard deinking process is often limited. A bleaching stage is therefore usually required in the production of high quality products including newsprint, tissue, and printing. Bleaching deinked pulp is similar to that of bleaching virgin pulps. Mechanical pulps are bleached with peroxide (about 1% on pulp, with 4% sodium silicate, 50°C) or dithionite (hydrosulfite, about 1% on pulp, 50 - 60 °C at pH 5 – 6 to mitigate air oxidation of dithionite). Sometimes these bleaching agents are added to the pulper to help with ink removal, but more efficient chemical usage is realized if the pulp is bleached after cleaning and screening.

In recent years, the utilization of wastepaper or old newspaper as filler in thermoplastic is attracted more and more attention due to their mechanical characteristic, renewability, and recyclability. There are many researches about newspaper as reinforcing filler in plastic composites. In 1993, Ren et al. have reported that maleic anhydride grafted polypropylene (MAPP) can be added to the newspaper fiber – polypropylene composites to improve the interfacial interaction of newspaper fiber and polypropylene [28]. Tensile strength and modulus of elasticity of the composites were significantly enhanced by the addition of MAPP. Later on in 1994, Sanadi et al. have reported a 40% by weight of recycled newspaper fiber in polypropylene resulted in a tensile strength of 34.1 MPa and an unnotched izod impact strength of 112 $J/mm^2$ [29]. Small quantities of MAPP and acrylic acid grafted polypropylene (AAPP) were used to improved in properties. Tensile strength as high as 57 MPa and an unnotched izod impact strength of 212 $J/mm^2$ were achieved with the addition of one of the MAPP, while smaller improvements were found with AAPP. Recently, Yuan et al. have studied the influence of MAPP on the properties of polypropylene / newspaper flour composites and the compatibilization mechanism [30]. Experimental results revealed that MAPP is a very good coupling agent for these composites since it can improve the compatibility of polypropylene and newspaper flour, and hence increase the mechanical properties. Differental scanning calorimetry and wide angle x – ray diffraction showed the cocrystallization between bulk PP and PP segment of MAPP.

## 2.5 Matrix Materials

The purpose of using polymer as a matrix is to hold the fibers together so that mechanical loads may be transferred from the weak matrices to the higher strength fibers. In addition, polymer matrix protecting the fibers from handling damages and environmental degradation and in many cases contributing some needed properties such as ductility, toughness, or electrical insulation. Service temperature is often the main consideration in the selection of a matrix material as well as processing temperature during fabrication.

Polymer matrices are made from either thermosets (e.g. epoxy, polyester, phenolic) or thermoplastics (e.g. polyimide, polysulfone, polyetherketone, polypropylene sulfide). Epoxies and polyesters are the most commonly polymer matrix materials for several decades, such as for fiberglass based composites. These thermosetting resins offer a combination of low cost, versatility in many processes, and good property performance.

For natural fiber polymer composites, uses of thermosetting resins as matrix materials can cause degradation of natural fibers. Since the processing temperature of thermosetting resins are higher than the limitation temperature of natural fibers.

Thermoplastics offer many advantages over thermosetting polymer. One of the advantages of thermoplastic matrix composites is design flexibility and ease of molding complex parts. Simple methods such as extrusion and injection molding are used for processing of the composites. Thermoplastics like PE, PP, PS, and PVC are often used as matrix materials because the processing temperature is restricted to temperature below 200°C to avoid thermal degradation of the natural fibers.

### 2.5.1 Polypropylene

Polypropylene is a linear hydrocarbon polymer. Polypropylene and polyethylene have many similarities in the properties, particularly in the swelling and solution behavior and their electrical properties. Polypropylene is cheaper than polyethylene because propylene gas is cheaper than ethylene gas and it is lighter, with the specific gravity about 0.90. The presence of a methyl group attached to alternate carbon atoms on the chain backbone can alter the properties of the polymer. For example it can cause a slight stiffness of the chain and it can interfere with the molecular symmetry. The first effect leads to increase the crystalline melting point whereas the interference with molecular symmetry would tend to depress it. In the case of the most regular polypropylene the net effect is a melting point some higher than that of the regular polyethylene. The methyl side groups can also influence some aspects of chemical behavior. For example the tertiary carbon atom provides a site for oxidation so that polypropylene is less sTable than polyethylene to the influence of oxygen. In addition, thermal and high energy treatment leads to chain scission rather than crosslinking. Moreover, the influence of the methyl group can lead to products of different tacticity, ranging from completely isotactic and syndiotactic structures to atactic molecules. The isotactic from is the most regular since the methyl groups are all disposed on one side of molecule. Isotactic molecule can crystallize in a helix with three molecules being required for one turn of the helix and both right – hand and left – hand helices occur but both forms can fit into the same crystal structure. Commercial polypropylene are usaually about 90 – 95% isotactic. In the products, atactis and syndiotactic structures may be present either as complete molecules or as blocks of vary length in chains of isotactic molecules. Isotactic structure is stiff, highly crystalline and with high melting point. Within the range of commercial polymers the greater the amount of isotactis material the greater the crystalline and hence the greater the softening point, stiffness, tensile strength, modulus and hardness, all other structure features being equal.

The influence of molecular weight on the bulk properties of polypropylene is often opposite to that experience with most other well – known polymers. Although an increase in molecular weight leads to an increase in melt viscosity and impact strength, in accordance with the most polymers, it also leads to a lower yield strength, lower hardness, lower stiffness and softening point. This effect is believed to be due to the fact that high molecular weight polymer does not crystallize so easily as lower molecular weight and it is the difference in the degree of crystallization which affect the bulk properties.

One unfortunate characteristic property of polypropylene is the dominating transition point which occurs at about 0°C with the result that the polymer becomes brittle as this temperature is approached. Products of improved strength and lower brittle points may be obtained by block copolymerization of polypropylene with small amounts (4 – 15%) of ethylene. Such materials are widely used and are often preferred to the homopolymer in injection molding and bottle blowing application.

## 2.6 Polymer Processing

### 2.6.1 Two Roll Mill

Before a polymer can be used to make product, it is usually necessary to mix it with ingredients, which serve a variety purpose. The simplest and basic machine for intensive mixing is a two roll mill. The two roll mill is comprised of a pair of rollers with axes horizontally disposed to each other, giving a vertical “ nip “ between them. The polymer matrix and additives are subjected to high shear in the nip as the rolls rotate in opposite directions.

The technique of this machine is to pass the appropriate loading of matrix material, usually raw polymer, through the nip a few times until it warms up, softens, and forms smooth band around one of the rolls. This process is assisted manually by cutting the band with a knife from one edge to two – third to three – quarters of its width, so that a flap of it is formed which can be folded to the other side. By cutting and folding many times from both sides, good distribution and dispersion are achieved.

### 2.6.2 Twin Screw Extruder

In principle, the extrusion process comprises the forcing of a plastic or molten material through a shaped die by means of pressure. Screws are used to progress the polymer in the molten or rubber state along the barrel of the machine. The most widely used type is the single screw extruder. Twin screw extruder is also used when superior mixing or conveying is important.

Twin screw extruder is devided into co – rotating and counter rotating types. As the name indicate, the difference is in whether the two screws rotate in the same or in opposite direction, i.e. both clockwise or counterclockwise, or one in each sense. Twin screw extruder acts as positive displacement pumps with little dependence on friction, and this is the main reason for their choice for heat sensitive materials such as poly (vinyl chloride) or PVC.

#### Co – Rotating Twin Screw Extruder

The co – rotating twin screw extruder transfers the melt from the screw channel of one screw to the other screw. The conveying mechanism – drag force – is comparable to that found in the single screw extruder. By being transferred from one screw channel to another, the melt does follow a longer path and is subjected to higher shear. The co – rotating twin screw extruder finds application primarily in compounding. Figure 2.5 presents the tightly intermeshing co - rotating twin screw extruder [12].

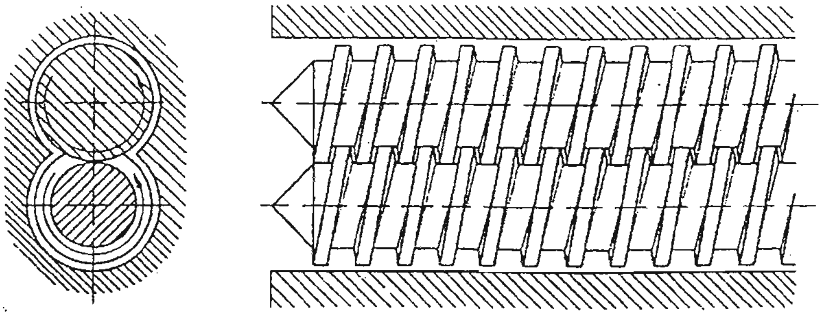


Figure 2.5 Tightly intermeshing co - rotating twin screw extruder.

Counter – Rotating Twin Screw Extruder

Each screw segment forms a close chamber that conveys the melt material from the hopper to the end of the screw without any noteworthy exchange with neighboring chambers. Drag forces are not needed for this positive conveying, with the result that little dissipation – induced heating occurs. Heating occurs largely via the heater bands on the barrel, whish can be precisely controlled and permit gentle heating of sensitive materials. While this conveying and melting mechanism assures well controlled, gentle handling of the material, the melt is usually inhomogeneous and insufficiently plasticated so that the use of mixing elements is also be recomended here. Figure 2.6 shows the counter – rotating twin screw extruder [12].

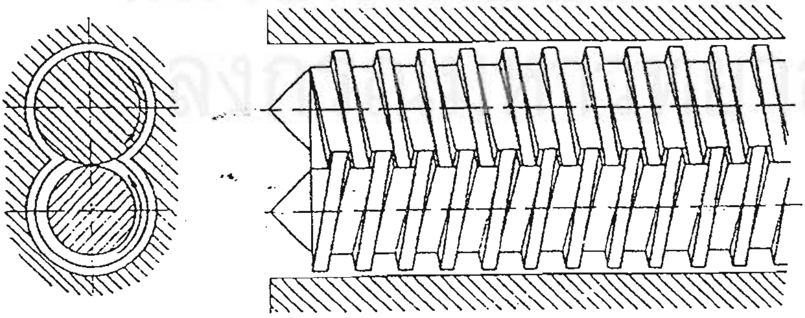


Figure 2.6 Tightly intermeshing counter – rotating twin screw extruder.

### 2.6.3 Injection Molding

In injection molding, granular polymers are heated and forced, or injected into a mold cavity, cooled, and removed. This process is used to produce many items, from toothbrush handles to automobile bumpers. An injection molding machine has two main sections : the injection unit and the clamp unit which houses the mould. All thermoplastics polymer (except with high viscosity like fluoroplastics, polyimides, and some aromatic polyesters) can be injection molded and many thermosetting polymer can be injected molded as well. Advantages of injection molding are high production rates, ability to inject around inserts, little or no finishing requirements, and recycling capability. The only major disadvantage is the high cost of equipments and mold. Figure 2.7 shows the principles of injection molding diagrammatically [12].

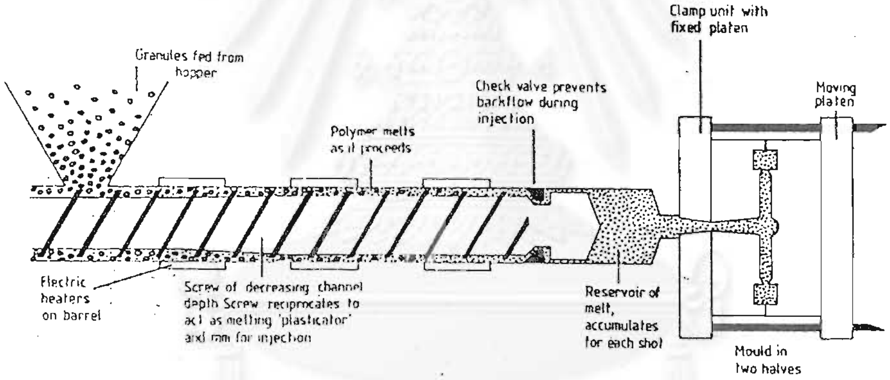


Figure 2.7 Injection moulding.

Modern injection – molding machines use the reciprocating screw for plastication, the same as for extrusion, but the screw is stopped and then used as a plunger. Plunging injects the hot polymer into the mold where it takes the shape of the cavity. When cooled, the parts are removed and gates, runners, and excess materials are removed and regrounded for recycling.

## 2.7 Surface Analysis : X – Ray Photoelectron Spectroscopy (XPS)

XPS is also known as ESCA which is an acronym for Electron Spectroscopy for Chemical Analysis for surface characterization. The XPS technique is spectroscopic technique in which a sample is bombared with soft x –rays, which can cause the emission of core, i.e., non – valence, electrons from the atoms of the sample.

As shown in Figure 2.8, X – ray can penetrate through matter, i.e., the sample surface up to a depth of few hundred mm. and interact with both valence and core electrons of the atoms resulting in the ejection of electron referred as "*photoelectron*"

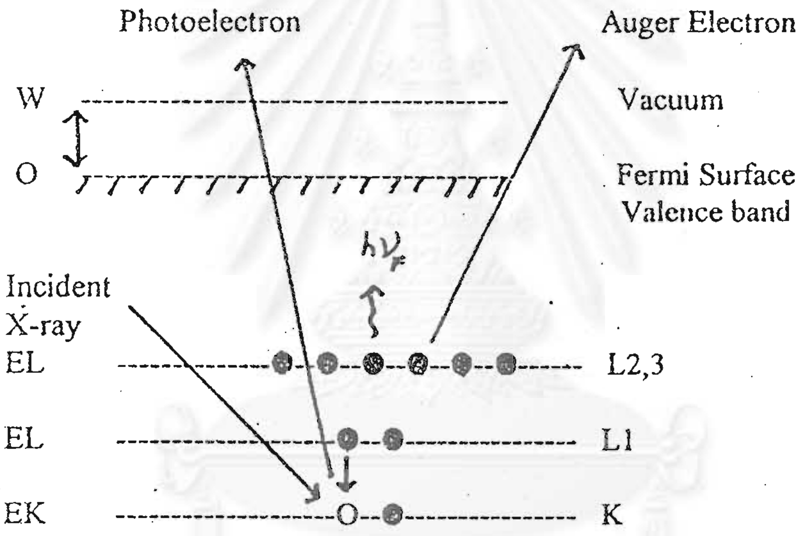


Figure 2.8 Schematic energy level diagram showing the photoelectronic, Auger and X – ray fluorescence processes.

The binding energies of the electron which reflect the attractive forces of the nucleus on the core electron are characteristic of the type of atoms present in the sample surface. Thus knowing the binding energy of a given photoelectron, one can identify the element involved. The binding energies of the photoelectron are obtained via the "Einstein Relation"

$$BE = h\nu - KE - \phi_s \qquad (3.1)$$

Where

$BE$ = binding energy (eV) of the photoelectron

$h\nu$ = incident energy of X – ray

$KE$ = kinetic energy of the photoelectron

$\phi_s$ = work function of spectrometer

A typical spectrum from a polymer is a plot between binding energy (eV) and a number of emitted electron per energy level (N(E)/E(counts)). Figure 2.9 shows a typical spectrum for XPS analysis of poly (ether sulphone). Table 2.4 presents binding energy of some elements and the core level.

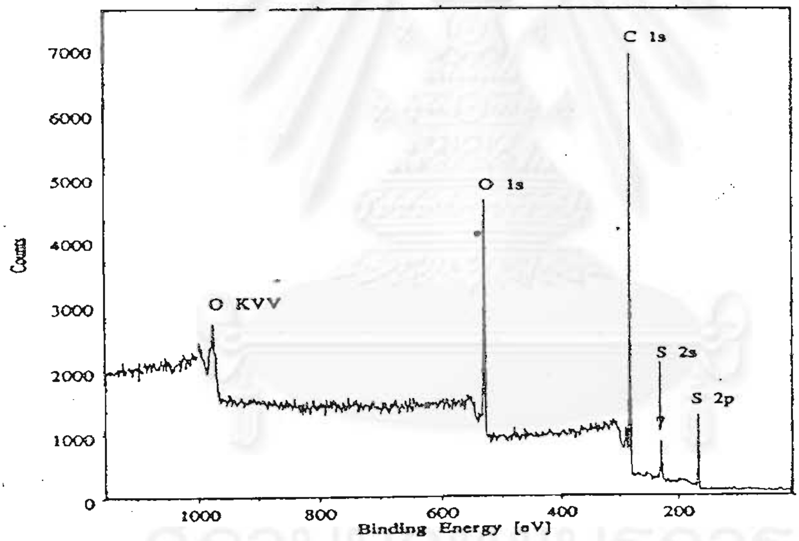


Figure 2.9 Typical spectrum for XPS analysis of poly(ether sulphone).

**Table 2.4** Typical Energy of Some Elements and the Core - Level

| Element | Core – level | BE (eV) |
|---|---|---|
| Li | 1s | 55 |
| C | 1s | 284 |
| N | 1s | 399 |
| O | 1s | 532 |
| F | 1s | 686 |
| Na | 2s | 63 |
| Si | 2p1/2, 2p3/2 | 100, 99 |
| S | 2p1/2, 2p3/2 | 165, 164 |
| Cl | 2p1/2, 2p3/2 | 202, 200 |
| Cu | 2p1/2, 2p3/2 | 951, 931 |

Also as shown in Figure 2.8, along with the photoionization several secondary processes also take place as also shown in Figure 2.8. One of them is the Auger emission. It may be considered as a two steps process. The core hole that is produced simultaneously with the photoemission of the core electron is immediately occupied by an electron from the outer level. The energy released in the process is used to eject a secondary electron referred as Auger elctron. X – ray fluorescence or XRF takes place if energy released by the decay of the outer level electron to fill the core hole is converted to the x – ray photon without the ejection of a second electron.

This technique is very well known because it is nondestructive method and suited to several types of polymer analysis and required only minimum sample preparation. Film. Solid, and powder samples may all be used. It has been applied to the study of surface modified polymers, detecting surface layers of additives or contaminants, or surface degradation as in weathering.

# CHAPTER III

# EXPERIMENTS

## 3.1 Materials

3.1.1 Polypropylene (PP 700J) provided by Thai Polyethylene Co., Ltd. was used as a matrix. Its melt flow index and density are 12 g/10 min. and 0.910 g/cm$^3$, respectively.

3.1.2 Maleic Anhydride Grafted Polypropylene (MAPP) was used as a coupling agent to improve the interfacial adhesion. It was supplied by Dupont Co., Ltd., USA, under the trade name of Fusabond MZ – 203D.

3.1.3 Sodium Hydroxide (NaOH) was a laboratory grade purchased from Merck Company.

3.1.4 Hydrogen Peroxide ($H_2O_2$) was a reagent grade purchased from Merck Company.

3.1.5 Dodecanoyl Chloride (Lauroyl Chloride) was a synthesis grade purchased from Merck Company.

3.1.6 Pyridine was a synthesis grade prrchased from Merck Company.

3.1.7 Newspapers were used as a reinforcing filler. They were collected mostly from Thai – Rat Newspaper.

3.1.8 All chemicals were used as received.

## 3.2 Equipments

The equipments below are listed consecutively based on the experimental procedure. The details of each step will be further described in the next section.

### 3.2.1 Two Roll Mill

The blending of polypropylene and newspaper pulp was first done in a Lab Tech two roll mill model LRM150.

### 3.2.2 Grinder

The grinding of composites was done by a Momunda grinder model NCMM 3695. They were stored at ambient condition prior to further processing.

### 3.2.3 Twin Screw Extruder

After grinding, the composites were extruded and pelletized by a Collin twin screw extruder model CD - 85560.

### 3.2.4 Injection Molding

The compounded pellets were injected by an Engel injection molding machine model ES 200/50.

### 3.2.5 Tensile Testing Machine

Tensile properties of the composite samples were measured by an Instron Universal Testing Machine model 4206, according to the ASTM D638.

### 3.2.6 Flexural Testing Machine

Flexural properties of the composite samples were carried out by a LLOYD Universal Testing Machine model LR10K, according to the ASTM D790.

### 3.2.7 Impact Tester

Impact tests of the composite samples were performed by a Zwick 5102 Pendulum Impact tester, according to the ASTM D256.

### 3.2.8 Fourier Transform Infrared Spectrometer (FTIR)

FTIR was used to study the structure and the functional group of the newspaper pulp. Spectra were obtained from a FTIR Nicolet Impact 400D.

### 3.2.9 Differential Scanning Calorimeter (DSC)

A Perkin Elmer DSC7 was used to study the thermal transitions behavior of the composite samples with the heating rate of 20°C/min.

3.2.10 Thermogravimetric Analyzer (TGA)

Thermal degradation temperature ($T_d$) of the composite samples was determined by a Perkin Elmer TGA7 under $N_2$.

3.2.11 Scanning Electron Microscope (SEM)

The fracture surfaces of the composite samples after the impact tests were observed with a Jeol JSM – 5410LV scanning electron microscope after coating with gold.

3.2.12 X – Ray Photoelectron Spectroscopy (XPS)

X – ray photoelectron spectra were recorded with a Perkin Elmer Physical Electronics 5100 with Al K$\alpha$ excitation (400 W).

## 3.3 Methodology

The flow chart of the entire manufacturing process is shown below in Figure 3.1.

3.3.1 Preparation of Newspaper Pulp from Old Newspaper

Small pieces of newspaper were pulped and deinked in 3 g/l sodium hydroxide (NaOH) solution. After that the deinked newspaper pulp were bleached in 3 g/l hydrogen peroxide ($H_2O_2$) solution for increasing the whiteness of newspaper pulp. After the preparation, the newspaper pulp was dried in an oven at 105°C overnight prior to use. The dried newspaper pulp was then devided into two sets. The first set was blended with polypropylene using MAPP as a coupling agent. The newspaper pulp in second set was modified by an esterification reaction, as describe in section 3.3.2, before blending with polypropylene.

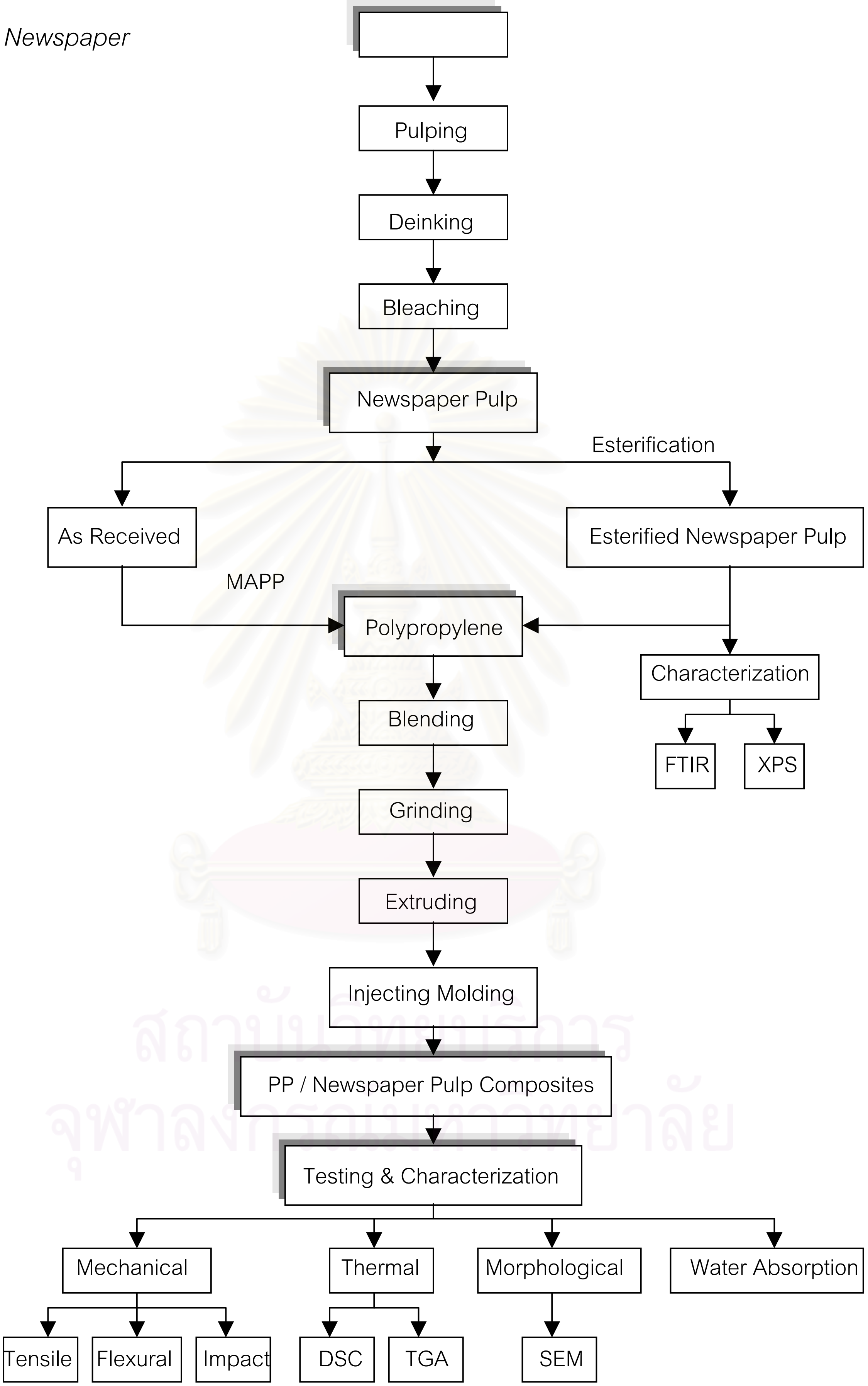


**Figure 3.1** The flow chart of manufacturing process.

### 3.3.2 Esterification of Newspaper Pulp

This method was adopted from Thiebaud et al. Method [22]. The procedure of esterification was as follows. Firstly, the newspaper pulp was dried overnight in an oven at 105°C to remove its moisture. The dried newspaper pulp (2.5 g) was placed in a three – necked flask equipped with a mechanical stirrer, a condenser, and a thermometer. 15 ml. of pyridine and the appropriate amount of 0.28 mol of dodecanoyl chloride were added. The reaction was allowed to proceed for 3 hours at 115°C. Upon completion the reaction, the mixture was cooled and poured with vigorous stirring into a glass beaker containing 200 ml ethanol to precipitate the esterified newspaper pulp and to eliminate any color impurities. The product was washed twice with 200 ml hot ethanol. The excess of ethanol was removed by an air stream and the esterified newspaper pulp was dried at 50°C overnight and weighed.

### 3.3.3 Preparation of the Polypropylene / Newspaper Pulp Composites

As already mentioned, newspaper pulp was devided into two sets. The first set was mixed with polypropylene, but the other set was reacted with dodecanoyl chloride and pyridine for esterification reaction prior to mixed with polypropylene. The blending of polypropylene and newspaper pulp was done at 175 – 180°C in a two roll mill. Newspaper pulp content was 5, 10, 15, and 20% by weight and added after polypropylene had melted and the mixing was carried out for 5 minutes. In case of polypropylene/newspaper pulp – MAPP, the MAPP content was 2, 5, 10, and 20% by weight of newspaper pulp. All compositions are tabulated in Table 3.1. After that, the resulting composite sheet was removed from the two roll mill and ground by a grinder.

For good dispersion, the premix was then proceeded on a twin screw extruder with the roter speed of 50 rpm. The processing temperatures were 70, 170, 175, 180, 185, and 190°C according to 6 zones of the extruder, respectively. The extruded strands were cooled in water, pelletized, and dried.

Finally, the compounded pellets were molded by an injection moulding. The nozzle temperature was 195°C and the injection pressure was about 100 bar. The composites were injected into standard ASTM test specimens. Mechanical properties, thermal properties, water absorption, and fracture surface of the composite samples were investigated.

**Table 3.1** Compositions of the Composites

| Batch | PP | Newspaper Pulp | Esterified Newspaper Pulp | MAPP |
|---|---|---|---|---|
| 1. | PP | - | - | - |
| 2. | PP | 5 | - | - |
| 3. | PP | 10 | - | - |
| 4. | PP | 15 | - | - |
| 5. | PP | 20 | - | - |
| 6. | PP | - | 5 | - |
| 7. | PP | - | 10 | - |
| 8. | PP | - | 15 | - |
| 9. | PP | - | 20 | - |
| 10. | PP | 5 | - | 10 |
| 11. | PP | 10 | - | 10 |
| 12. | PP | 15 | - | 10 |
| 13. | PP | 20 | - | 10 |
| 14. | PP | 10 | - | 2 |
| 15. | PP | 10 | - | 5 |
| 16. | PP | 10 | - | 20 |

### 3.3.4 Characterization of Newspaper Pulp

Newspaper pulp was characterized by using FTIR and XPS. For FTIR characterization, transmission spectra were obtained with the KBR technique. Each spectrum was recorded at a resolution of 4 cm$^{-1}$, with a total of 32 scans and a frequency range of 4000 – 400 cm$^{-1}$.

XPS is a surface analysis technique. Spectra were obtained at two different take - off angles, 15° and 75° (between the plane of the surface and the entrance lens of the detector optics). Vacuum – dried newspaper pulp was ground into powder. The powder was then pressed onto a double – sided tape attached on flat Mylar (PET) film. Excess powder was removed by compress air blow.

### 3.3.5 Characterization of Polypropylene / Newspaper Pulp Composites

#### 3.3.5.1 Mechanical Properties

Tensile tests with using dumbell shaped specimens were conducted using a crosshead speed of 50 mm/min and a guage length of 50 mm, according to the ASTM D638. Flexural tests, using three point bending mode, were performed, according to the ASTM D790. Rectangular test specimens with dimensions of 10.0 wide, 60.0 mm long and 3.4 mm thick were tested using a crosshead speed of 20 mm/min and a span length of 48 mm. Impact tests were performed using the ASTM D256 test method by izod pendulum. Condition during all tests were 23°C. At least five specimens of each composites were tested and the results were averaged to obtain a mean value.

#### 3.3.5.2 Thermal Properties

For DSC measurements, sample sizes with an average weight of 10 mg encapsulated in a hermitically sealed aluminium pan were prepared for each sample. The same temperature history was applied to all samples : first heating from 50°C to 250°C at a heating rate of 20°C/min under nitrogen atmosphere, followed by quenching the sample to 50°C to remove any previous thermal history, and finally heating to 250°C at a scanning rate of 20°C/min. From these thermograms the melting temperature ($T_m$), crystallization temperature ($T_c$), and heat of fusion ($\Delta H_f$) were determined. The degree of crystallinity of the composite was calculated using the following formula:

$$\chi_c = \frac{\Delta H_{f,sc}}{\Delta H_{f,c}} \times 100 \tag{3.1}$$

Where, $\Delta H_{f,sc}$ = heat of fusion for the semi – crystalline polymer (J/g)

$\Delta H_{f,c}$ = heat of fusion for the completely crystalline polymer (J/g)

Thermogravimetric analyser (TGA) was used to examined thermal degradation tenperature ( $T_d$ ) of the composites. Each sample of approximately 5 mg was heated with a heating rate of 20°C/min under nitrogen atmosphere from 50°C to 650°C.

### 3.3.5.3 Morphological Studies

Scanning electron microscope (SEM) at acceleration voltage of 15 KV was used to study the impact fractured surface of the composites in order to understand the failure mechanism of the composites in the presence of newspaper. The fractured surface of the sample was coated with gold before being scanned. The morphology such as phase structure, dispersion, and adhesion of the components were investigated.

### 3.3.5.4 Determination of Water Absorption

Water absorption of the composites were measured according to the ASTM D570. At least five dumbell shaped specimens for each composite were tested. They were dried in an oven for 24 hours at 50°C, cooled in a dessicator, and immediately weighed. The dried weight was designated as $W_1$. After that, they were immersed in distilled water for a set time and temperature. The specimens were removed, wiped dried, weighed, and immediately returned to the water bath. The procedure was repeatedly performed untill no weight changes were observed. Water absorption of each sample was calculated as the weight difference and is reported as percent increase of the initial weight, according to equation (3.2) as follows :

$$\%\ \text{Water Absorption} = \frac{W_2 - W_1}{W_1} \times 100 \qquad (3.2)$$

**When $W_1$ = initial or dried weight**

$W_2$ = final or wet weight

# CHAPTER IV

# RESULTS AND DISCUSSION

## 4.1 Characterization of Newspaper Pulp

In these composites, newspaper pulp was used as a reinforcing filler. FTIR characterization was used to determine the chemical structure and functional group of newspaper pulp and esterified newspaper pulp with dodecanoyl chloride (dodecanoated newspaper pulp). In order to study the surface chemistry of newspaper pulp and esterified newspaper pulp and to support the FTIR results, XPS technique was used.

### 4.1.1 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of newspaper pulp and esterified newspaper pulp are shown in Figure 4.1 along with the FTIR of cotton fiber as a reference or a representative of a cellulose fiber.

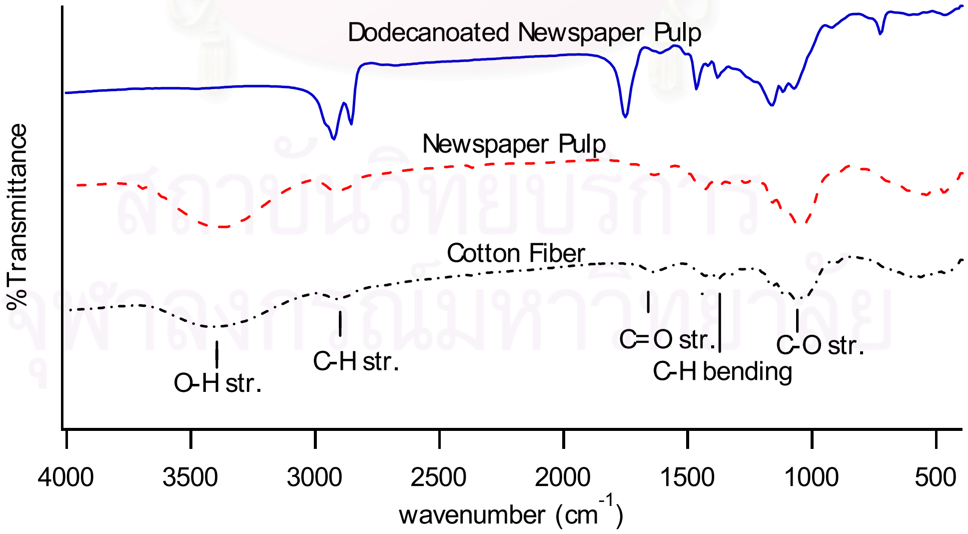
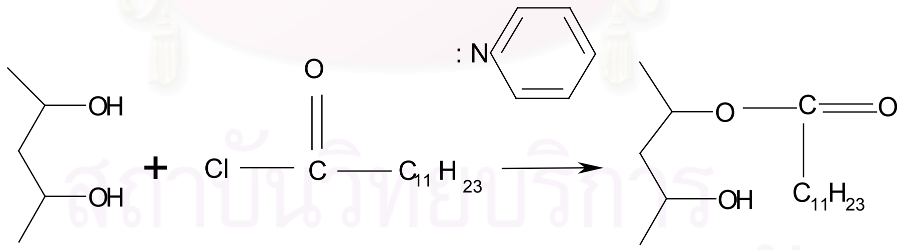


**Figure 4.1** FTIR spectra of newspaper pulp and dodecanoated newspaper pulp.

In the spectrum of newspaper pulp, the characteristic broad peak between 958 – 1190 CM$^{-1}$ is attributed to C – O bond stretching. Another strong broad band due to hydroxyl bond stretching appears at 3000 – 3600 CM$^{-1}$. Small peak at 1620 - 1640 CM$^{-1}$ defines as C = O stretching of the aldehyde at the end chain of cellulose. In addition, the spectrum of newspaper pulp is similar to the spectrum of cotton fiber because the chemical structure of both newspaper and cotton is cellulose.

Because the substitution reaction on hydroxyl groups of cellulose with long chain of dodecanoyl chloride, the hydroxyl peak intensity decreases after esterification of newspaper pulp with dodecanoyl chloride. The strong carbonyl bond stretching appears at 1746 – 1790 CM$^{-1}$ confirm the esterification of newspaper pulp, as shown in Figure 4.1. Another strong and high intensity band observed in the esterified newspaper pulp at 2800 – 2950 CM$^{-1}$ is C – H stretching which is corresponding to the methyl / methylene groups of dodecanoyl chloride. This peak, in fact, can also be observed in the newspaper pulp and cotton fiber spectrum with low intensity, and also defines as the methylene groups in cellulose structure. Figure 4.2 presents the chemical structure and esterification reaction of newspaper pulp and dodecanoyl chloride.

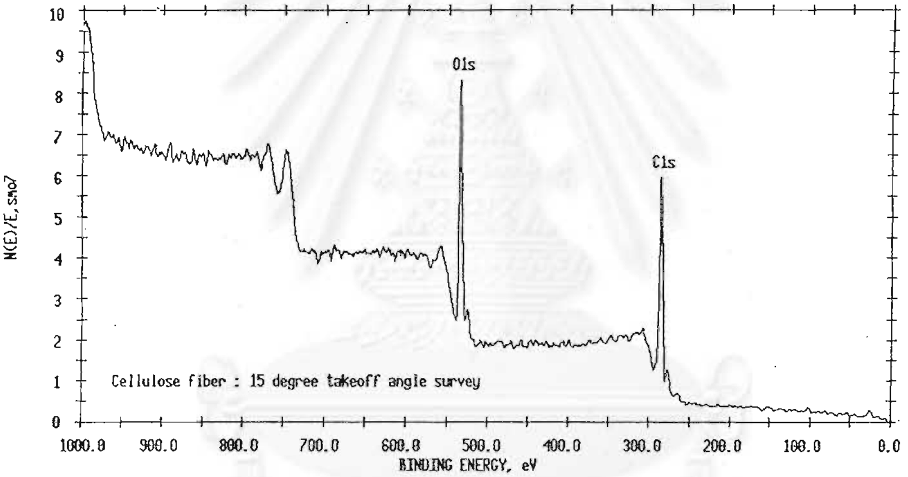


Newspaper Pulp    Dodecanoyl Chloride    Esterified Newspaper Pulp

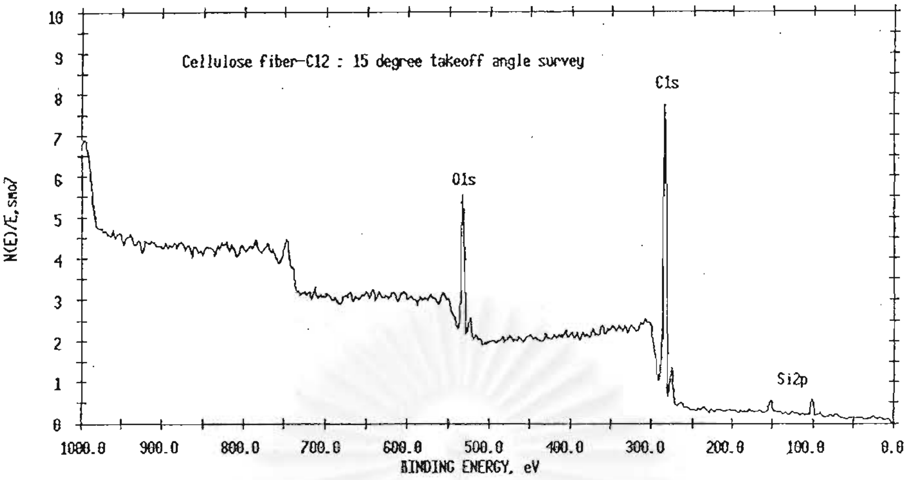
Figure 4.2 The chemical structure and esterification reaction of newspaper pulp and dodecanoyl chloride.

### 4.1.2 X – Ray Photoelectron Spectroscopy (XPS)

XPS was used for the surface characterization of newspaper pulp and esterified newspaper pulp. Figure 4.3 (a) – (b) shows the survey scan spectrum of newspaper pulp and esterified newspaper pulp, respectively. As can be seen, the peak position of carbon and oxygen found in newspaper pulp and esterified newspaper pulp are located at about 285 eV and 533 eV, respectively. Although, the position of carbon and oxygen peaks of esterified newspaper pulp are similar to those of the newspaper pulp, their intensity or peak height are different from those of the newspaper pulp.



(A)



(B)

Figure 4.3 XPS spectra of (a) untreated newspaper pulp and (b) esterified newspaper pulp.

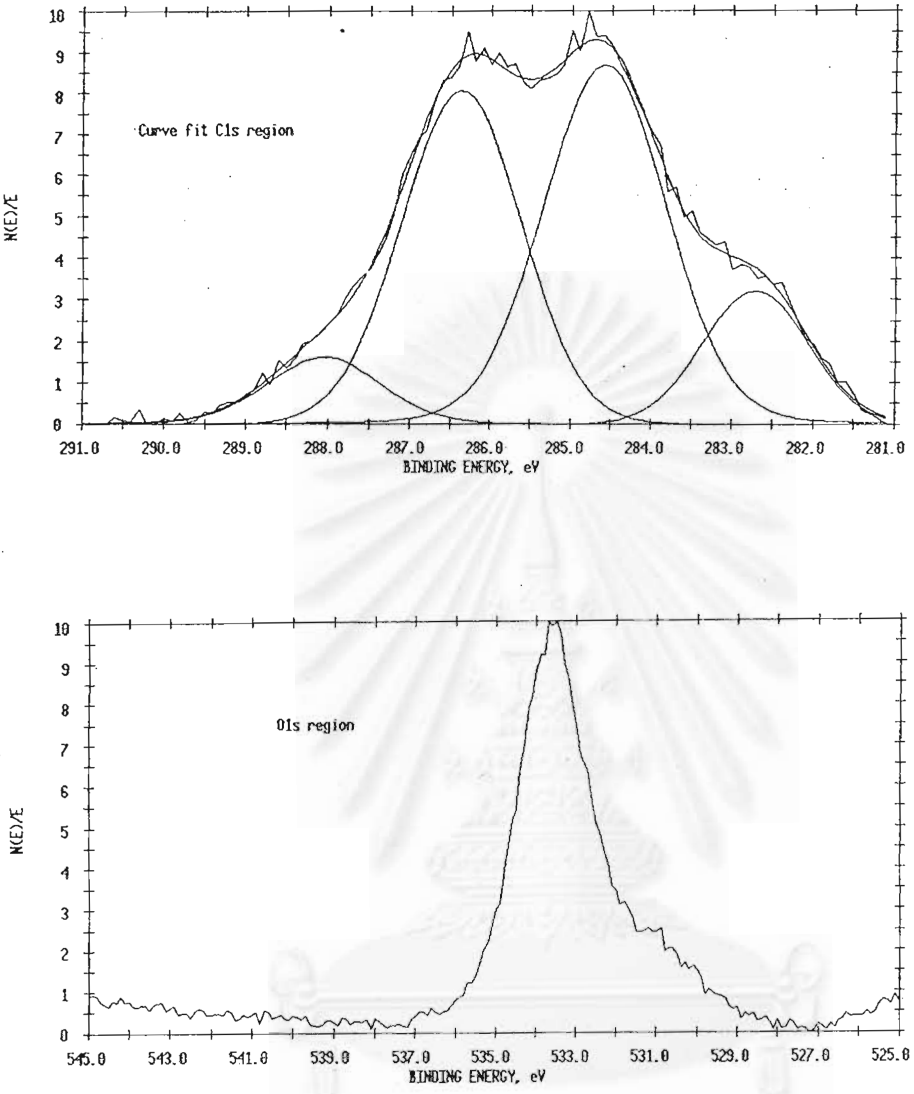
Computerized peak separation and peak area measurements were applied to determine the chemical composition of the modified surfaces. After running the detail scan (Figure 4.4(a) and (b)) for each peak, the concentration of carbon and oxygen atoms for newspaper pulp and esterified newspaper pulp can be determined from the curve fitting of the total area under the peaks. Their values are shown in Table 4.1. Obviously, the concentration of carbon atom in esterified newspaper pulp is higher than the concentration of carbon atom in newspaper pulp. And vice versa, the concentration of oxygen atom in esterified newspaper pulp is lower than the concentration of oxygen atom in newspaper pulp

Table4.1 Atomic Concentration of Newspaper Pulp and Esterified Newspaper Pulp

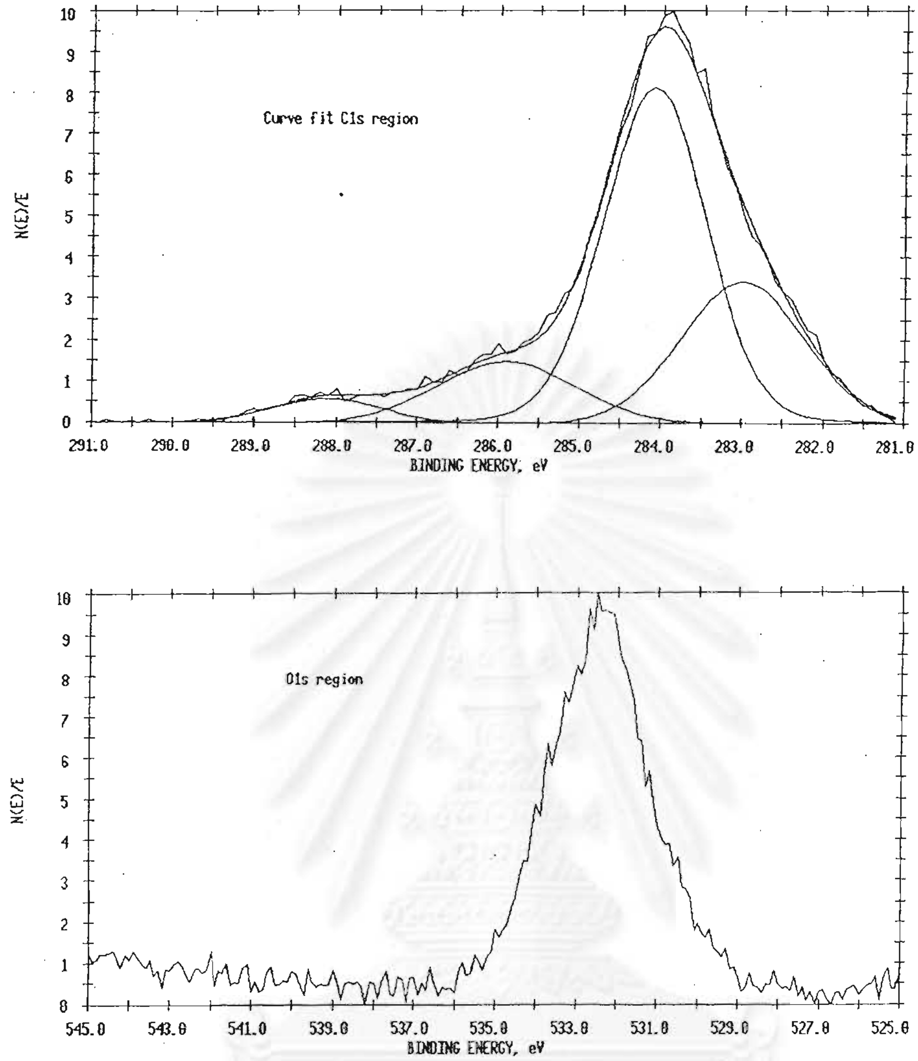
| Newspaper | Concentration (%) | |
|---|---|---|
| | C1s | O1s |
| 1. Newspaper Pulp | 68.45 | 31.55 |
| 2. Dodecanoated Newspaper Pulp | 83.31 | 16.69 |

As can be seen in Table 4.1, comparing to newspaper pulp, the carbon concentration of the esterified newspaper pulp increased 14.86%, whereas its oxygen concentration decreased 14.86%.  The increasing in carbon concentration and decreasing in oxygen concentration of esterified newspaper pulp comfirm the results from FTIR that the esterification reaction of newspaper pulp with dodecanoyl chloride has been successful.  The increasing in carbon concentration can be defined as methylene groups ($-CH_2$) in the long chain fatty acid ester grafted with cellulose structure in newspaper pulp, as depicted in Figure 4.2.  Also, the decreasing in oxygen concentration is due to the disappearance of hydroxyl groups (-OH) on the cellulose that has been changed to ester bond by the esterification reaction.  Inconclusion, the change in atomic concentration of carbon and oxygen atoms is because of the reaction between acid chloride and hydroxyl group on the surface of newspaper pulp.

To confirm that surface modification by esterification has been achieved, the peak separation of the detail scan at the carbon atom region was performed as iillustrated in Figure 4.4 (a) and (b).  Figure 4.4 (a) shows the O1s and C1s spectra of untreated newspaper pulp, while the oxygen peak is symmetrical and consists of only one peak, the carbon peak can be separated into four components $C_1$, $C_2$, $C_3$, $C_4$ with binding energies 282.72, 284.58, 286.36, and 288.05 eV, respectively.  They can be assigned as follows : $C_1$  represents the carbon atoms bonded to hydrogen, $C_2$ represents the carbon atoms bonded to carbon, $C_3$ represents the carbon atoms bonded to a single nonketonic oxygen atom (C-O), and $C_4$ represents the carbon atoms bonded to two nonketonic oxygen atoms(O-C-O) and $C_4$ represents the carbon atoms bonded to a nonketonic and a ketonic oxygen atoms (O-C=O)


Curve fit C1s region
N(E)/E
10
9
8
7
6
5
4
3
2
1
0
291.0
290.0
289.0
288.0
287.0
286.0
285.0
284.0
283.0
282.0
281.0
BINDING ENERGY, eV
O1s region
N(E)/E
545.0
543.0
541.0
539.0
537.0
535.0
533.0
531.0
529.0
527.0
525.0
BINDING ENERGY, eV

(A)



(B)

Figure 4.4 The resolved C1s and O1s spectra of (a) untreated newspaper pulp and (b) esterified newspaper pulp.

Similarly, the carbon 1s and oxygen 1s spectra of esterified newspaper pulp are composed in Figure 4.4 (b). Again here, the carbon spectrum consisits of four peaks, while only one symmetrical oxygen peak is observed. Each carbon peak can be designated in the same manner. The binding energy and intensity of carbon and for untreated and treated newspaper pulp are quantified and summarized in Table 4.2. From the Table, the peak at 285 eV characteristic for C-C has increased significantly from 2788 counts / sec of untreated newspaper pulp to 4527 counts / sec of esterified newspaper pulp. Moreover, the peak at about 286 eV designated for C-O has also decreased drastically from 4527 counts / sec of untreated newspaper pulp to only 826 counts / sec of esterified newspaper pulp. These results indicate that the aliphatic hydrocarbon is existed on the surfaces of the treated newspaper pulp, these explaining its hydrophobic properties.

**Table 4.2** Elemental Composition of Untreated and Treated (esterified) Newspaper Pulp

| Elements | Designated Peak | **Newspaper Pulp** | | Esterified Newspaper Pulp | |
|---|---|---|---|---|---|
| | | Binding Energy (eV) | Intensity (Counts/sec) | Binding Energy (eV) | Intensity (Counts/sec) |
| $C_1$ | C-H | 282.72 | 1031 | 283.00 | 1897 |
| $C_2$ | C-C | 284.58 | 2788 | 284.09 | 4527 |
| $C_3$ | C-O | 286.36 | 2586 | 285.90 | 826 |
| $C_4$ | O-C-O | 288.05 | 527 | 288.10 | 325 |

### 4.2 Mechanical Properties of Polypropylene/Newspaper Pulp Composites

Comparison of polypropylene and polypropylene / newspaper pulp composites on the mechanical properties is presented in this section. Measurements of the mechanical properties such as tensile, flexural, and impact properties are important in determining the utilization of these composites in daily life. Thus this section will focus on the effect of newspaper pulp content, compatibilizer content, and surface modification on the tensile, flexural, and impact properties of the polypropylene / newspaper pulp composites.

### 4.2.1 Tensile Properties

The most common method of investigating mechanical properties of composites is to carry out stress – strain or more precisely load – extension measurement using a tensile tester. Determination of the stress – strain or load – extension behavior of material is useful as it provides information concerning important mechanical properties such as Young's modulus, yield strength, and stress at break.

The stress – strain or load – extension curve can be readily obtained for polymer by subjecting a specimen to a tensile force applied at a constant rate of testing. In Figure 4.5, load is plotted against extension. For polypropylene curve, initially the stress is proportional to the strain and the tensile modulus can be obtained from the slope. This characteristic defines as elastic deformation. After that the strain is increased, the curve decreases in slope untill it reaches a maximum. This is known as the yield point. Although not obviously, polypropylene has reached its yield point at about 1.1 KN and further elongates untill breaks. In other words plastic deformation occurs. During elastic deformation the cross sectional area of the specimen decreases uniformally as length increases. The polypropylene curve shows its elongation at break at about 11 mm. This is a general characteristic for most ductile polymer.

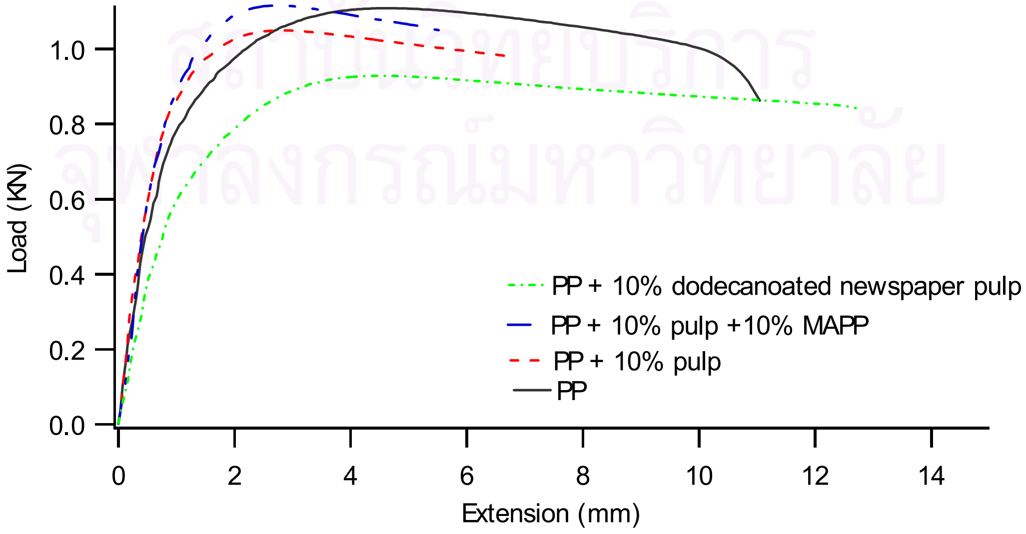


**Figure 4.5** Load – extension of the composites.

In the case of the composite without MAPP and composite with MAPP, it can be observed that the increase in load or stress of these composites is much faster than that of the pure polypropylene. This suggested that the stiffness of these composites is improved by the addition of newspaper pulp. After a prolonged testing period, the stress changes to a non – linear behavior which illustrates the viscoelastic properties of the composites. The characteristic curves of these two composites are similar, but the tensile modulus and maximum load of the composite with MAPP are higher than those of the composite without MAPP. This is because the addition of MAPP can improve compatibility and interfacial bonding between the polypropylene and newspaper pulp. After reaching their maximum load, the plastic deformation starts to occur. These composites fracture more rapidly than polypropylene. The elongation at break of the composite without MAPP and composite with MAPP are about 5 and 7 mm, respectively. These composites curves are different from the polypropylene curve since the influence of newspaper pulp that reduces the ductility and enhances the stiffness of polypropylene. From the area under the curves, polypropylene is tougher than these two composites. The characteristic of whitening observed in both composites upon stretching can be explained in terms of crazing of the polypropylene matrix, cavitation, or dewetting of newspaper pulp. The crazes appear as small crack – like entities which are usually initiated on the specimen surface and are oriented perpendicular to the tensile axis.

For polypropylene / esterified newspaper pulp composites, the load – extension curve shows lower tensile modulus than the composite with and without MAPP, and even lower than that of polypropylene. The increasing of stress is much slower than both composites and polypropylene. From the observation, the composite with esterified newspaper pulp is softer than both composites and polypropylene. After the stress reaches its maximum or at the yield point of about 0.9 KN, the stress whitening or crazing can be observe as well. The difference between the composite with esterified newspaper pulp, the composite with MAPP, and the composite without MAPP is the extension or elongation at break. Among them, the elongation at break of the composite with esterified newspaper pulp is highest.  In fact, its extension is also greater than that of the pure polypropylene.

Therefore, it can be concluded that the composite with esterified newspaper pulp has lower the tensile strength and Young's modulus than any other composites including polypropylene.  However, the elongation at break of the esterified newspaper pulp composite is much greater than that of pure polypropylene, the composite without MAPP, and the composite with MAPP.  The composite with MAPP has highest in the tensile strength , followed by the composite without MAPP, polypropylene and the composite with esterified newspaper pulp.  The weekness of the composite without MAPP implies poor interfacial bonding between newspaper pulp and polypropylene.

Effect of newspaper pulp content on tensile properties

The effect of newspaper pulp content on the tensile modulus of the composite without MAPP, the composite with MAPP, and the composite with esterified newspaper pulp is shown in Figure 4.6 and Table 4. 3.  Newspaper pulp  content is varied from 5% to 20% by weight of polypropylene, with 5% increasing interval.  For both compatibilized and uncompatibilized composites, tensile modulus increases with increasing the newspaper pulp content.  This is due to the reinforcing effect of newspaper pulp.

In contrast, the tensile modulus of the composite with esterified newspaper pulp decreases with increasing newspaper pulp content which is actually lower than that of polypropylene.  This is owing to the plasticizing effect of long chain hydrocarbon of dodecanoyl chloride grafted on newspaper pulp.  Obviously, as shown in Figure 4.4, the decrease in tensile modulus is compensates by the increase in elongation.  In this case, the esterified newspaper pulp does not function as a reinforcing filler, but a plasticizer, for polypropylene.

Comparing between the composite with MAPP and without MAPP, as would be expected the tensile modulus of the composite with 10% MAPP is greater than that of the composite without MAPP, except at 5% newspaper pulp loading. At this composition, the tensile modulus of the composite with 10% MAPP is slightly lower than that of the composite without MAPP. Overall, the tensile modulus of polypropylene increases 66.67% with the addition of 20% newspaper pulp with MAPP, and decreases with the addition of 20% esterified newspaper pulp by 55.03%.

As shown in Figure 4.7 and Table 4.4, the influence of newspaper pulp content on the stress at upper yield or tensile stress at yield is varies upon the type of composites. In the case of the composite with esterified newspsper pulp, the tensile stress at yield decreases significantly with increasing newspaper pulp content. Whereas for the composite without MAPP, the tensile stress at yield slightly decreases up to 10% newspaper pulp loading and remains constant at about 30 MPa afterwards. Obviously, the tensile stress at yield of the composite with esterified newspaper pulp is much lower than that of the composite without MAPP in all of newspaper pulp content.

Unlike both of them, at low concentration the newspaper pulp – MAPP seems to have no effect on the tensile stress at yield of the polypropylene. But the tensile stress at yield starts increasing with increasing newspaper pulp content after 15% newspaper pulp – MAPP was added to the polypropylene. Tensile stress at yield of the composite with MAPP reaches its maximum of about 37 MPa at 20% newspaper pulp content. The incompatibility of polypropylene and newspaper pulp contribute to the lower tensile stress at yield. In the case of the composite with esterified newspaper pulp, the decreasing in tensile stress at yield can be attributed to the internal plasticization provided by the long chain fatty acid ester.

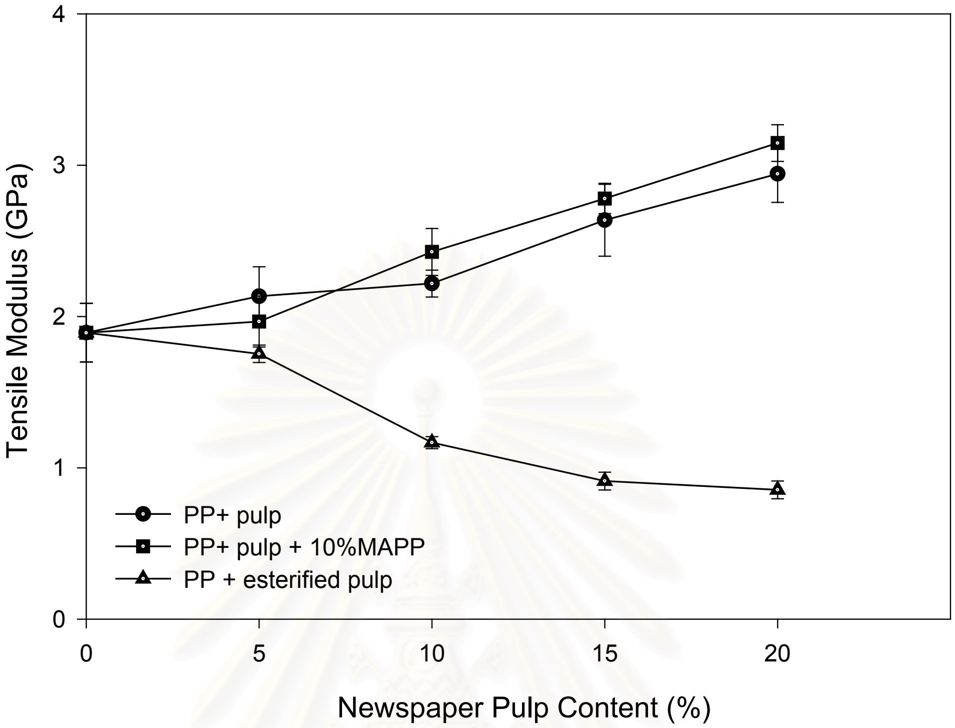


**Figure 4.6** Tensile modulus of the polypropylene / newspaper pulp composites.

Table 4.3 Tensile Modulus of the Polypropylene / Newspaper Pulp Composites

| Newspaper Pulp Content (%) | Tensile Modulus (GPa) | | |
|---|---|---|---|
| | Without MAPP | With MAPP | With Esterified Newspaper Pulp |
| 0 (PP) | 1. 89 ± 0.19 | 1.89 ± 0.19 | 1.89 ± 0.19 |
| 5 | 2.13 ± 0.20 | 1.97 ± 0.17 | 1.84 ± 0.22 |
| 10 | 2.22 ± 0.09 | 2.43 ± 0.15 | 1.17 ± 0.04 |
| 15 | 2.64 ± 0.24 | 2.78 ± 0.10 | 0.91 ± 0.5 |
| 20 | 2.94 ± 0.19 | 3.15 ±0.12 | 0.85 ± 0.06 |

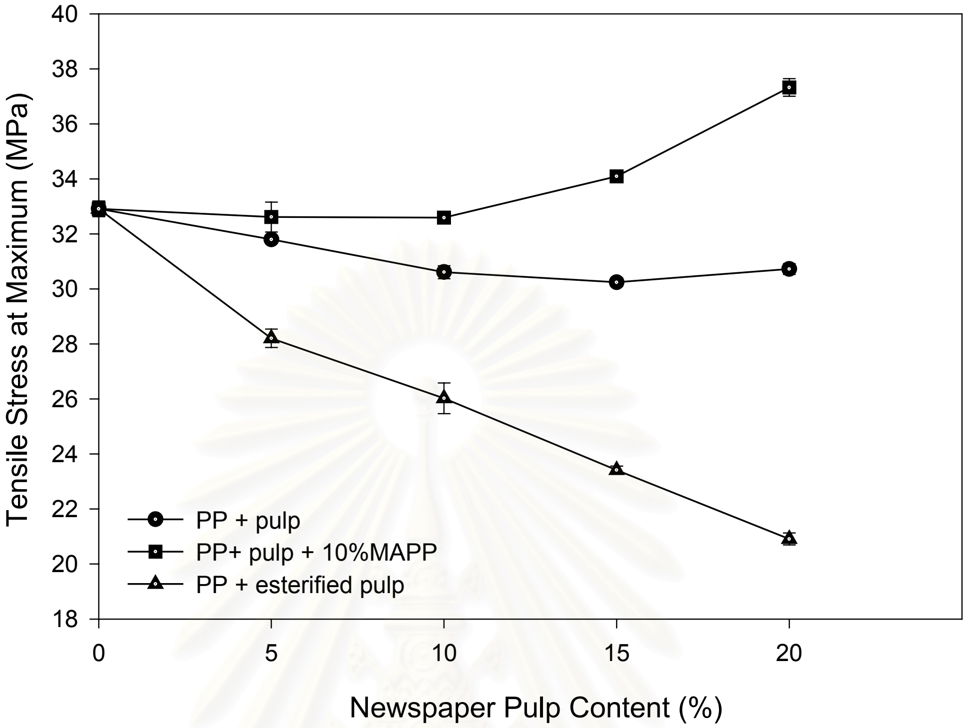


**Figure 4.7** Tensile stress at maximum of the polypropylene / newspaper pulp composites.

**Table 4.4** Tensile Stress at Maximum of the Polypropylene / Newspaper Pulp Composites.

| Newspaper Pulp Content (%) | Tensile Stress at Maximum (MPa) | | |
|---|---|---|---|
| | Without MAPP | With MAPP | With Esterified Newspaper Pulp |
| 0 (PP) | 32.91 ± 0.28 | 32.91 ± 0.28 | 32.91 ± 0.28 |
| 5 | 31.80 ± 0.15 | 32.90 ± 0.53 | 28.20 ± 0.33 |
| 10 | 30.61 ± 0.24 | 33.39 ± 0.57 | 26.02 ± 0.56 |
| 15 | 30.24 ± 0.15 | 34.09 ± 0.20 | 23.39 ± 0.15 |
| 20 | 30.73 ±0.19 | 37.33 ±0.32 | 20.91± 0.21 |

Figure 4.8 and Table 4.5 present the effect of newspaper pulp content on the tensile stress at break. Both the composite without MAPP and the composite with MAPP show the increasing in tensile stress at break with the increase in the newspaper pulp content. As can be seen, similar to the tensile modulus and tensile stress at yield, the tensile stress at break of the composite with MAPP is higher than that of the composite without MAPP in every compositions. The addition of 20% newspaper pulp – MAPP increases tensile stress at break or tensile strength by 47.48%, whereas only 18.89% increasing is observed for the composite without MAPP. In fact the increasing in tensile stress at break of composite without MAPP starts to level off after 5% loading of newspaper pulp.

In the case of the composite with esterified newspaper pulp, the tensile stress at break slightly increases when 5% newspaper pulp was added and then gradually decreases upon increasing the newspaper pulp content. The decreasing in tensile strength seems to level off at 15% newspaper pulp loading.

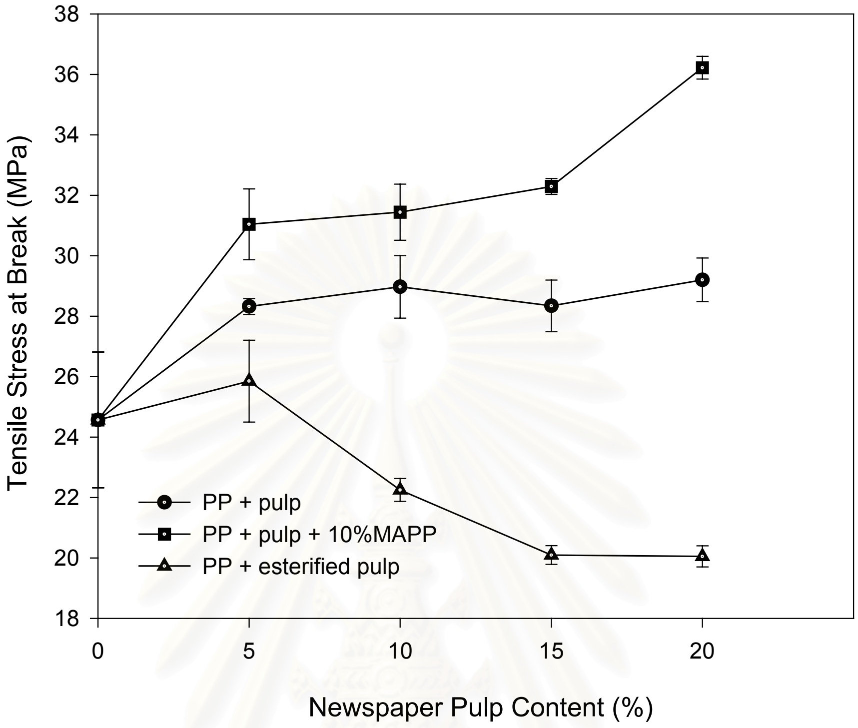


**Figure 4.8** Tensile stress at break of the polypropylene / newspaper pulp composites

**Table 4.5** Tensile Stress at Break of the Polypropylene / Newspaper Pulp Composites

| Newspaper Pulp Content (%) | Tensile Stress at break (MPa) | | |
|---|---|---|---|
| | Without MAPP | With MAPP | With Esterified Newspaper Pulp |
| 0 (PP) | 24.56 ± 2.24 | 24.56 ± 2.24 | 24.56 ± 2.24 |
| 5 | 28.32 ± 0.26 | 31.04 ± 1.17 | 25.85 ±1.36 |
| 10 | 28.97 ± 1.04 | 31.44 ± 0.92 | 22.25 ± 0.34 |
| 15 | 28.34 ± 0.85 | 32.29 ± 0.26 | 20.09 ± 0.31 |
| 20 | 29.20 ± 0.72 | 36.22 ± 0.38 | 20.05 ± 0.35 |

Effect of surface modification on tensile properties

Surface modification of newspaper pulp is very nescessary due to the incompatibility between the polypropylene and newspaper pulp which contributing to the unsatisfactory mechanical properties. In this part, the tensile properties of the composite using MAPP as a coupling agent between the polypropylene and the newspaper pulp are compared with that of the composite using esterified newspaper pulp.

As shown in Figure 4.6 through 4.8, using of MAPP as a coupling agent helps improving the tensile properties of polypropylene / newspaper pulp composites. Since MAPP enhances the compatibility between polypropylene and newspaper pulp, the tensile strength and stiffness of this composite is higher than those of the composite without MAPP. In contrast, the surface modification of newspaper pulp with the esterification reaction can not improve the tensile strength and stiffness, but the elongation at break, of the composite. The tensile modulus, for example, is lowest compared to the other two composites. From Figure 4.4 the stress – strain behavior illustrates that the esterified newspaper pulp composite is soft and ductile.

In conclusion, the improvement of compatibility between polypropylene and newspaper with MAPP is better than the esterification reaction. MAPP can improve the interfacial adhesion between the two components and hence the modulus, the tensile stress at yield,and the tensile stress at break are higher than the polypropylene. In the case of composite with esterified newspaper pulp, this compatibility might be overiden by the plasticizing effect of long chain fatty acid ester of dodecanoyl chloride.

Effect of compatibilizer on tensile properties

All composite materials, wheather fibrous or particulate, require good bonding between the polymer and the reinforcement. This is needed for mechanical reasons and to ensure effective load transmission through the reinforcing phase. In order to improve the compatibility and interfacial adhesion of polypropylene and newspaper pulp, MAPP was added during mixing. For comparison of the effect of MAPP content on the tensile properties of the composite, the newspaper pulp content at 10% was used in all of the composites. The MAPP content used are 2%, 5%, 10%, and 20% by weight of newspaper pulp.

As shown in Figure 4.9 and Table 4.6, it is interesting to observe that the tensile modulus is not significantly influenced by the quantity of the MAPP added. This observation suggested that the stiffness of the composite is mainly reinforced by the fiber or newspaper pulp itself than by the MAPP. Clearly, MAPP has little effect on the tensile modulus of the polypropylene / newspaper pulp composite except at the 10% MAPP in which the composite shows highest in tensile modulus.

The effect of MAPP content on the tensile stress at yield is presented in the Figure 4.10 and Table 4.7. Obviously, the tensile stress at yield increases with an increase in the MAPP content. At 20% MAPP, the polypropylene / newspaper pulp composite shows the highest tensile stress at yield of about 34.5 MPa. Unlike the case of tensile modulus, the increasing of tensile stress at yield due to the addition of MAPP into the polypropylene / newspaper pulp composite confirms the results that MAPP takes part in the interfacial adhesion improvement between the polypropylene and newspaper pulp. Good interfacial bonding is actually responsible directly for the load – extension tolerance of the composite. As described earlier, the tensile stress at yield of the composite with MAPP is greater than that of the composite without MAPP. This is because the presence of MAPP can improve the interfacial adhesion of the two components. As a result, the tensile stress at yield is better. In this case, tensile stress at yield increases 12.22% compared to the composite without MAPP.

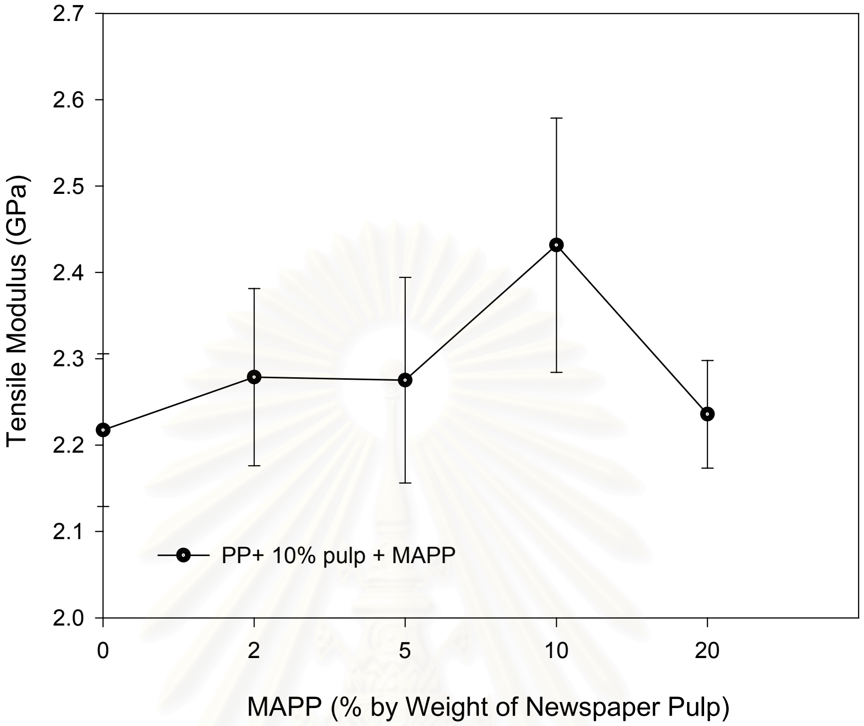


**Figure 4.9** Tensile modulus of the composites with different MAPP content.

Table 4.6 Tensile Modulus of the Composites with Different MAPP Content

| MAPP Content (%) | Tensile Modulus (GPa) |
|---|---|
| 0 | 2.22 ± 0.09 |
| 2 | 2.28 ± 0.10 |
| 5 | 2.28 ± 0.12 |
| 10 | 2.43 ± 0.15 |
| 20 | 2.16 ± 0.08 |

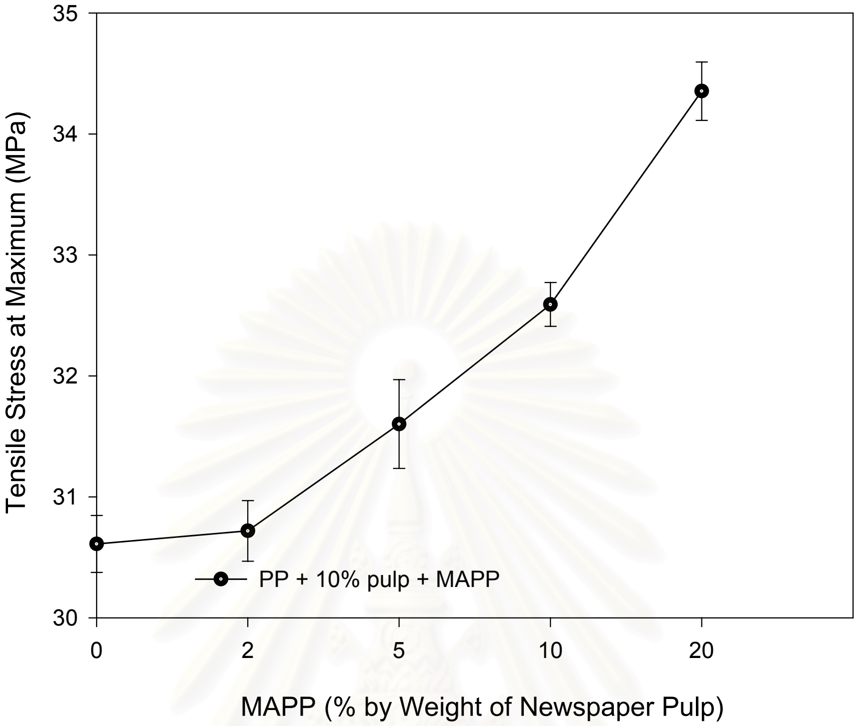


**Figure 4.10** Tensile stress at maximum of the composites with different MAPP content.

**Table 4.7** Tensile Stress at Maximum of the Composites with Different MAPP content

| MAPP Content (%) | Tensile Stress at Maximum (MPa) |
|---|---|
| 0 | 30.61 ± 0.24 |
| 2 | 30.72 ± 0.25 |
| 5 | 31.60 ± 0.37 |
| 10 | 33.39 ± 0.57 |
| 20 | 34.35 ± 0.24 |

Figure 4.11 and Table 4.8 display the effect of MAPP content on the tensile stress at break of the polypropylene / newspaper pulp composite. Although at 2% MAPP the tensile stress at break of the composite is lower than the composite without MAPP. The tensile stress at break starts rising again when the MAPP content increases from 5% up to 20%. Thus, in general, the addition of MAPP also helps increasing the tensile strength of the composites. Similar to the case of tensile stress at yield, this result can be explained that MAPP promotes the compatibility between the polypropylene and newspaper pulp.

In conclusion, MAPP affects only tensile strength and tensile stress at yield. Because MAPP can improve the compatibility between the polypropylene and newspaper pulp, hence, the tensile strength is better than the composite without MAPP. In contrast to its effect on tensile strength, coupling agent has a relative small effect on the tensile modulus of polypropylene / newspaper pulp composite.

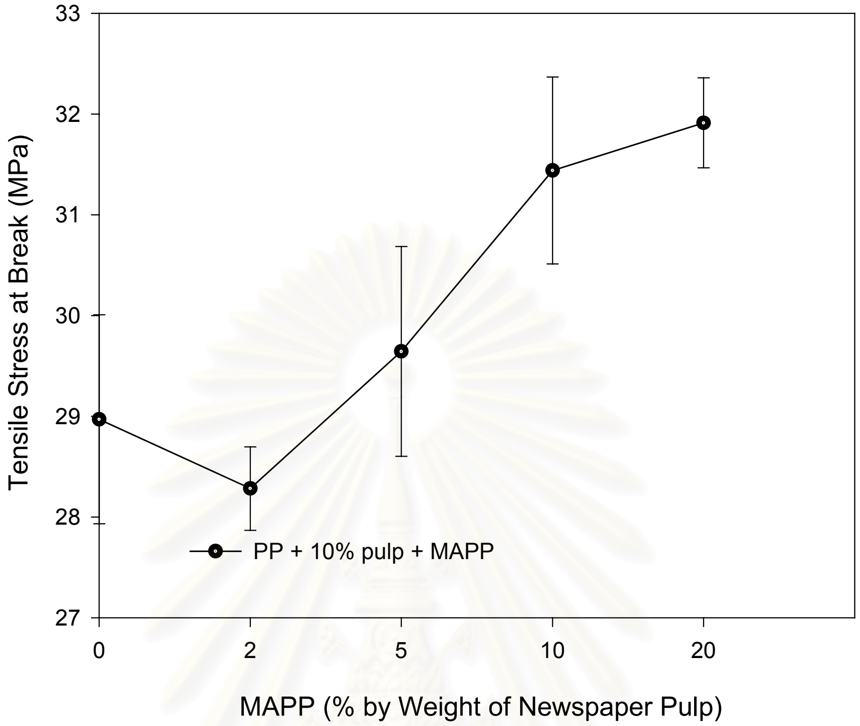


**Figure 4.11** Tensile stress at break of the composites with different MAPP content.

Table 4.8 **Tensile Stress at Break of the Composites with Different MAPP content**

| MAPP Content (%) | Tensile Stress at Break (MPa) |
|---|---|
| 0 | 28.97 ± 1.04 |
| 2 | 28.28 ± 0.41 |
| 5 | 29.61 ± 1.06 |
| 10 | 31.44 ± 0.93 |
| 20 | 31.91 ± 0.45 |

### 4.2.2 Flexural Properties

#### Effect of newspaper pulp content on flexural properties

Figure 4.12 and Table 4.9 show the effect of newspaper pulp content on the flexural modulus of the composite. The flexural modulus of the composite without MAPP and the composite with MAPP behaves in the same fashion that the flexural modulus increases as the amount of newspaper pulp content increases. In the case of the composite with esterified newspaper pulp, the flexural modulus decreases when increasing the newspaper pulp content. These results appear in the same trend as those previously reported on the tensile properties. Likewise, it can then explained that the increasing in flexural modulus is owing to the reinforcing effect of newspaper pulp, whereas the reducing in flexural modulus of esterified newspaper pulp composite might be due to the plasticizing effect from dodecanoated ester attached to the newspaper pulp.

The effect of newspaper pulp content on the flexural yield strength of the composite is presented in Figure 4.13 and Table 4.10. Similar to the flexural modulus, the flexural yield strength of the composite without MAPP and the composite with MAPP increases with increasing the newspaper pulp content. But the flexural yield strength of the composite with MAPP is higher than that of the composite without MAPP. The highest flexural yield strength about 58 MPa is of the 20% newspaper pulp – MAPP composite. On the other hand, the addition of esterified newspaper pulp decreases the flexural yield strength of the polypropylene. Not so surprisingly, the flexural yield strength decreases as a function of newspaper pulp content possibly because of the plasticizing effect of long chain fatty acid ester.

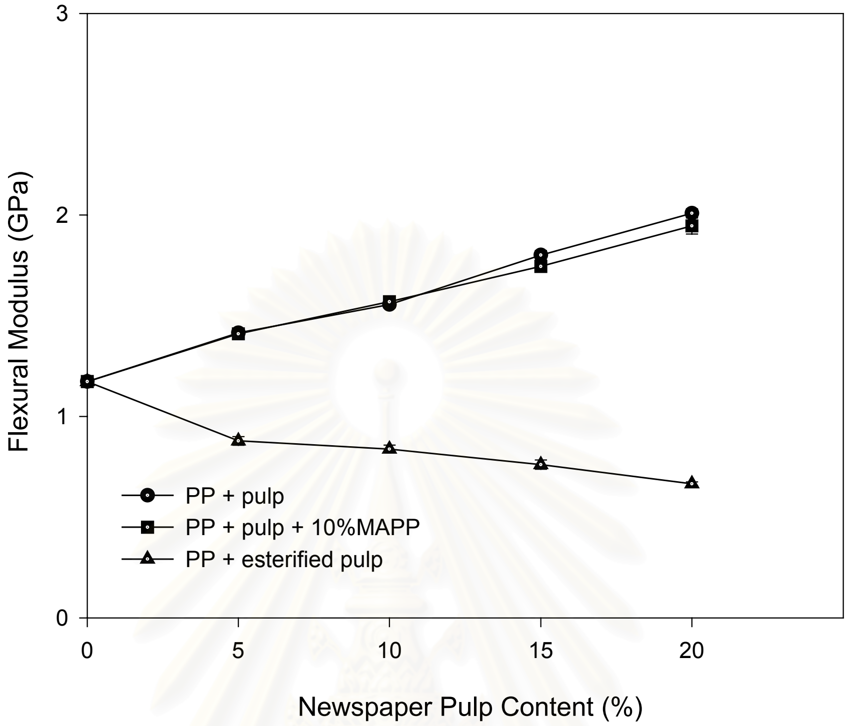


**Figure 4.12** Flexural modulus of the polypropylene / newspaper pulp composites.

Table 4.9 **Flexural Modulus of the Polypropylene / Newspaper Pulp Composites**

| Newspaper Pulp Content (%) | Flexural Modulus (GPa) | | |
|---|---|---|---|
| | Without MAPP | With MAPP | With Esterified Newspaper Pulp |
| 0 (PP) | 1.17 ± 0.01 | 1.17 ± 0.01 | 1.17 ± 0.01 |
| 5 | 1.41 ± 0.01 | 1.41 ± 0.02 | 0.88 ± 0.02 |
| 10 | 1.55 ± 0.01 | 1.57 ± 0.01 | 0.84 ± 0.02 |
| 15 | 1.80 ± 0.02 | 1.75 ± 0.02 | 0.76 ± 0.02 |
| 20 | 2.01 ± 0.02 | 1.94 ± 0.04 | 0.66 ± 0.01 |

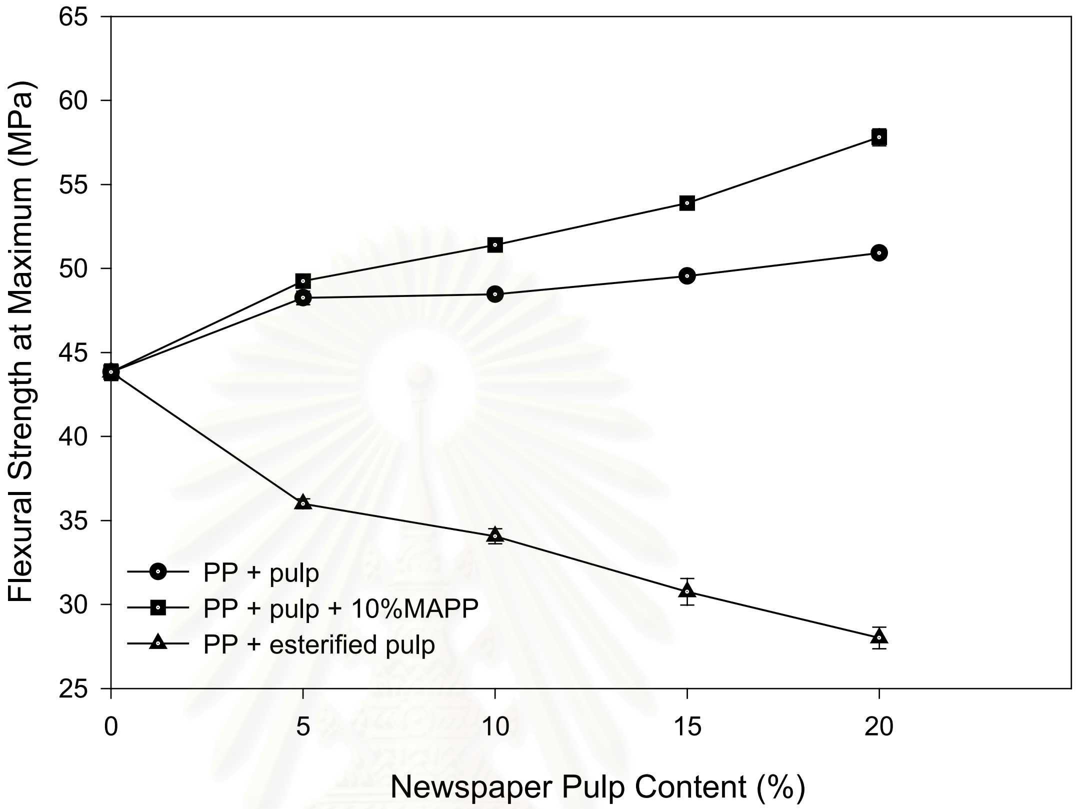


**Figure 4.13** Flexural strength at maximum of the polypropylene / newspaper pulp composites.

**Table 4.10** Flexural Strength at Maximum of the Polypropylene / Newspaper Pulp Composites

| Newspaper Pulp Content (%) | Flexural Strength at Maximum (MPa) | | |
|---|---|---|---|
| | Without MAPP | With MAPP | With Esterified Newspaper Pulp |
| 0% (PP) | 43.82 ± 0.48 | 43.82 ± 0.48 | 43.82 ± 0.48 |
| 5% | 48.25 ± 0.41 | 49.24 ± 0.20 | 35.99 ± 0.29 |
| 10% | 48.45 ± 0.26 | 51.40 ± 0.33 | 34.06 ± 0.44 |
| 15% | 49.54 ± 0.16 | 53.82 ± 0.17 | 30.75 ± 0.79 |
| 20% | 50.92 ± 0.27 | 57.80 ± 0.51 | 28.01 ± 0.65 |

### Effect of surface modification on flexural properties

Because of the poor compatibility between polypropylene and newspaper pulp, it is nearly impossible to prepare the composite with good mechanical properties without any interface modification. However, surface modification of newspaper pulp by MAPP has no effect on the flexural modulus, but the flexural yield strength, as shown in Figure 4.12 and 4.13, respectively. Clearly from Figure 4.12, the flexural modulus of the composite with and without MAPP is superimposed to each other through the whole range of newspaper pulp content. Unlike the flexural modulus, the addition of MAPP produces a significant inprovement in the flexural strength. This is because the stiffness or modulus of the composite is mainly due to the fiber or newspaper pulp itself; while the flexural yield strength improvement is also caused by the interfacial adhesion between the two phases which should be enough during being stretched.

In contrast, the surface modification with the esterification reaction can not improve either flexural modulus or flexural yield strength of the composite. Both values decreases drastically upon increasing newspaper pulp content. In other words, the flexural properties of polypropylene and newspaper pulp can not be improved by the addition of esterified newspaper pulp, but the MAPP – newspaper pulp.

### Effect of compatibilizer on flexural properties

From the effect of surface modification on flexural properties it can be concluded that MAPP improve the interfacial adhesion between polypropylene and the newspaper pulp. In this section, the effect of MAPP content is studied.

Figure 4.14 and Table 4.11 show the effect of MAPP content on the flexural modulus of the composite. It is interesting to see that the flexural modulus is not significantly affected by the amount of MAPP added. This result is in good agreement with the effect of MAPP content on the tensile modulus. The same conclusion can be addressed that the stiffness of the composite is mainly due to the volume fraction and the strength or modulus of newspaper pulp itself rather than the degree of used coupling agent or MAPP content. This explanation is based on the rule of mixture, a simple composite theory, which always assumes perfect bonding or adhesion between two phases, or neglects the effect of interfacial bond strength of the composite.

The influence of MAPP content on the flexural yield strength is presented in Figure 4.15 and Table 4.12. The flexural yield strength remarkably increases with increasing the MAPP content. By adding 20% MAPP, the newspaper pulp can enhance the flexural yield strength up to 7.97% compared to the unmodified – surface composite (0% MAPP). Therefore, from Figure 4.14 and 4.15 it can be concluded that MAPP affects only the flexural yield strength but has no effect on the flexural modulus. As mentioned, the same trend is also found in the case of tensile properties.

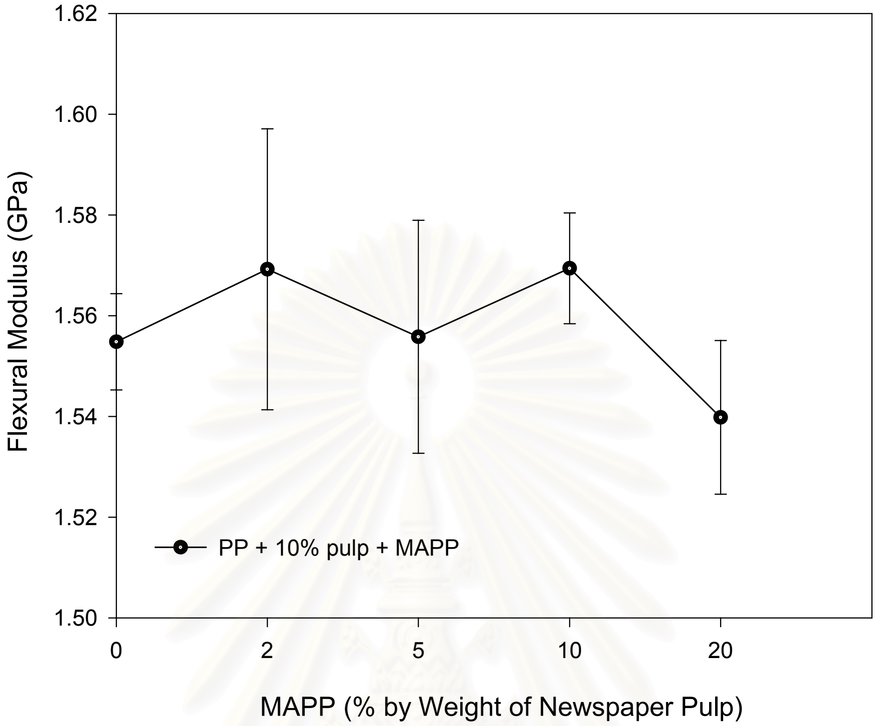


**Figure 4.14** Flexural modulus of the composites with different MAPP content.

Table 4.11 Flexural Modulus of the Composites with Different MAPP content

| MAPP Content (%) | Flexural Modulus (GPa) |
|---|---|
| 0 | 1.55 ± 0.01 |
| 2 | 1.57 ± 0.03 |
| 5 | 1.56 ± 0.02 |
| 10 | 1.57 ± 0.01 |
| 20 | 1.54 ± 0.02 |

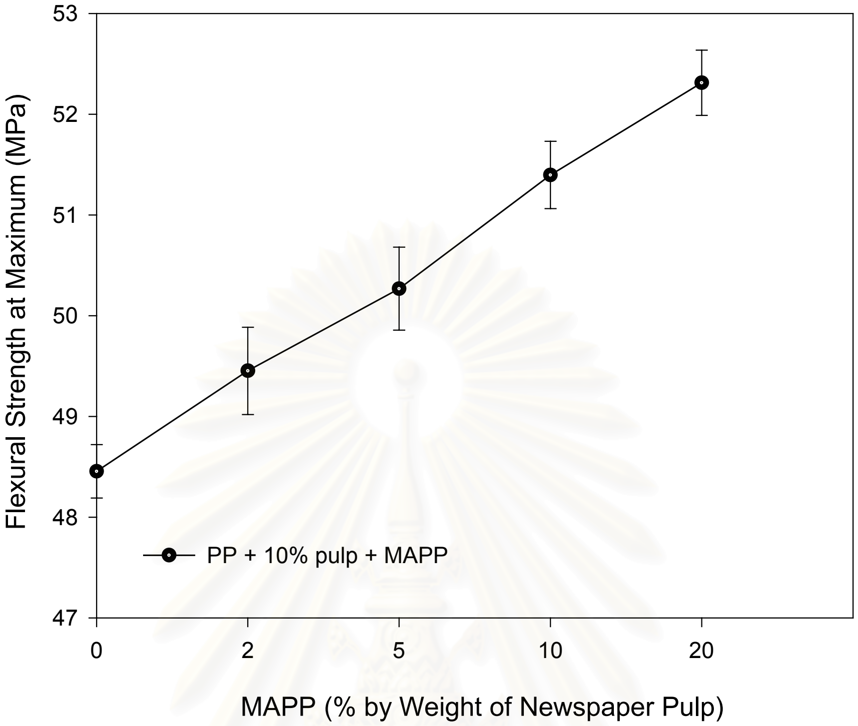


**Figure 4.15** Flexural strength at maximum of the composites with different MAPP content.

Table 4.12 Flexural Strength at Maximum of the Composites with Different MAPP content

| MAPP Content (%) | Flexural Strength at Maximum (MPa) |
|---|---|
| 0 | 48.45 ± 0.26 |
| 2 | 49.54 ± 0.43 |
| 5 | 50.27 ± 0.41 |
| 10 | 51.40 ± 0.30 |
| 20 | 52.31 ± 0.32 |

### 4.2.3 Impact Properties

#### Effect of newspaper pulp content on impact strength

Figure 4.16 and Table 4.13 show the notched Izod impact strength of the composite without MAPP, the composite with MAPP and the composite with esterified newspaper pulp. Unlike tensile and flexural properties, increasing the amount of newspaper pulp has no effect on the impact strength of both composite with MAPP and without MAPP. Although slight increase in impact strength at 5% newspaper pulp loading has been found in both composites, 9.92% and 6.38%, respectively, with further increase the newspaper pulp content, the impact strength does not increase. In fact, their impact strength values seem to decrease slightly at high newspaper pulp content (20%).

The composite with esterified newspaper pulp shows the lowest impact strength in all of newspaper pulp content and the impact strength is also lower than the polypropylene. Similar to other mechanical strength previously discussed, the plasticizing effect from long chain fatty acid ester plays an important role in decreasing all the strength of polypropylene / newspaper pulp composites.

#### Effect of surface modification on impact strength

As can be seen in the Figure 4.16 and Table 4.13, the two methods of surface modification, the addition of MAPP and the esterification reaction, can not improve the impact strength of the composites. In particular, there is no difference in impact strength between the composite with MAPP and without MAPP.

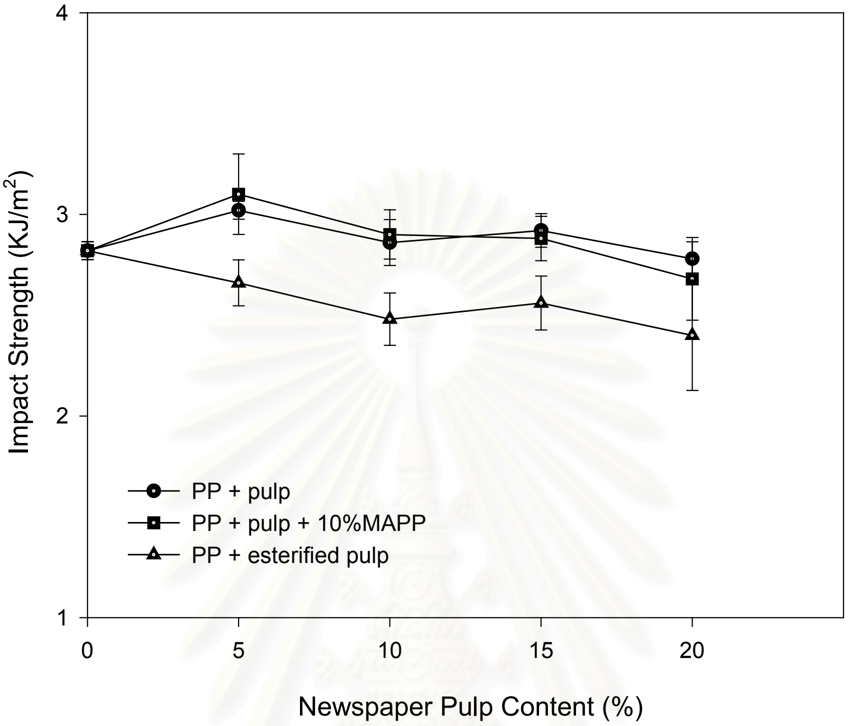


**Figure 4.16** Impact strength of the polypropylene / newspaper pulp composites.

**Table 4.13** Impact Strength of the Polypropylene / Newspaper Pulp Composites

| Newspaper Pulp Content (%) | Impact Strength (KJ/m$^2$) | | |
|---|---|---|---|
| | Without MAPP | With MAPP | With Esterified Newspaper Pulp |
| 0 (PP) | 2.82 ± 0.18 | 2.82 ± 0.18 | 2.82 ± 0.18 |
| 5 | 3.00 ± 0.71 | 3.10 ± 0.20 | 2.66 ± 0.11 |
| 10 | 2.86 ± 0.11 | 2.90 ± 0.12 | 2.48 ± 0.13 |
| 15 | 2.88 ± 0.13 | 2.60 ± 0.07 | 2.48 ± 0.25 |
| 20 | 2.78 ± 0.13 | 2.56 ± 0.21 | 2.40 ± 0.27 |

Effect of compatibilizer on the impact strength

The MAPP compatibilizer has little or no effect on the notched Izod impact strength. From the Figure 4.17 and Table 4.14, the MAPP content of 2% and 5% can not improve the impact strength of the composite and the values are lower than that of the composite without MAPP. The improvement of the impact strength can be observed when the MAPP content increased to 10% and 20%. At 20% MAPP, the polypropylene / newspaper pulp composite gives the highest impact strength. In conclusion, the amount of MAPP has little or no effect on the impact strength compared to the composite without MAPP.

The overall results of the impact properties lead to the conclusion that the newspaper pulp and the addition of MAPP have a little effect on the impact strength of the polypropylene composite.

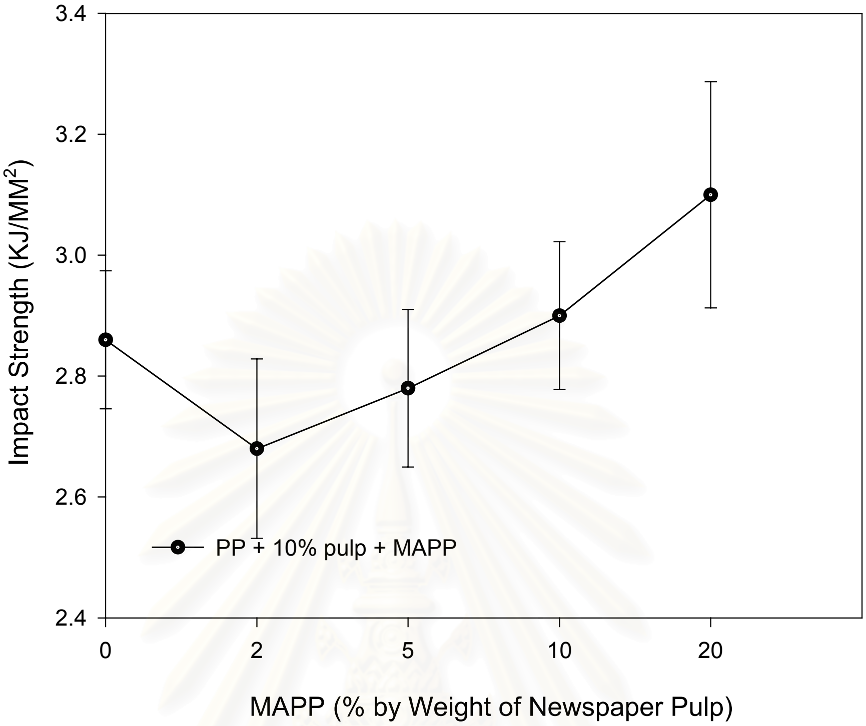


**Figure 4.17** Impact strength of the composite with different MAPP content.

Table 4.14 **Impact Strength of the Composite with Different MAPP Content**

| MAPP Content (%) | Flexural Modulus (GPa) |
|---|---|
| 0 | 2.86 ± 0.11 |
| 2 | 2.68 ± 0.15 |
| 5 | 2.78 ± 0.13 |
| 10 | 2.90 ± 0.12 |
| 20 | 3.10 ± 0.19 |

## 4.3 Thermal Characterization

In this section, the study of polypropylene and its composite with newspaper pulp was undertaken to further understanding of the effect of newspaper pulp, compatibilizer content, and surface modification on thermal properties of the composite.

### 4.3.1 Thermogravimetric Analysis (TGA)

Thermal degradation and weight loss as a function of temperature were studied using a Perkin Elmer TGA7 in a nitrogen atmosphere. A heating rate of 20°C was used to heat the sample from 50°C to 600°C. Sample weighing 5 mg were used.

Figure 4.18 represents a typical TGA thermogram of newspaper pulp and esterified newspaper pulp. Newspaper pulp shows an initial weight loss at 100°C as a result of water loss. With a further rise in temperature from 100°C to 400°C, newspaper pulp exhibits no changes in weight and is stable to 275°C. Thermal degradation of newspaper pulp begins near 280°C, with the weight decreasing rapidly to 380°C.

The thermogravimetric analysis of esterified newspaper pulp shows the thermal degradation of esterified begins near 190°C and the weight decreasing to 420°C. Although, the onset degradation temperature of esterified newspaper pulp is lower than newspaper pulp, but the thermal stability of esterified newspaper pulp is up to 420 °C

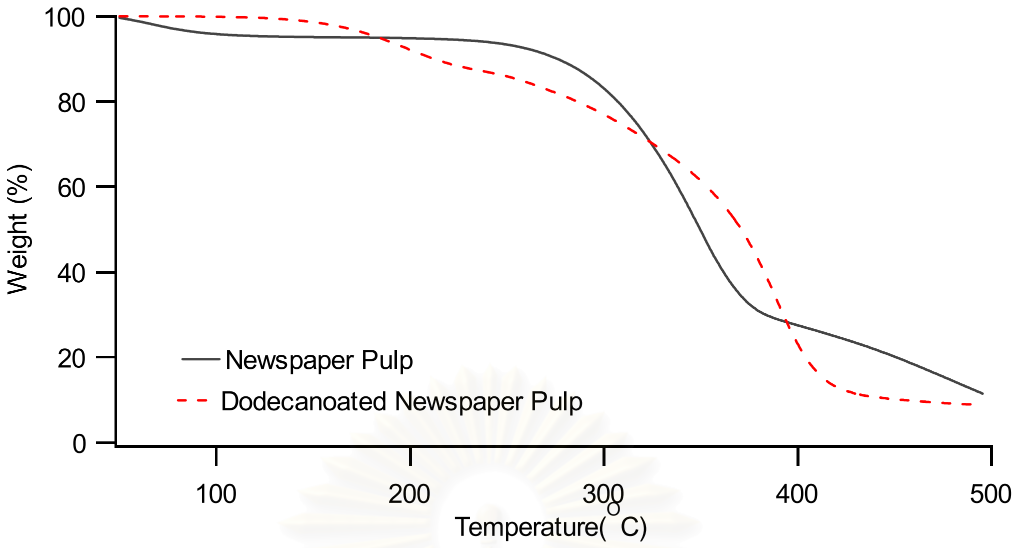


Figure 4.18 Weight loss as a function of temperature for newspaper pulp and esterified newspaper pulp.

Effect of Newspaper Pulp Content

Figure 4.19 shows a TGA thermogram for polypropylene / newspaper pulp composites containing different amounts of newspaper pulp. Polypropylene shows an initial weight loss at 354$^{o}$C, with the weight decreasing rapidly to 460$^{o}$C. In the polypropylene composite with 5% newspaper pulp, the onset of the degradation starts at 363.45 $^{o}$C whereas that of the polypropylene composite with 10% newspaper pulp is about 363.75$^{o}$C. The degradation or decomposition of polymer occurs when the polymer has received enough energy to break intramolecular bond. Since the intramolecular bond is very strong bond, so the degradation occurs at high temperature. When newspaper pulp was added to polypropylene, the composite needs more energy in decomposition than pure polypropylene. Because the portion of energy is used to decompose the newspaper pulp prior to decompose polypropylene. Hence, polypropylene part in the composite is decomposed at higher temperature. In according to the TGA thermogram, the degradation temperature of the composite with newspaper pulp is greater than that of polypropylene. In conclusion, the composite with newspaper pulp has better thermal stability than the pure polypropylene. When comparing the effect of newspaper pulp content on the degradation temperature, no significant difference between the composite with 5% and 10% newspaper pulp can be observe, except the higher amount of residue found in the 10% newspaper pulp composite. This residue is corresponding directly to the quantity of newspaper pulp contained in the composites which turned into ash after being decomposed. In contrast, polypropylene has no residue left after decomposition since its chemical compositions completely decompose into volatile materials.

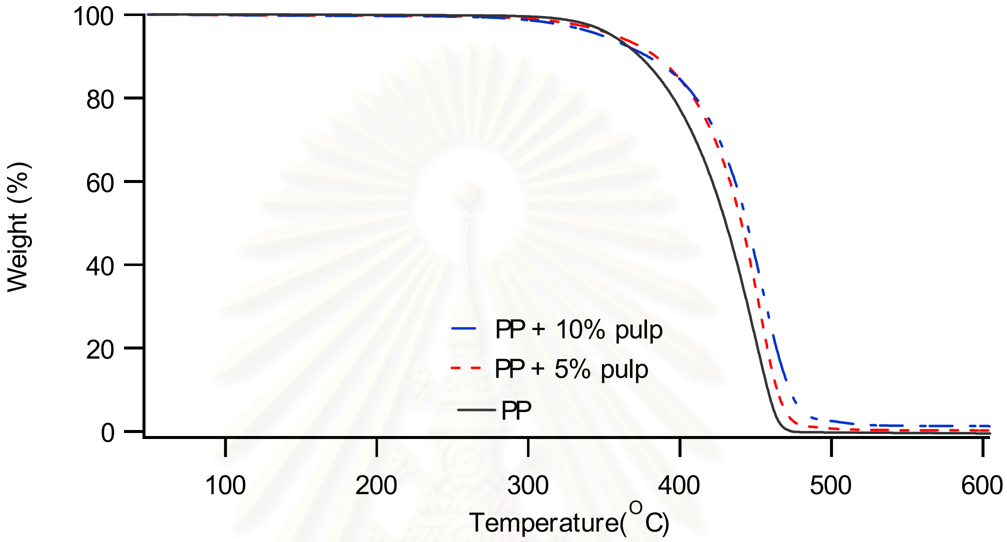


**Figure 4.19** Weight loss as a function of temperature for the composites without MAPP

**Table 4.15** The Onset Degradation Temperature of the Composite without MAPP

| Newspaper Pulp Content (%) | Td (Onset) (°C) |
|---|---|
| 0 (PP) | 354.49 |
| 5 | 363.45 |
| 10 | 363.75 |

<u>Effect of Compatibilizer</u>

Thermal degradation of the polypropylene / 10% newspaper pulp composite with various amounts of MAPP is shown in Figure 4.20. The onset degradation temperature of the composite with different amounts of MAPP is presentd in Table 4.16. From the thermograms there is no difference between the onset degradation temperature of the composite with and without MAPP. In addition, increasing the amount of MAPP has no effect on the onset and final degradation temperatures of the composite, since the degradation temperature of MAPP is about 364°C similar to the degradation temperature of the composite without MAPP. Hence, the addition of MAPP can not effect on the thermal stability of the composite. From this study, the newspaper pulp has the great influence on the thermal stability of the composite, not MAPP, as described earlier in the composite without MAPP.

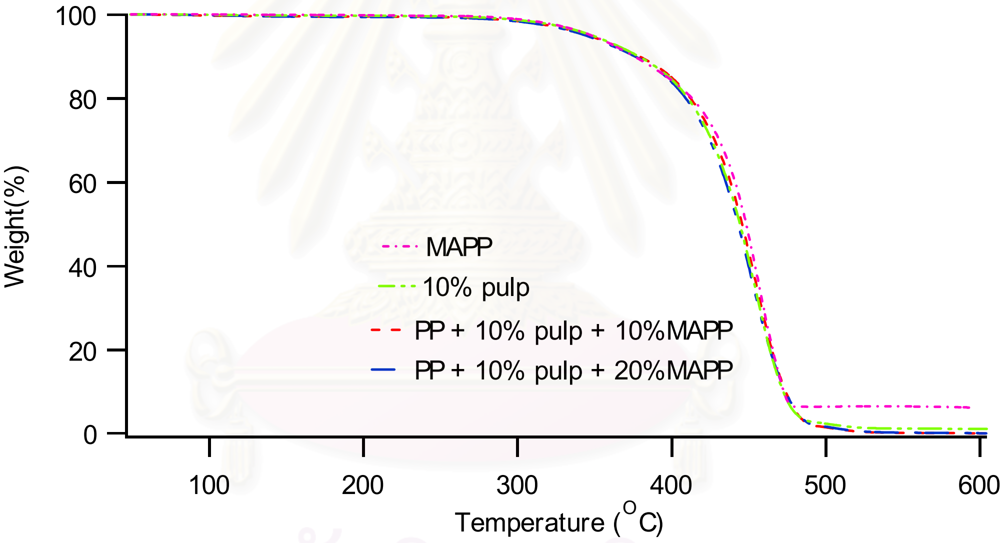


**Figure 4.20** Weight loss as a function of temperature for the composite with MAPP.

**Table 4.16** The Onset Degradation Temperature of the Composite with MAPP

| MAPP Content (%) | Td (Onset) (°C) |
|---|---|
| 0 | 363.75 |
| 10 | 364.50 |
| 20 | 364.10 |

Effect of Esterified Newspaper Pulp

Figure 4.21 shows the effect of esterified newspaper pulp on the thermal stability of the composite. The onset of degradation temperature is presented in Table 4.17. The composite with esterified newspaper pulp has higher degradation temperature than polypropylene in all esterified newspaper pulp loading. In order words, these composites are higher thermal stability than polypropylene. From the thermogram, it can be seen that the composite with 5% of esterified newspaper pulp has the highest stability followed by 10% and 15% esterified newspaper pulp composites, respectively.

Like the case of the composite with newspaper pulp, these composites need higher energy in decomposition than polypropylene owing to the portion of energy used to decompose esterified newspaper pulp before the decomposition of polypropylene. Hence, the decomposition or degradation occurs at high temperature than pure polypropylene.

In addition, the degradation temperature of the composite with esterified newspaper pulp is greater than the composite with newspaper pulp in every compositions. This is because the esterified newspaper pulp has higher thermal stability.

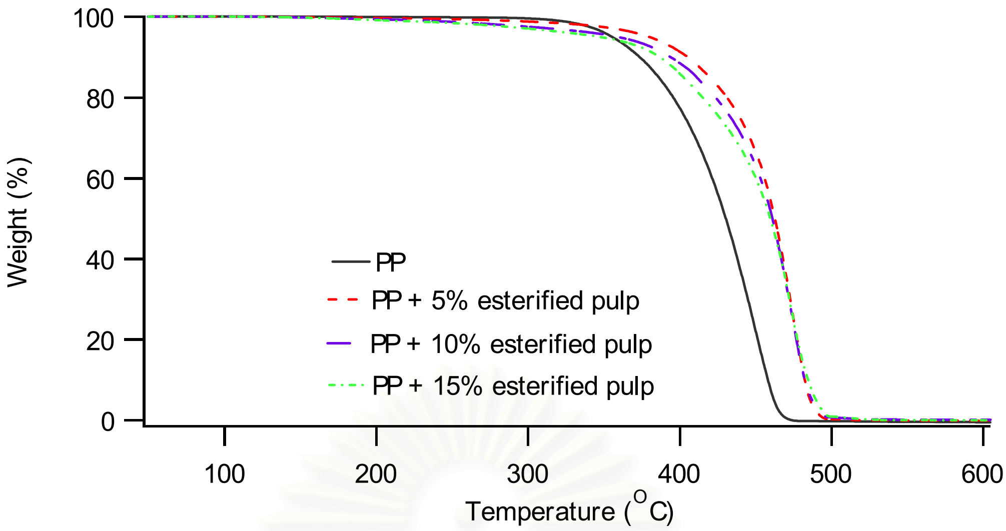


**Figure 4.21** Weight loss as a function of temperature for the composite with esterified newspaper pulp.

**Table 4.17** The Onset Degradation Temperature of the Composite with Esterified Newspaper Pulp

| Newspaper Pulp Content (%) | Td (Onset) (°C) |
|---|---|
| 0 (PP) | 354.49 |
| 5 | 381.84 |
| 10 | 376.76 |
| 15 | 372.43 |

Comparison of the thermal stability in the composite without MAPP, the composite with 10% MAPP, and the composite with esterified newspaper pulp is shown in Figure 4.22. Table 4.18 presents the onset degradation temperature of these composites. At 10 wt% newspaper pulp, the degradation temperature of these composite is shifted to the higher temperature than the polypropylene. This because of the presence of newspaper pulp and esterified newspaper pulp. Among them, the composite with esterified newspaper pulp shows the highest thermal stability. The composite without MAPP and the composite with MAPP show the same degradation temperature. Polypropylene is lowest thermal stability.

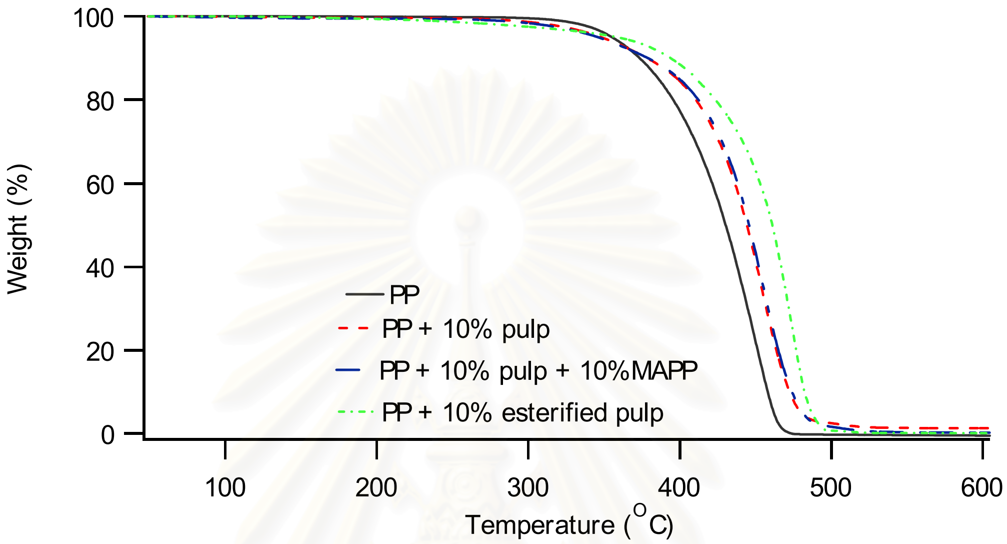


**Figure 4.22** Weight loss as a function of temperature for the composite without MAPP, the composite with MAPP, and the composite with esterified newspaper pulp.

**Table 4.18** The Onset Degradation Temperature of the Composite without MAPP, the Composite with MAPP, and the Composite with Esterified Newspaper Pulp

| Type of Composites | Td (Onset) (°C) |
|---|---|
| Polypropylene | 354.59 |
| Composite without MAPP | 363.75 |
| Composite with MAPP | 364.10 |
| Composite with esterified Newspaper pulp | 376.76 |

### 4.3.2 Differential Scanning Calorimeter (DSC)

Thermal transition temperature was characterized by a differential scanning calorimetry (DSC). The melting temperature (Tm) of the composite was taken as the maximum of the endothermic peak from the second heating while the crystallization temperature (Tc) was taken as the maximum of the exothermic peak from the cooling cycle.

### Effect of Newspaper Pulp Content on Thermal Properties

The second heating of DSC thermograms for polypropylene and polypropylene / newspaper pulp composites are illustrated in Figure 4.23. It is found that Tm of the composite do not show the significant change from the pure polypropylene, only 3°C shifted is observed. However, Tc is clearly shifted to the higher temperature with the addition of newspaer pulp as shown in Figure 4.24. These shifts in Tm and Tc seem to be independent on the newspaper pulp content.

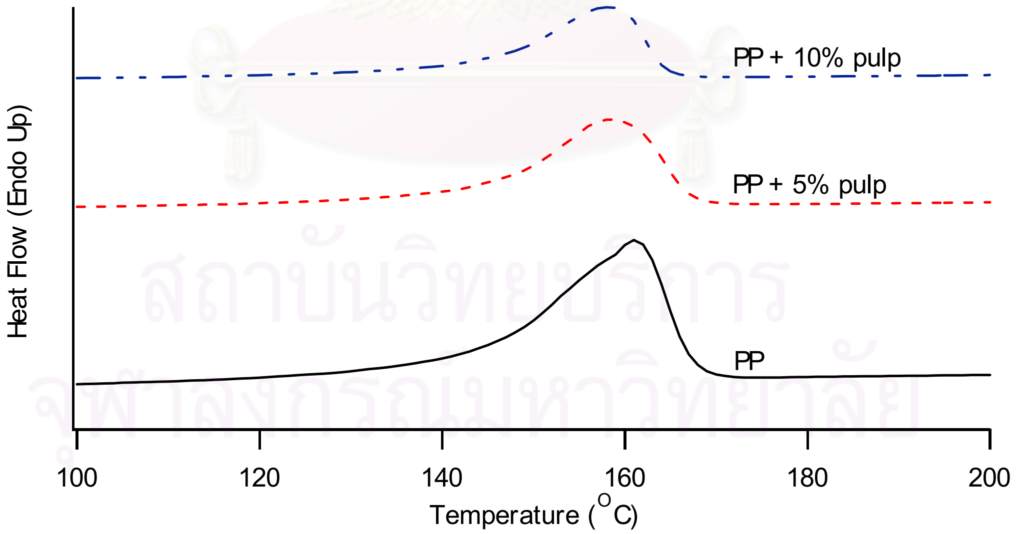


Figure 4.23 The melting temperature for polypropylene and polypropylene / newspaper

pulp composites.

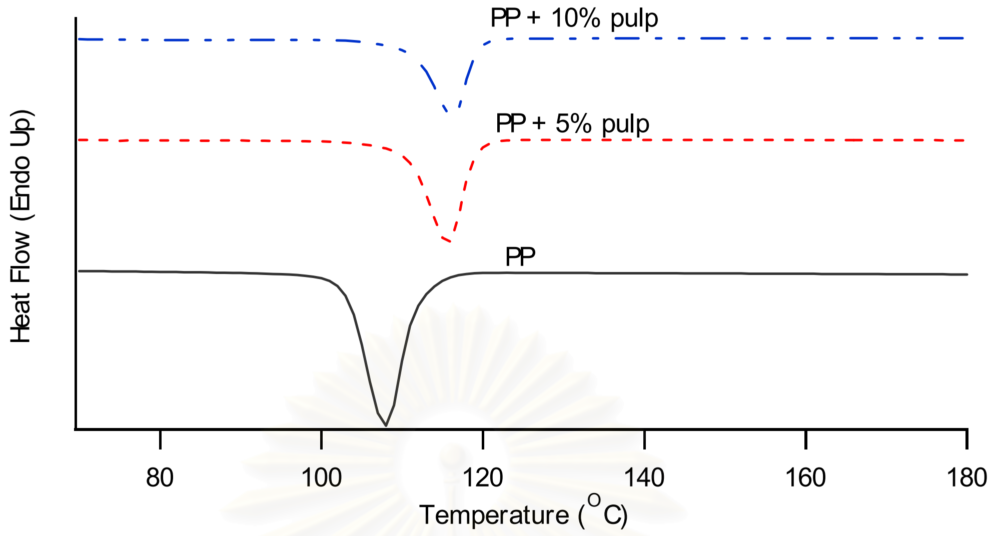


**Figure 4.24** The crystallization temperature for polypropylene and polypropylene / newspaper pulp composites.

It is well known that the area enclosed under this melting endothermic peak, (called the heat of fusion), can be used to calculate the degree of crystallinity. Therefore, by knowing the heat of fusion of fully crystalline polypropylene, the degree of crystallinity can be determined. Table 4.19 summarizes the melting temperature, crystallization temperature, heat of fusion, and degree of crystallinity of polypropylene and polypropylene / newspaper pulp composites. The heat of fusion for 100% crystalline polypropylene used to calculated the degree of crystallinity of polypropylene is 230 J/g [20].

**Table 4.19** Thermal Properties and Degree of Crystallinity for Polypropylene and Polypropylene / Newspaper Pulp Composites

| Newspaper Pulp Content (%) | Tm (°C) | Tc (°C) | $\Delta H_f$ (J/g) | | Degree of Crystallinity (%) | |
|---|---|---|---|---|---|---|
| | | | J/g (Total) | J/g (PP) | $\Delta H_{f,c}$=230J/g | |
| | | | | | /Total | /PP |
| 0 | 161.00 | 107.97 | 82.94 | 82.94 | 36.06 | 36.06 |
| 5 | 158.59 | 115.57 | 72.56 | 76.38 | 31.55 | 33.21 |
| 10 | 158.33 | 116.37 | 54.71 | 60.79 | 23.79 | 26.43 |

Although there is no other endothermic peak occurred upon heating the polypropylene composites to 200°C, this does not mean that the composites are compatible. The endothermic transition occurred is solely attributed from the polypropylene since the newspaper pulp, like any other cellulose fibers, has no melting temperature.

As mentioned earlier, addition of newspaper pulp causes an increasing in Tc . It might be implied that newspaper pulp functions as a nucleating agent allowing polypropylene to form its crystals on the nucleating sites very fast and at higher temperature compared to pure polypropylene. In other words, these nucleating agents provide nuclei for heterogeneous crystallization, raising the crystallization rate, and crystallization temperature. More and smaller spherulites are consequently produced resulting in the lowering of Tm and degree of crystallinity. However, as the number of nuclei increases, there seems to be no effect on Tc .

The heat of fusion of polypropylene decreases as the newspaper pulp content increases as shown in Table 4.19. The incorporation of newspaper pulp in a polypropylene matrix changes the crystallinity of the pure polypropylene. The added newspaper pulp appears to acts as an impurity, interfering with the crystalline formation of polypropylene by interrupting the close packing of polypropylene segments. As a result, the degree of crystallinity decrease.

As shown in Figure 4.23 and Table 4.19, there is no significant difference in the Tm between polypropylene and its composites. The Tm of each composite remains close to the Tm of pure polypropylene, regardless of the newspaper pulp content. Only 3°C lowering in Tm is observed.

The difference in Tm between the pure polypropylene and polypropylene containing newspaper pulp, however, might be able to explain in terms of its crystal structure. In general, several difference types of spherulites may be formed on crystallization of polypropylene. The normal crystalline form of polypropylene is a so – called $\alpha$ - polypropylene with a monoclinic unit cell. However, formation of $\beta$ - polypropylene, a polymorphic form of polypropylene sometimes found in melt cooled polymer, may be promoted by the use of certain nucleating agent. The difference in crystal formation may be responsible for the shifted in Tm of polypropylene phase. Further investigation by x – ray diffraction technique is needed in order to understand more of the polypropylene crystal including its crystal structure.

### Effect of Compatibilizer

Figure 4.25 and 4.26 present the effect of MAPP content on the melting temperature and the crystallization temperature of polypropylene and the 10 wt% newspaper pulp / polypropylene composite. As can be seen, the increasing in the amount of MAPP has no effect on both Tm and Tc.

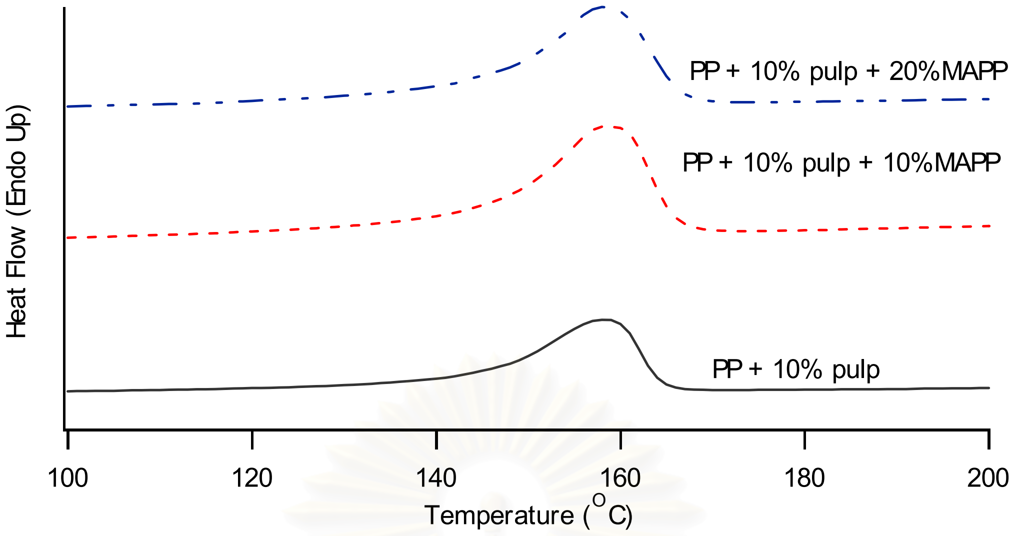


**Figure 4.25** The melting temperature for the composites with MAPP.

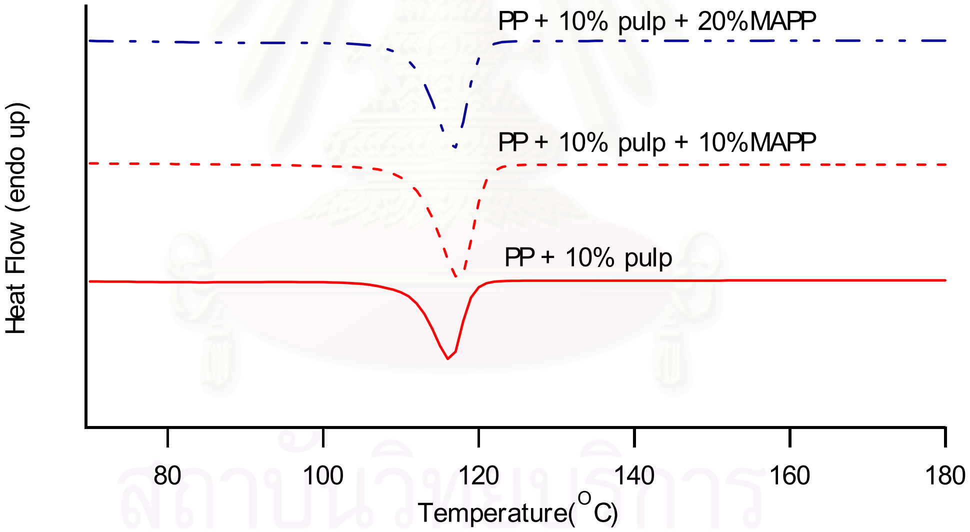


**Figure 4.26** The crystallization temperature for polypropylene and the composites with MAPP.

The effect of MAPP content on the degree of crystallinity of polypropylene is also presented in Table 4.20. Degree of crystallinity increases with the MAPP content increases. This result can be explained that MAPP has an excellent compatibilizing effect on the composite. Unlike the composite without MAPP, the newspaper pulp does not act as impurity. Treatment of newspaper pulp with MAPP provides covalent bonds across the interface, permitting segmental crystallization and thus cohesive coupling between newspaper pulp and polypropylene matrix [31]. More precisely, polypropylene segments of MAPP form miscible blends with the bulk polypropylene. Hence, the degree of crystallinity of polypropylene also increases ; as a result, they require more energy to melt or change their structure.

**Table 4.20** Thermal Properties and Degree of Crystallinity for the Composites With MAPP

| MAPP Content (%) | Tm (°C) | Tc (°C) | $\Delta H_f$ (J/g) | | Degree of Crystallinity (%) | |
|---|---|---|---|---|---|---|
| | | | J/g (Total) | J/g (PP) | $\Delta H_{f,c}$=230J/g | |
| | | | | | /Total | /PP |
| 0 | 158.33 | 116.37 | 54.71 | 60.79 | 23.79 | 26.43 |
| 10 | 158.48 | 117.36 | 75.34 | 83.72 | 32.76 | 36.40 |
| 20 | 158.20 | 116.64 | 76.17 | 84.64 | 33.11 | 36.80 |

**Effect of Esterified Newspaper Pulp**

Figure 4.27 and 4.28 show the melting temperature and the crystallization temperature of polypropylene and the composite with esterified newspaper pulp. As can be seen, comparing to the pure polypropylene, only a small decrease of the melting temperature when the amount of esterified newspaper pulp increased is observed. The crystallization temperature increases with the addition of esterified newspaper pulp.

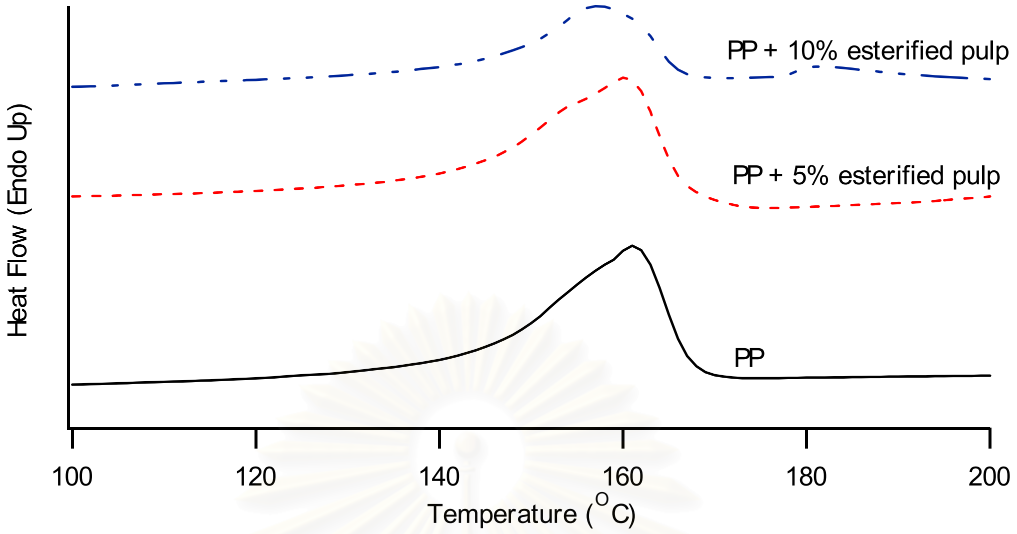


Figure 4.27 The melting temperature for polypropylene and the composites with esterified newspaper pulp.

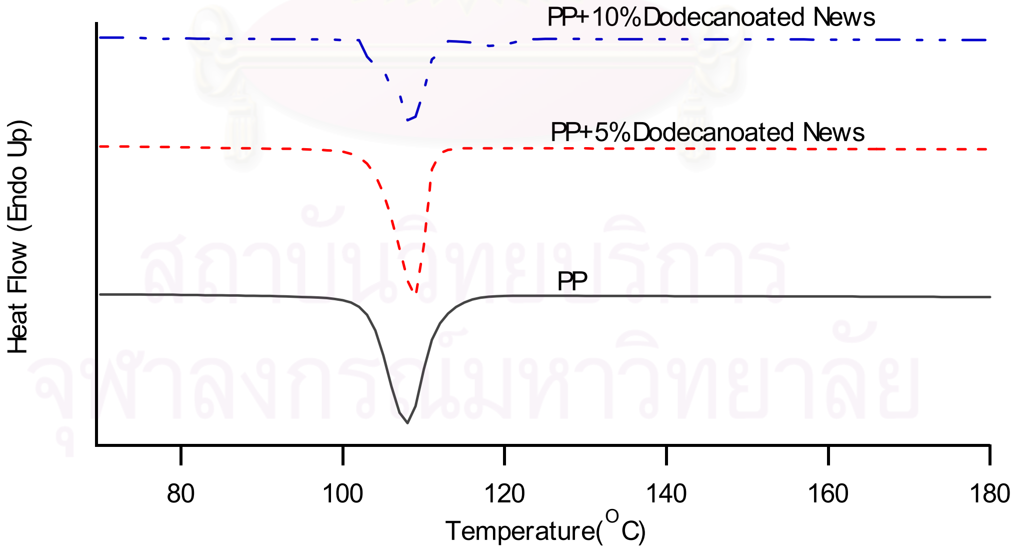


**Figure 4.28** The crystallization temperature for polypropylene and the composites with esterified newspaper pulp.

Table 4.21 presents thermal properties and degree of crystallinity for polypropylene and the composites with esterified newspaper pulp. From the Table, the heat of fusion increases when the esterified newspaper pulp is about 5 wt%. That means the degree of crystallinity of polypropylene increases. When the esterified newspaper pulp increases to 10 wt%, the heat of fusion and the degree of crystallinity decreases. But the degree of crystallinity is close to that of polypropylene, and higher than the case of composite without MAPP.

At 5% newspaper pulp loading, the increase in the degree of crystallinity can be explained in the same fashion as the composite containing MAPP that the esterified newspaper pulp does not act as impurity. The long chain fatty acid ester form miscible blends with the polypropylene matrix owing to segmental crystallization between the esterified newspaper pulp phase and polypropylene phase. This co – crystallization is however decreased when 10% esterified newspaper pulp is added. This result is in good agreement with the slight decrease in Tm. Since at 10% esterified newspaper pulp, the nucleating sites significantly increase, the more the nucleating sites, a large number of small and less perfect crystals are obtained. As a result, the composite show a little lower in Tm and also a 7% drop in degree of crystallinity.

**Table 4.21** Thermal Properties and Degree of Crystallinity for Polypropylene and the Composites with Esterified Newspaper Pulp

| Esterified Newspaper Pulp | Tm (°C) | Tc (°C) | $\Delta H_f$ (J/g) | | Degree of Crystallinity (%) |
|---|---|---|---|---|---|
| | | | J/g | J/g | $\Delta H_{f,c}$=230J/g |

| Content(Wt %) | | | (Total) | (PP) | /Total | /PP |
|---|---|---|---|---|---|---|
| 0 | 161.00 | 107.97 | 82.94 | 82.94 | 36.06 | 36.06 |
| 5 | 160.09 | 109.13 | 94.61 | 99.59 | 41.13 | 43.30 |
| 10 | 157.83 | 108.53 | 70.45 | 82.89 | 30.63 | 36.04 |

Comparison of the melting temperature for polypropylene, the composite without MAPP, the composite with MAPP, and the composite with esterified newspaper pulp is presented in Figure 4.29. About 3°C lowering in Tm comparing to polypropylene is observed.

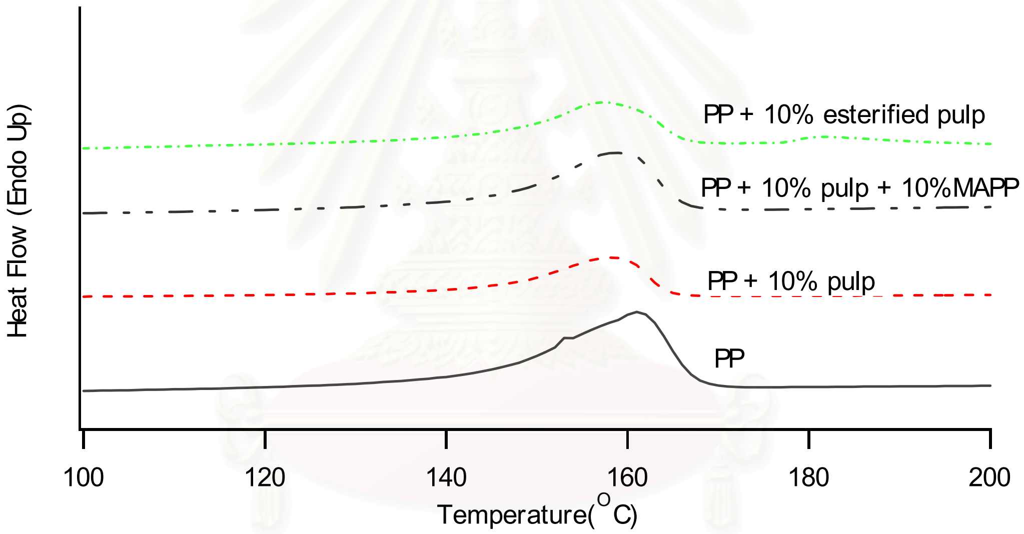


Figure 4.29 **Comparison of the melting temperature for polypropylene and the composites.**

For the comparison of the crystallization temperature, polypropylene has lowest crystallization temperature as shown in Figure 4.30. For different types of newspaper pulp / polypropylene composites, they have higher in the crystallization temperature. The number, size, perfection, and morphology of nuclei formed depends upon the crystallization temperature. But the crystallization temperature does not mean the degree of crystallinity. The heat of fusion can determine the degree of crystallinity. A higher degree of crystallinity means that they must require more energy to melt their crystalline structure. Comparison of thermal properties and degree of crystallinity between polypropylene and the composites is summarized in Table 4.22

As explained earlier, all different types of newspaper pulp, both treated and untreated, might be considered as undeliberately added nucleatin agent leading to the greater in Tc compared to the pure polypropylene. Comparing to pure polypropylene, a larger number and smaller spherulites of polypropylene phase in newspaper / polypropylene composites caused by nucleating agent can be taken into account for the lowering in Tm of all the composites.

The decrease in the degree of crystallinity of the untreated newspaper pulp / polypropylene composite is because newspaper pulp interfere with the crystallite formation of polypropylene by blocking an interchain bonding. However, the degree of crystallization of the composites is enhanced when newspaper pulp is treated with MAPP or with esterification reaction. The segmental crystallization of polypropylene can be induced by polypropylene segment of MAPP and long chain fatty acid ester of esterified newspaper pulp, resulting in an increase in the degree of crystallinity compared to the untreated newspaper pulp / polypropylene composite.

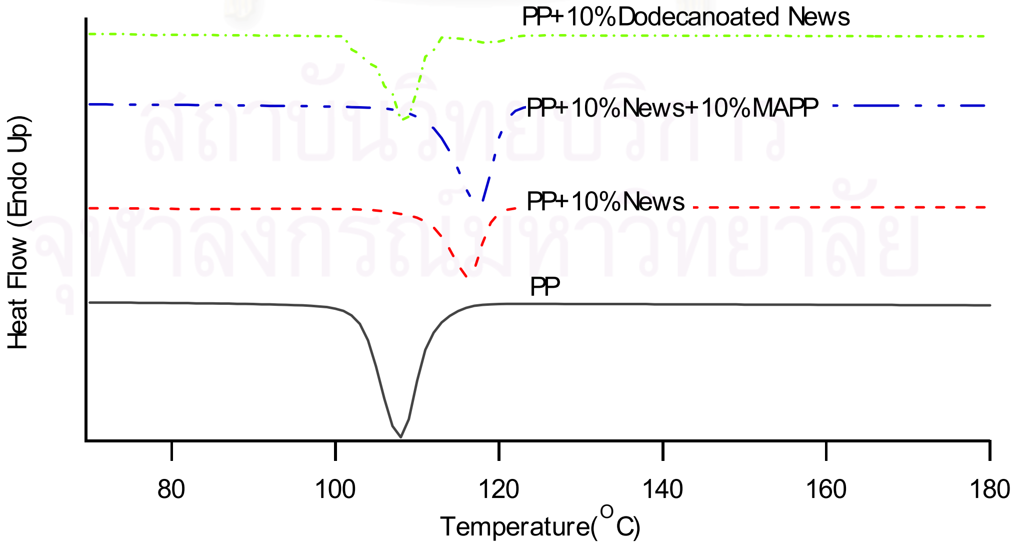


**Figure 4.30** Comparison of the crystallization temperature between polypropylene

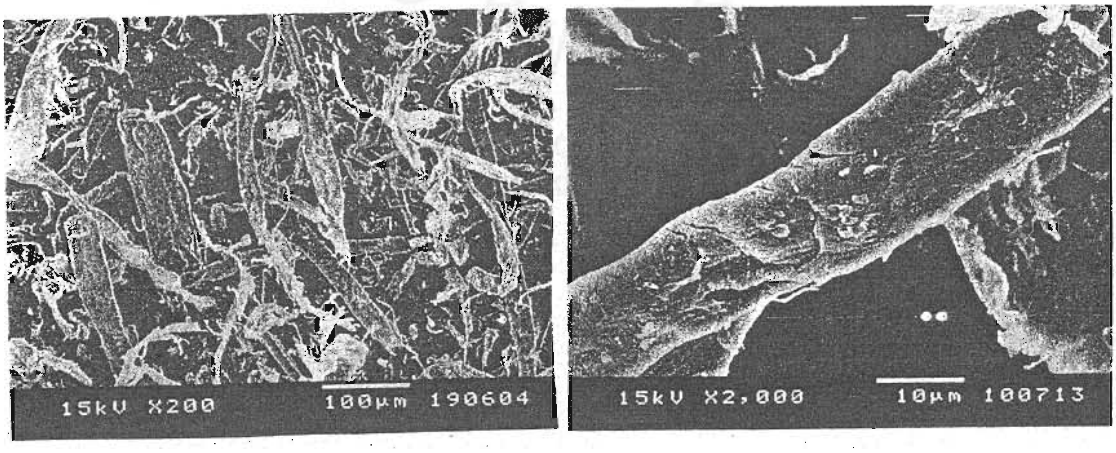
and the composites.

**Table 4.22** Comparison of thermal properties and degree of crystallinity between polypropylene and the composites

| Type of Composites | Tm ($^{o}$C) | Tc ($^{o}$C) | $\Delta H_f$ (J/g) | | Degree of Crystallinity (%) | |
|---|---|---|---|---|---|---|
| | | | J/g(Total) | J/g (PP) | $\Delta H_c$=230J/g | |
| | | | | | /Total | /PP |
| Polypropylene | 161.00 | 107.97 | 82.94 | 82.94 | 36.06 | 36.06 |
| Composite without MAPP | 158.33 | 116.37 | 54.71 | 60.79 | 23.79 | 26.43 |
| Composite with MAPP | 158.48 | 117.36 | 75.34 | 83.72 | 32.76 | 36.40 |
| Composite with esterified newspaper pulp | 157.83 | 108.53 | 70.45 | 82.89 | 30.63 | 36.04 |

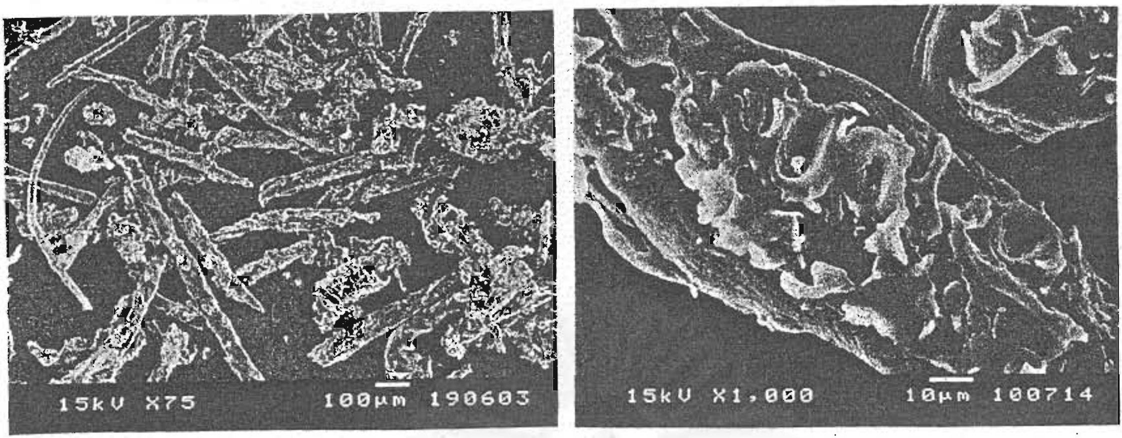
## 4.4 Morphological Studied of Polypropylene / Newspaper Pulp Composites

The SEM micrographs of the newspaper pulp and esterified newspaper pulp are shown in Figure 4.31 and 4.32, respectively. After deinking and bleaching processes, old newspaper is transformed into newspaper pulp. At low magnification, SEM micrographs of both esterified and unesterified newspaper pulp show that their pulps are not quite uniform but varying in its shape and size. Its diameter ranges from about 15 μm to 60 μm. Comparative, the surface of esterified newspaper pulp however is rougher than that of unesterified newspaper pulp, as confirmed by higher magnification of SEM micrographs. As presented in Figure 4.32(b), the surface of esterified newspaper pulp exhibited very rough and distinct surface, indicating the grafted dodecanoated on the surface, as opposed to the smoother surface of the unesterified newspaper pulp. Nevertheless, the surface of unesterified newspaper pulp is not very smooth compared to other cellulose fibers [32]. This is due to the fact that these newspaper pulp are regenerated from the newspaper ; the deinking and bleaching techniques can cause some damages such as tiny cracks left on the pulp surface. This defect might, in turn, results in lower mechanical properties compared to other natural fiber composites. Since other surface modification, using a MAPP as a coupling agent, was carried out by reactive blending technique, the SEM micrograph of MAPP – newspaper pulp cannot be obtained.



(A) (B)

Figure 4.31 SEM micrographs of newspaper pulp.

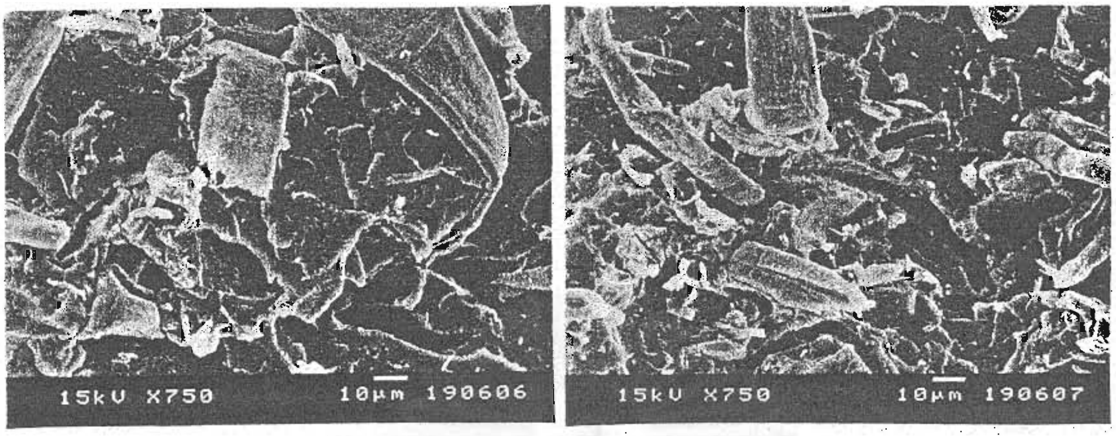


(A) (B)

Figure 4.32 SEM micrographs of esterified newspaper pulp.

In order to understand the effect of surface modifications , MAPP and esterification reaction, on the morphology of polypropylene / newspaper pulp composites, impact fractured surfaces of the composites were examined by scanning electron microscope (SEM).

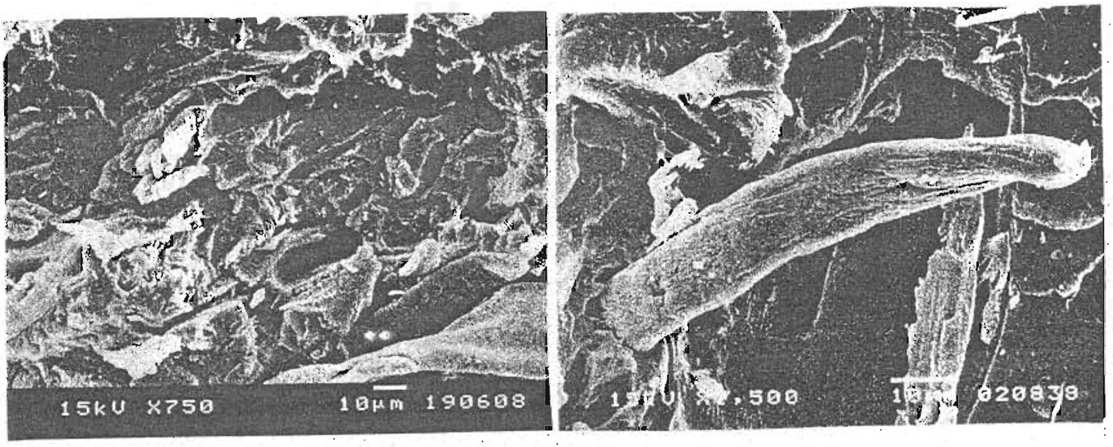
The SEM micrographs of the impact fractured surface of the composite without MAPP are shown in Figure 4.33 and 4.34. As shown in Figure 4.33 (a) and (b) due to a number of the hydrogen bonds formed between the newspaper pulp (cellulose) and the difference in character between the hydrophilic newspaper pulp and the hydrophobic polypropylene matrix, the newspaper pulp tends to agglomerate and becomes unevenly distributed throughout the matrix.



(A) (B)

Figure 4.33 SEM micrographs of impact fractured surfaces for the composite without MAPP.

These two micrographs reveal poor wetting of newspaper pulp by the polypropylene matrix. Without effective wetting of the fiber, strong interfacial adhesion cannot exists. Lack of interfacial interaction leads to a separation between the matrix and the newspaper pulp. In other words, fracture will occur at the interface of newspaper pulp and polypropylene. As shown in Figure 4.34 (a) and (b), newspaper pulp is easily pulled out from the polypropylene matrix because of the insufficient adhesion. As a result, it is obvious that the matrix contains holes of a shape identical to that of the newspaper pulp.

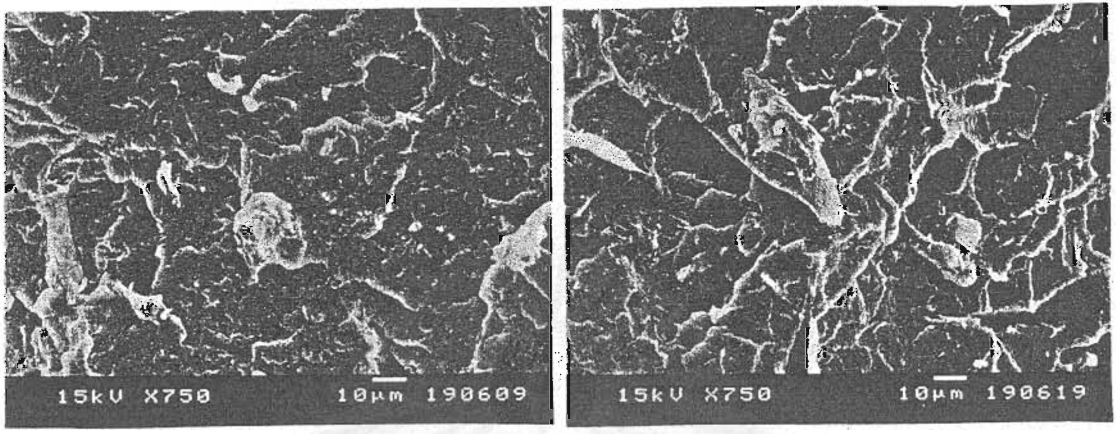


(A) (B)

Figure 4.34 SEM micrographs of impact fractured surfaces for the composite without MAPP showing hole and fiber pull – out.

Therefore, maleic anhydride polypropylene copolymer (MAPP) is used in the polypropylene / newspaper pulp composite as a coupling agent for improving compatibility between two components. The morphology of the fractured surface of 10% newspaper pulp / polypropylene composite is obviously different from the composite containing MAPP. For the composite without MAPP, the dispersion of the newspaper pulp is observed to be without adherence to the polypropylene matrix ( Figure 4.33 and 4.34). However, as shown in Figure 4.35 (a) and (b), by adding the MAPP into the composite, the newspaper pulp shows better dispersion with improve adhesion to the matrix. A good compatibility and enhanced wettability between the two phases is evidenced by a number of firmly embedded newspaper pulp that cannot be pulled out easily during the fracture process. In contrast to the sharp interface of uncompatibilized composite, there is more diffused interface or a co – continuous phase formation occurred in the case of compatibilized composite. As shown in Figure 4.36, the entire newspaper pulp is covered by layer of polypropylene matrix that has been pulled out together with the newspaper pulp.

Another distinct difference is that there is no trace of holes or fiber – pulled out from the matrix, unlike the composite without MAPP, more uniform fractured surface is observed. These results imply that the interfacial bond strength of the newspaper pulp / polypropylene composite can be improved by the addition of MAPP, as confirmed by the enhanced tensile properties discussed earlier. Conclusively, SEM micrographs ensure the role of a coupling agent in reducing the interfacial energy and thus promoting the interfacial adhesion between the newspaper pulp phase and polypropylene phase.



(A) (B)

Figure 4.35 SEM micrographs of impact fractured surfaces for the composite with MAPP. (x750)

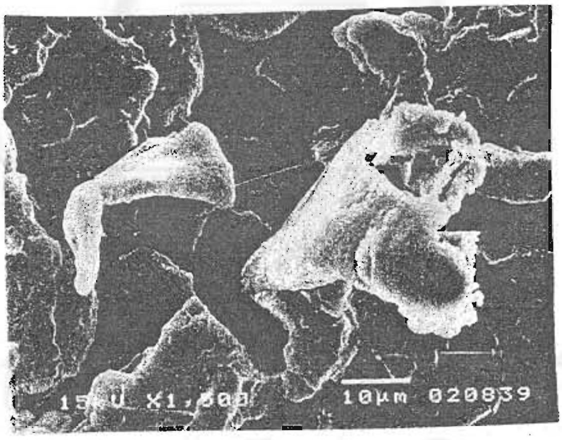
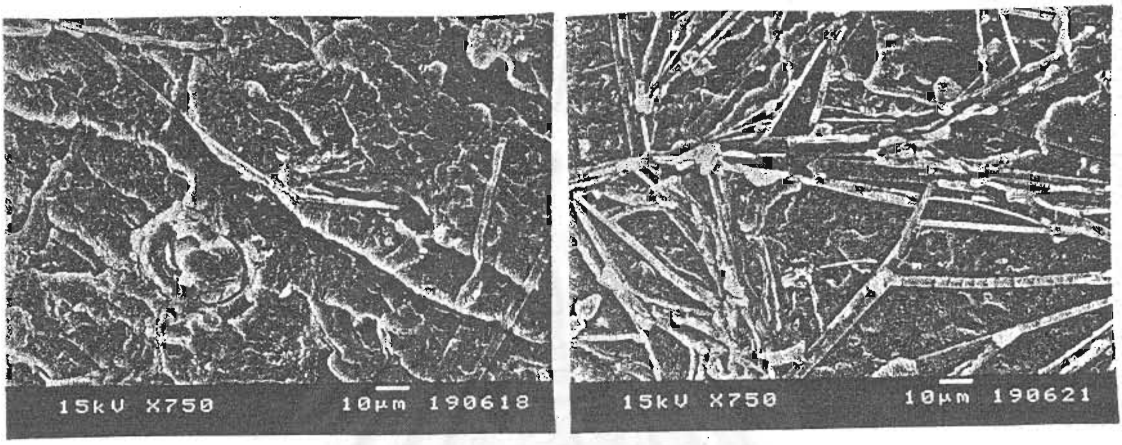


Figure 4.36 SEM micrographs of impact fractured surfaces for the composite with MAPP at higher magnification. (x1500)

In other case, esterified newspaper pulp was used as a reinforcing filler in polypropylene. SEM micrograph for the composite with esterified newspaper pulp or dodecanoated newspaper pulp are shown in Figure 4.37. In contrast to the composite without MAPP, the same result is observed between the esterified newspaper pulp /

polypropylene composite and MAPP – newspaper pulp / polypropylene composite that the treated newspaper pulp does not agglomerate within the matrix. As seen in Figure 4.37 (a) and (b) well dispersion of esterified newspaper pulp in polypropylene matrix is obtained.



(A) (B)

**Figure 4.37** SEM micrographs of impact fractured surfaces for the composite with esterified newspaper pulp.

This result means good wetting of esterified newspaper pulp by the polypropylene matrix. And the compatibility between esterified newspaper pulp and polypropylene is increased. Similar to the composite containing MAPP, there is no holes or traces of fiber pull - out from the polypropylene matrix. However, an interesting feature is also observed. As can be seen from Figure 4.37 (a) and (b), several " fibrill – liked" fractured surfaces occurred across the surface. In fact, the density of these "fibrill" is not dependent upon the esterified newspaper pulp content. More investigation is needed to be able to understand this phenomena.

In conclusion, in order to obtain composite with satisfactory mechanical properties, good dispersion of fibers in the matrix, effective wetting of fibers by matrix, and strong interfacial adhesion are required [29,30]. Therefore, if untreated newspaper pulp is used, poor wetting will occur. This is owing to the large difference in surface energy between newspaper pulp and polypropylene matrix. By treating with MAPP or esterification reaction, their surface energy is lower to a level much closer to the surface energy of the matrix. Thus better wetting is obtained.

## 4.5 Water Absorption of Polypropylene / Newspaper Pulp Composites

Water absorption as a percentage of dry weight at 23°C of pure polypropylene and polypropylene / newspaper pulp composite is plotted against time of immersion in Figure 4.38 through 4.43. The water absorption affects on the dimensional stability of the composite which is one of the important properties determining the performance of end – use composite products. The following discussion will addressed the effects of newspaper pulp content and surface modification of newspaper pulp by reactive blending with MAPP and esterification reaction with dodecanoyl chloride on the ability to absorb water of the polypropylene composites.

### Effect of Newspaper Pulp Content on the Water Absorption of the Composite

The plot of water absorption versus time for the composite without MAPP or uncompatibilized composite is shown in Figure 4.38. As can be observed, water absorption of the composites depends on the exposure time and the newspaper pulp content. Unlike the pure polypropylene with almost 0% of water absorption, the percentage of water absorption increases with the increasing of newspaper pulp content and in the range of 0.11 –0.41%. The composite with 20 wt% newspaper pulp shows the highest percentage of water absorption. The water absorption rate of the polypropylene / newspaper pulp composite is rapid at the initial stage exposure time, 2 –10 hours, after that water absorption is gradually increased upon reaching its equilibrium.

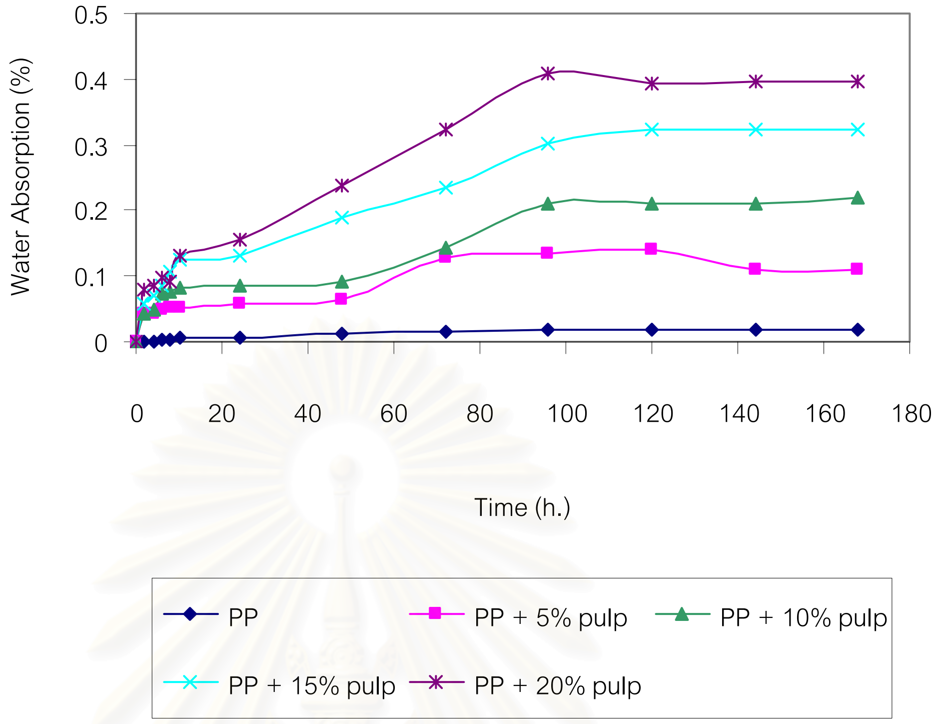


**Figure 4.38** Water absorption as a function of time for the composite without MAPP.

Polypropylene shows low percentage of water absorption about 0.01 – 0.02% due to its hydrophobic. When newspaper pulp is added, higher water absorption is received. This is because the chemical composition of newspaper pulp is cellulose, which comprises of a lot of hydroxyl groups. These hydroxyl groups have an ability to form hydrogen bonds with water, hence, the polypropylene / newspaper pulp composite exhibits higher water absorption than the polypropylene.

## Effect of MAPP on the Water Absorption of the Composite

Figure 4.39 displays water absorption as a function of time for the polypropylene / newspaper pulp composites with 10% MAPP. Comparing to Figure 4.38, the composite with MAPP has lower water absorption than the composites without MAPP. This result implies that MAPP can help reducing the ability to absorb water of newspaper pulp in the composite. As shown in Figure 4.39, maleic anhydride segment in MAPP can interact with hydroxyl group on cellulose of newspaper pulp so the ability of hydroxyl group to form hydrogen bond with water is reduced. Hence, the water absorption is lower in the composite with MAPP. For example, water absorption of 20% newspaper pulp / polypropylene composite is decreased from 0.41% to 0.26% after adding 10% MAPP. In fact, water absorption of the whole series of newspaper pulp / polypropylene composite containing MAPP decrease approximately by 37%, compared to uncompatibilized composites.

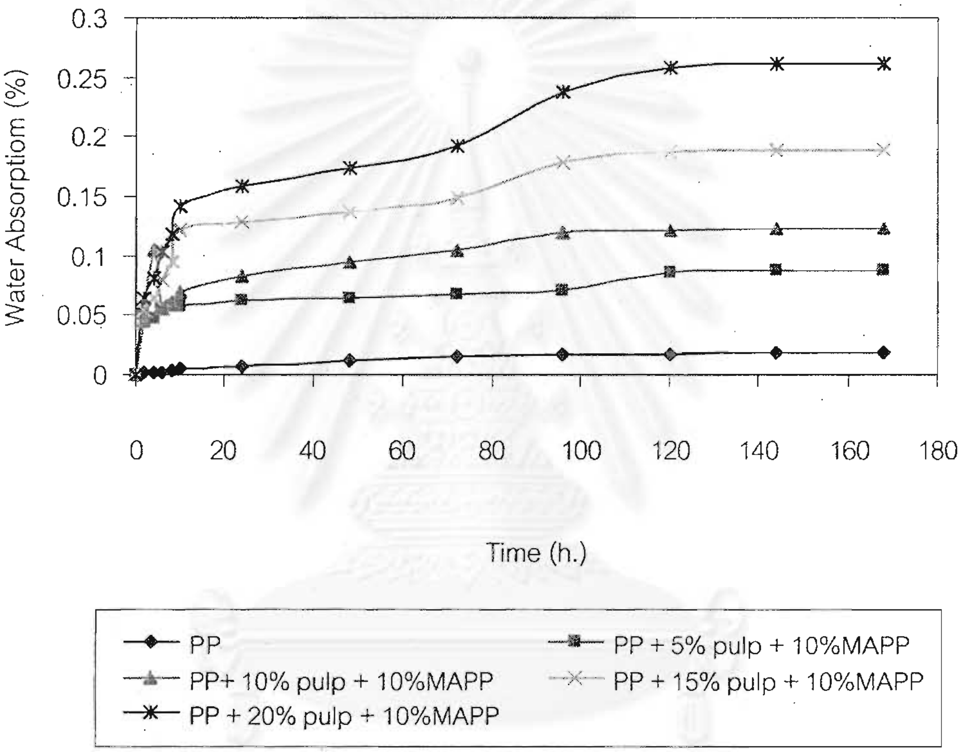


Figure 4.39 Water absorption as a function of time for the composite with MAPP.

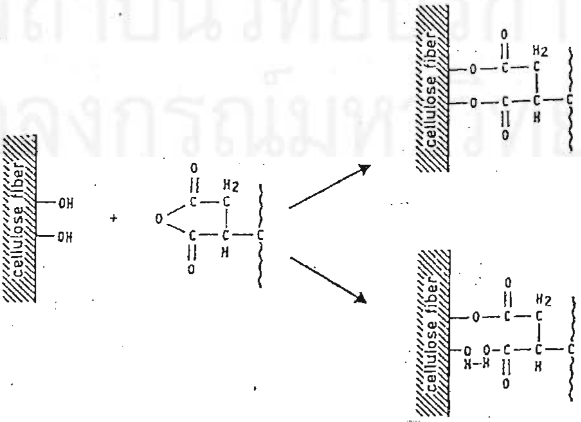


Figure 4.40 Reaction of MAPP on cellulose fiber.

The effect of MAPP content on the water absorption of the composite is shown in Figure 4.41. The composite with 10 wt% newspaper pulp at 2, 5, 10, and 20 %MAPP shows little difference in the percentage of water absorption. Their absorption slightly decreases with increasing MAPP content, as can be seen from the water absorption at equilibrium of 2% MAPP and 10% MAPP polypropylene / newspaper pulp composites.

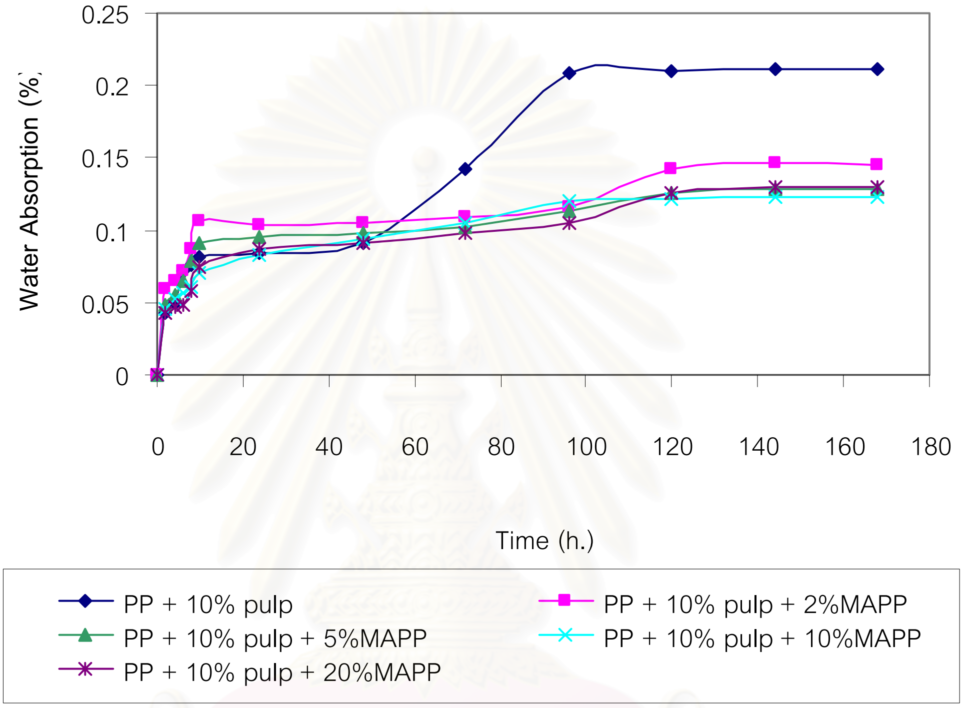


**Figure 4.41** Water absorption as a function of time for the composite with different MAPP content.

Effect of Esterified Newspaper Pulp on the Water Absorption of the Composites

Water absorption isotherm of the composite with esterified newspaper pulp is shown in Figure 4.42. Similar trend to other composites shown in previous Figures, water absorption of these composite increases with the increasing of the esterified newspaper pulp content. Besides, these esterified newspaper pulp / polypropylene composites reach their own equilibrium of water absorption within the same period of time, as other composites, that is approximately 120 hours of exposure. However, an interesting result is observed. Comparing to other composites investigated, water absorption of esterified newspaper pulp / polypropylene composite is very low, within the range of 0.01 – 0.08%.

Figure 4.2 shows the esterification reaction between cellulose and dodecanoyl chloride. Clearly, the hydroxyl groups in the newspaper pulp has changed to ester bonds with long chain fatty acid ester which is, of course, more hydrophobic than hydroxyl groups. As a result, their water absorption decreases. In other words,the esterification reaction renders newspaper pulp more hydrophobic by reducing the possibility of hydrogen bond formation between hydroxyl groups in the newspaper pulp and water, resulting in reducing the water absorption.

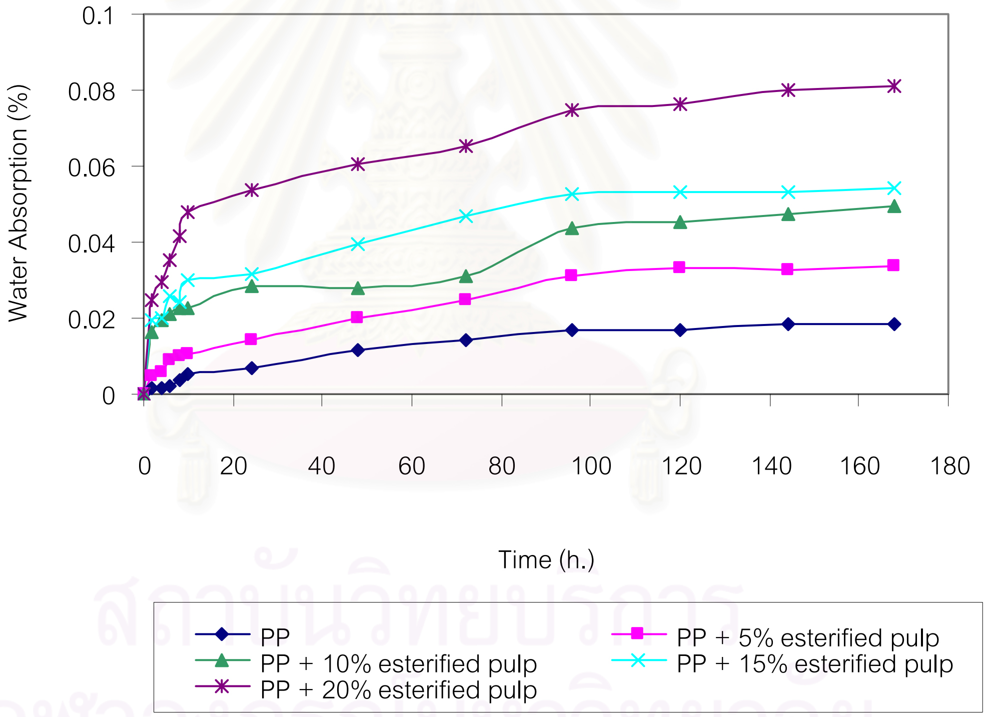


Figure 4.42 Water absorption as a function of time for the composite with esterified newspaper pulp.

Effect of Surface Modification on Water Absorption of the Composite

To clarify the effect of surface modification methods used in this research, Figure 4.43 shows the comparison of percentage of water absorption for polypropylene, the composite without MAPP, the composite with MAPP, and the composite with esterified newspaper pulp. Obviously, at 10 wt% newspaper pulp, the composite with esterified newspaper pulp has the lowest water absorption. These water absorption isotherms reveal an interesting result that the esterification reaction can make the newspaper pulp more hydrophobic than the addition of the MAPP. From these results, it can be implied that the dimensional stability of the composite with esterified newspaper pulp is better than the composite with MAPP and the composite without MAPP.

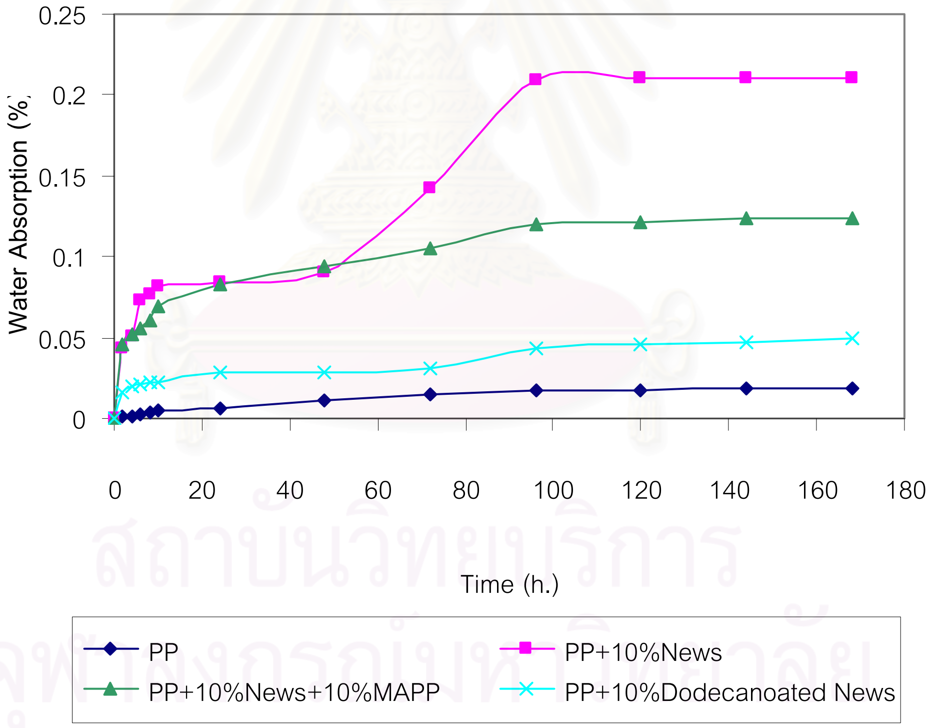


Figure 4.43 Water absorption as a function of time for polypropylene, the composite without MAPP, the composite with MAPP, and the composite with esterified newspaper pulp.

# CHAPTER V

# CONCLUSIONS AND RECOMMENDATIONS

## Conclusions

As an effort to reuse old newspaper, a newspaper pulp reinforced polypropylene composite was made. Like other natural fibers reinforced composites, this composite offers a number of benefits including high specific stiffness and strength, low density, and biodegradability. Although, this composite has many advantages, but it has a main problem in preparation of this composites. This problem is the incompatibility and poor interfacial adhesion between the newspaper pulp and polypropylene, resulting in poor mechanical properties. Thus maleic anhydride polypropylene copolymer (MAPP) was used as a coupling agent to improve the compatibility and interfacial bond strength between the two phases. For comparison, the esterification reaction using dodecanoyl chloride was adopted to modify surface of the newspaper pulp prior to mix with the polypropylene matrix.

This work has focused on the effect of surface modifications on the mechanical properties, thermal properties, morphological studies, and water absorption of the composite. The properties of the composite without MAPP, the composite with MAPP, and the composite with esterified newspaper pulp are summarized in Table 5.1.

Table 5.1 Conclusive Properties of the Polypropylene / Newspaper Pulp Composites

| Properties | Composite Without MAPP | | Composite With MAPP | | Composite with Esterified Newspaper Pulp | |
|---|---|---|---|---|---|---|
| | 5% | 20% | 5% | 20% | 5% | 20% |
| Tensile Properties | * | * | *** | ***** | - | - |
| Flexural Properties | * | *** | *** | ***** | - | - |
| Thermal Properties (Td) | * | * | *** | *** | ***** | *** |
| Water Absorption (hydrophobicity) | - | - | *** | * | ***** | *** |

- = low * = medium *** = good ***** = very good

1. The composite with MAPP shows the highest tensile properties and the tensile properties increase with increasing the newspaper pulp content. This is because MAPP can improve interfacial adhesion between the two components. In the case of the composite with esterified newspaper pulp, the tensile properties decrease with increasing newspaper pulp content which are actually lower than those of polypropylene. This is due to the plasticizing effect of long chain fatty acid ester.

2. Similar to the case of the tensile properties, the composite with MAPP shows the highest flexural properties, whereas the composite with esterified newspaper pulp has the lowest flexural properties.

3. In view of thermal propertes, TGA results shows that the thermal stability of the composite without MAPP, the composite with MAPP, and the composite with

esterified newspaper pulp are higher than that of pure polypropylene. Among them, the composite with esterified newspaper pulp shows the highest thermal stability.

4. The composite with esterified newspaper pulp exhibits lowest water absorption which leads to the interesting conclusion that the surface modification by esterification reaction can make the newspaper pulp more hydrophobic than the addition of MAPP.

5. In conclusion, it can be summarized that the mechanical as well as thermal properties of the composite can be improved by selecting a suitable surface modification. In this work the surface modification using maleic anhydride grafted polypropylene is the excellent method for improving the properties of the polypropylene / newspaper pulp composite.

## Recommendations

The natural fiber composite with an outstanding combination of properties is not dream today. By using proper processing technique, fiber surface modifications or coupling agents can lead to make the composite with optimum properties. From this work, there are several suggestions for future work as follows :

1. In this work, the newspaper was deinked and bleached prior to use. In fact little difference can be observed between the newspaper pulp before and after deinking and bleaching processes. When high quantity of deinked newspaper pulp was added to the polypropylene, the color of the composites became darker eventually. So, deinking and bleaching of the newspaper are not necessary.

2. In this work, the newspaper pulp content was varied from 5 to 20 wt%. Hence, in the future the composite with higher newspaper content should be prepared in order to investigate the optimizing condition.

3. At present, the newspaper pulp is used as a reinforcing filler in polypropylene matrix. The selection of new matrix such as other thermopastics, PE, PVC, PS is an interesting way for improving the mechanical properties of these thermoplastics.

4. Newspaper and natural fiber are suitable for using in thermoplastics since the processing temperature is about 200°C. The real challenge is to improve the thermal stability of these fibers so that they can be used with engineering polymers and further improving the advantage of both the polymers and the fiber.

5. According to the thermal and dimensional stability including its cost of production, commercial application of the esterified newspaper pulp / PP composites may probably be limited.

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# Appendix A : Equipments

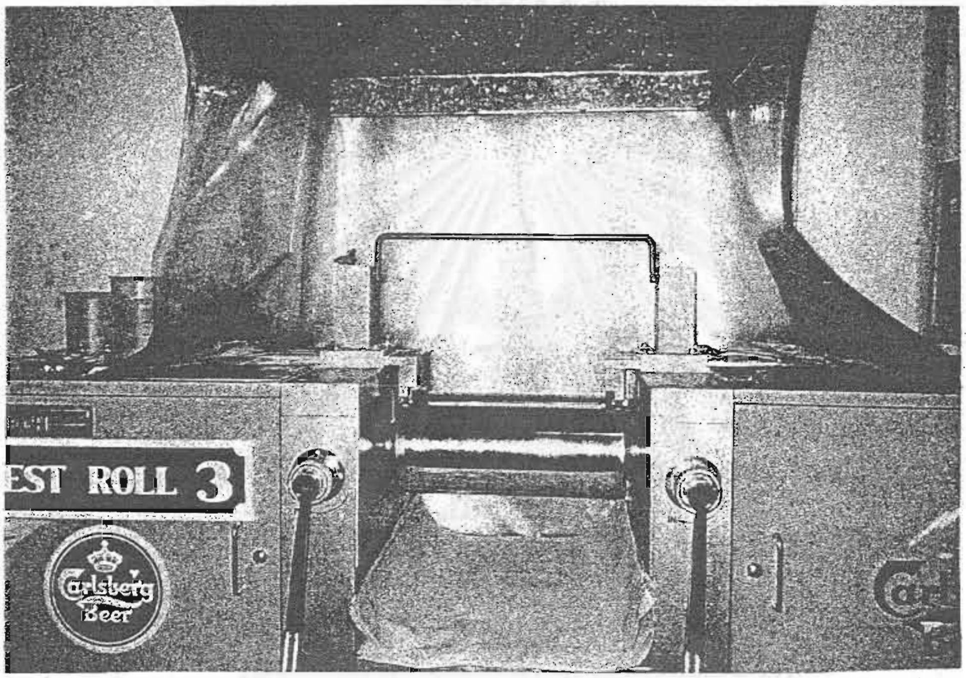

Figure A1 Two Roll Mill.

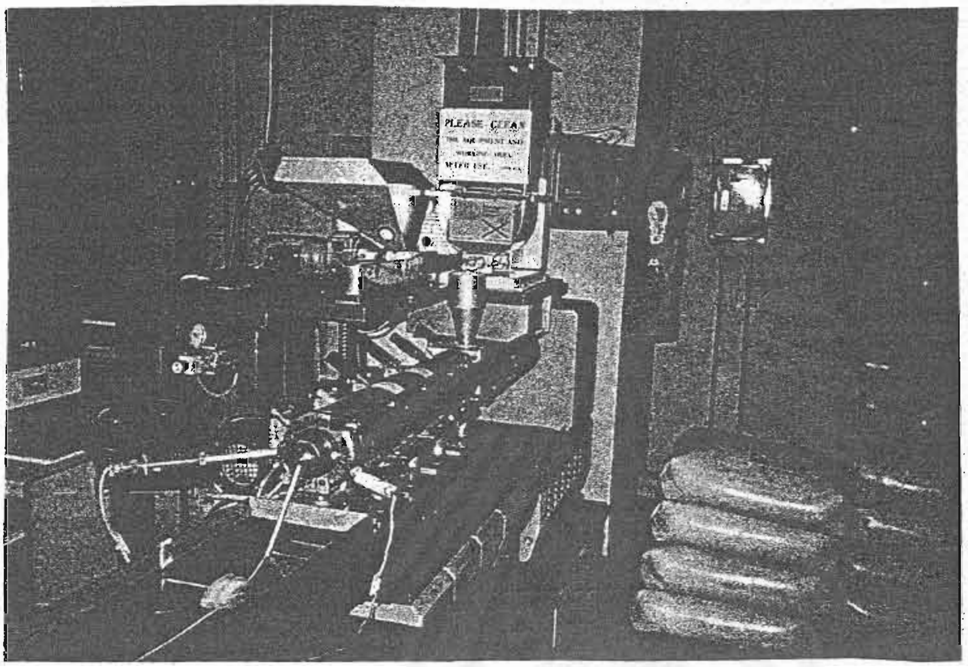

Figure A2 Twin Screw Extruder.

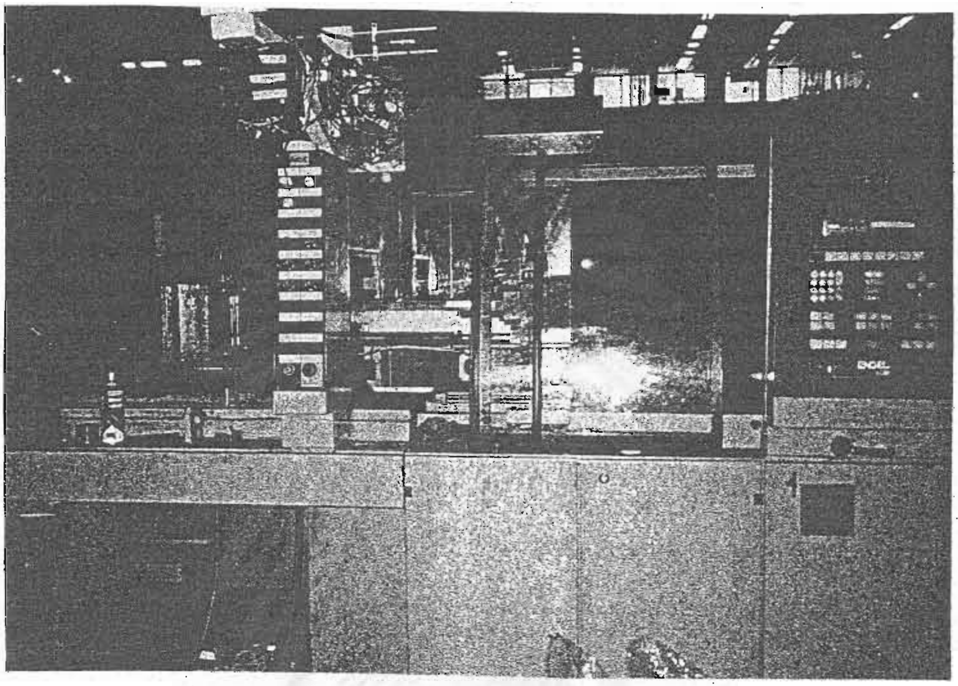

Figure A3 Injection Molding.

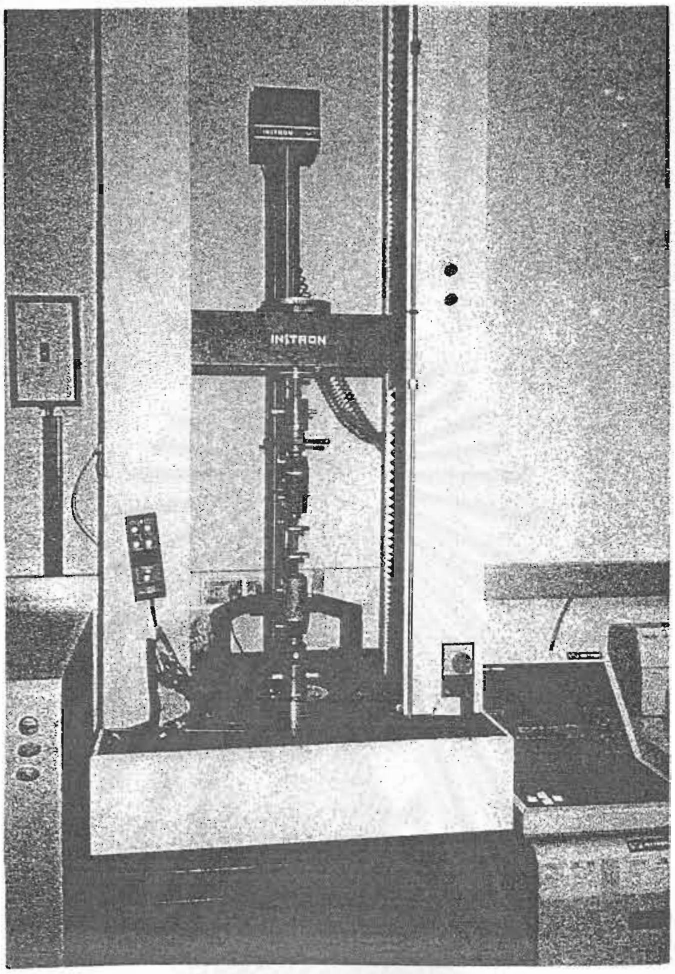

Figure A4 Tensile Testing Machine.

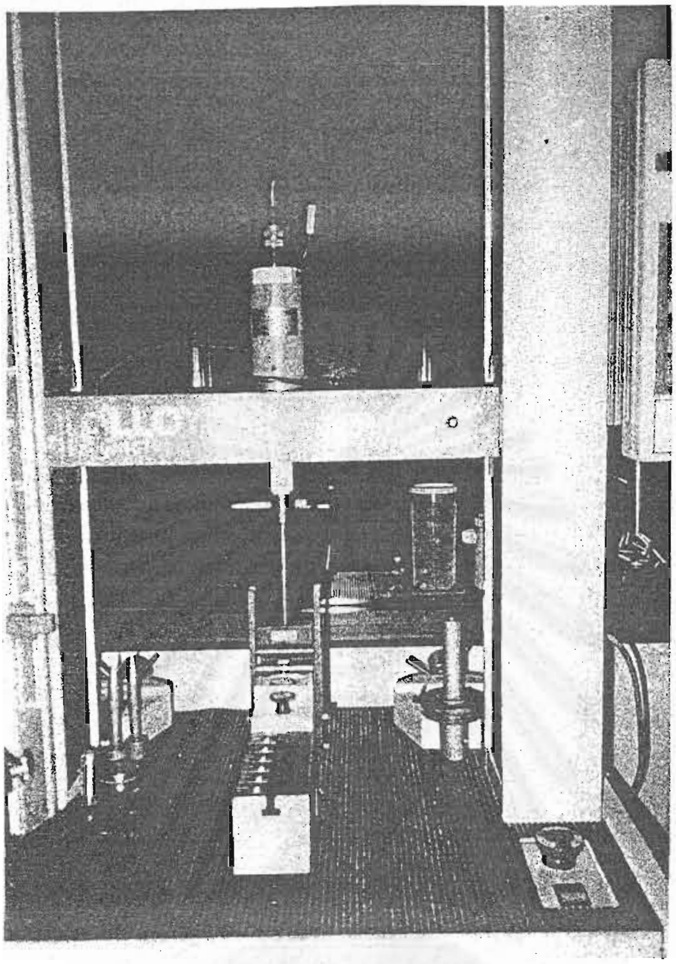

Figure A5 Flexural Testing Machine.

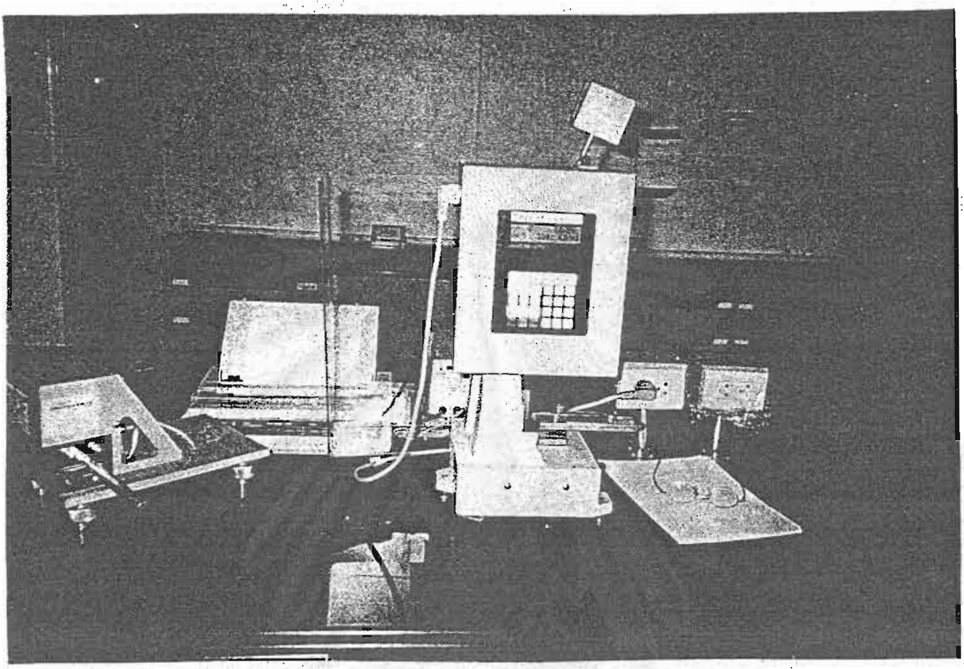

Figure A6 Impact Tester.

Figure A7 Differential Scanning Calorimeter (DSC).

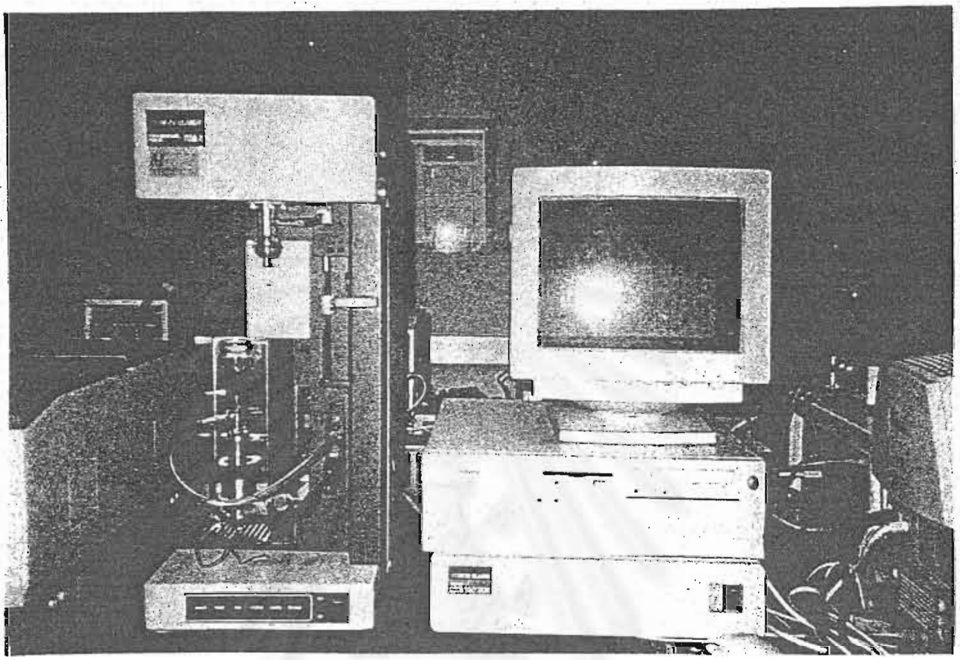

Figure A8 Thermogravimetric Analyzer (TGA).

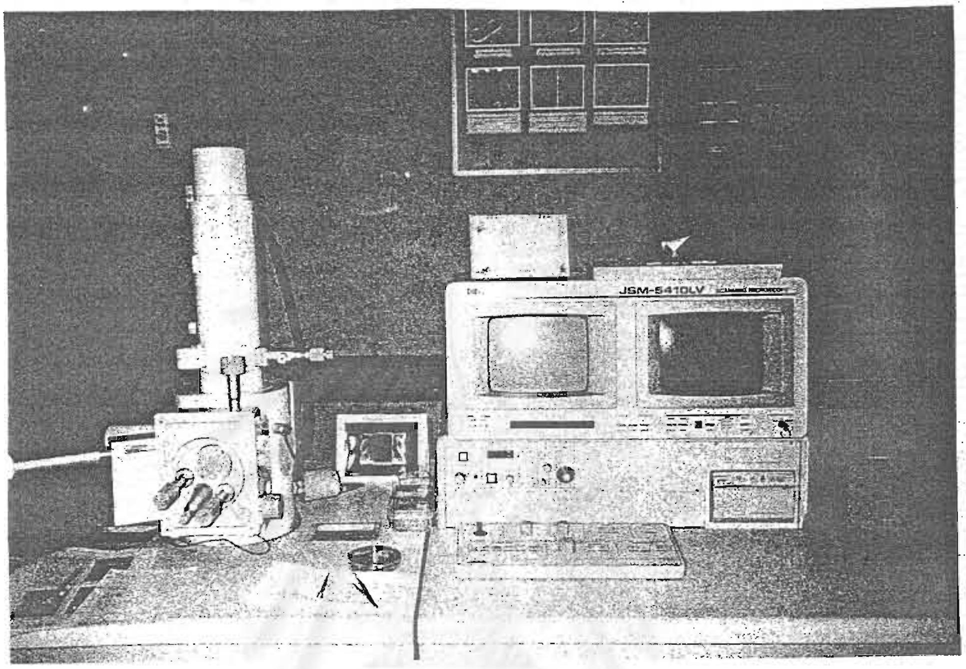

Figure A9 Scanning Electron Micrroscope (SEM).

# Appendix B : Mechanical Properties

Table B1 Tensile Modulus (GPa) of the Polypropylene / Newspaper Pulp Composites

| Tensile Modulus | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sample | Trial No. | | | | | Mean | SD |
| | 1 | 2 | 3 | 4 | 5 | | |
| PP | 1.991 | 1.868 | 1.981 | 2.055 | 1.567 | 1.89 | 0.19 |
| 5% pulp | 2.172 | 2.422 | 1.950 | 1.950 | 2.170 | 2.13 | 0.20 |
| 10% pulp | 2.109 | 2.169 | 2.347 | 2.232 | 2.230 | 2.22 | 0.09 |
| 15% pulp | 2.859 | 2.602 | 2.512 | 2.883 | 2.323 | 2.64 | 0.24 |
| 20% pulp | 2.739 | 2.780 | 3.082 | 3.177 | 2.936 | 2.94 | 0.19 |
| 5% esterified pulp | 1.662 | 1.783 | 2.220 | 1.800 | 1.730 | 1.84 | 0.22 |
| 10% esterified pulp | 1.102 | 1.165 | 1.179 | 1.210 | 1.174 | 1.17 | 0.04 |
| 15% esterified pulp | 0.891 | 0.941 | 0.959 | 0.818 | 0.952 | 0.91 | 0.50 |
| 20% esterified pulp | 0.872 | 0.910 | 0.887 | 0.758 | 0.844 | 0.85 | 0.06 |
| 5% pulp + 10% MAPP | 2.020 | 1.703 | 2.163 | 2.006 | 1.940 | 1.97 | 0.17 |
| 10% pulp + 10% MAPP | 2.250 | 2.388 | 2.390 | 2.480 | 2.850 | 2.43 | 0.15 |
| 15% pulp + 10% MAPP | 2.731 | 2.808 | 2.706 | 2.942 | 2.705 | 2.78 | 0.10 |
| 20% pulp + 10% MAPP | 3.250 | 3.140 | 3.197 | 2.940 | 3.200 | 3.15 | 0.12 |
| 10% pulp + 2% MAPP | 2.150 | 2.200 | 2.300 | 2.340 | 2.400 | 2.28 | 0.10 |
| 10% pulp + 5% MAPP | 2.230 | 2.360 | 2.210 | 2.150 | 2.440 | 2.28 | 0.12 |
| 10% pulp + 20% MAPP | 2.256 | 2.241 | 2.132 | 2.120 | 2.068 | 2.16 | 0.08 |

**Table B2** Tensile Stress at Maximum ( MPa) of the Polypropylene / Newspaper Pulp Composites

| Tensile Stress at Maximum | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sample | Trial No. | | | | | Mean | SD |
| | 1 | 2 | 3 | 4 | 5 | | |
| PP | 32.592 | 33.115 | 33.261 | 32.894 | 32.709 | 32.91 | 0.28 |
| 5% pulp | 31.732 | 31.918 | 31.581 | 31.934 | 31.832 | 31.80 | 0.15 |
| 10% pulp | 30.269 | 30.855 | 30.808 | 30.564 | 30.553 | 30.61 | 0.24 |
| 15% pulp | 30.472 | 30.324 | 30.184 | 30.112 | 30.120 | 30.24 | 0.15 |
| 20% pulp | 31.031 | 30.624 | 30.514 | 30.699 | 30.757 | 30.73 | 0.19 |
| 5% esterified pulp | 28.332 | 28.136 | 27.719 | 28.189 | 28.637 | 28.20 | 0.33 |
| 10% esterified pulp | 25.120 | 26.230 | 26.541 | 25.890 | 26.340 | 26.20 | 0.56 |
| 15% esterified pulp | 23.305 | 23.372 | 23.297 | 23.662 | 23.331 | 23.39 | 0.15 |
| 20% esterified pulp | 20.643 | 21.064 | 20.882 | 21.182 | 20.7763 | 20.91 | 0.21 |
| 5% pulp + 10% MAPP | 32.890 | 33.410 | 32.530 | 33.180 | 33.220 | 32.90 | 0.53 |
| 10% pulp + 10% MAPP | 33.630 | 33.809 | 33.706 | 33.398 | 32.409 | 33.39 | 0.57 |
| 15% pulp + 10% MAPP | 33.878 | 34.125 | 34.423 | 34.009 | 34.037 | 34.09 | 0.20 |
| 20% pulp + 10% MAPP | 37.538 | 37.347 | 36.944 | 37.275 | 37.084 | 37.33 | 0.32 |
| 10% pulp + 2% MAPP | 30.781 | 31.129 | 30.551 | 30.068 | 30.522 | 30.72 | 0.25 |
| 10% pulp + 5% MAPP | 31.588 | 31.407 | 31.256 | 32.218 | 31.538 | 31.60 | 0.37 |
| 10% pulp + 20% MAPP | 34.539 | 34.211 | 34.294 | 34.064 | 34.655 | 34.35 | 0.24 |

**Table B3** Tensile Stress at Break (MPa) of the Polypropylene / Newspaper Pulp Composites

| Tensile Stress at Break | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sample Code | Trial No. | | | | | Mean | SD |
| | 1 | 2 | 3 | 4 | 5 | | |
| PP | 26.400 | 25.982 | 24.212 | 25.391 | 20.828 | 24.56 | 2.24 |
| 5% pulp | 28.224 | 28.394 | 27.969 | 28.688 | 28.315 | 28.32 | 0.26 |
| 10% pulp | 30.170 | 28.679 | 27.848 | 28.211 | 29.939 | 28.97 | 1.04 |
| 15% pulp | 28.335 | 27.335 | 29.651 | 27.932 | 28.436 | 28.34 | 0.85 |
| 20% pulp | 28.549 | 28.840 | 28.930 | 30.401 | 29.276 | 29.20 | 0.72 |
| 5% esterified pulp | 26.774 | 25.453 | 27.712 | 24.597 | 24.709 | 25.85 | 1.36 |
| 10% esterified pulp | 22.353 | 21.586 | 22.544 | 22.368 | 22.382 | 22.25 | 0.34 |
| 15% esterified pulp | 20.580 | 19.962 | 19.752 | 20.170 | 20.008 | 20.09 | 0.31 |
| 20% esterified pulp | 19.651 | 20.020 | 20.205 | 20.551 | 19.815 | 20.05 | 0.35 |
| 5% pulp + 10% MAPP | 29.132 | 30.660 | 31.843 | 31.843 | 31.699 | 31.04 | 1.17 |
| 10% pulp + 10% MAPP | 32.362 | 30.891 | 31.439 | 30.199 | 32.304 | 31.44 | 0.92 |
| 15% pulp + 10% MAPP | 32.160 | 32.564 | 31.900 | 32.391 | 32.420 | 32.29 | 0.26 |
| 20% pulp + 10% MAPP | 36.631 | 36.602 | 35.823 | 36.112 | 35.938 | 36.22 | 0.38 |
| 10% pulp + 2% MAPP | 28.402 | 28.509 | 27.629 | 28.162 | 28.708 | 28.28 | 0.41 |
| 10% pulp + 5% MAPP | 29.305 | 31.400 | 29.132 | 29.564 | 28.637 | 29.61 | 1.06 |
| 10% pulp + 20% MAPP | 31.958 | 32.045 | 31.439 | 31.554 | 32.564 | 31.91 | 0.45 |

**Table B4** Flexural Modulus (GPa) of the Polypropylene / Newspaper Pulp Composites

| Flexural Modulus | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sample | Trial No. | | | | | Mean | SD |
| | 1 | 2 | 3 | 4 | 5 | | |
| PP | 1.182 | 1.185 | 1.167 | 1.178 | 1.151 | 1.17 | 0.01 |
| 5% pulp | 1.418 | 1.405 | 1.415 | 1.428 | 1.408 | 1.41 | 0.01 |
| 10% pulp | 1.564 | 1.542 | 1.549 | 1.564 | 1.555 | 1.55 | 0.01 |
| 15% pulp | 1.816 | 1.832 | 1.776 | 1.781 | 1.795 | 1.80 | 0.02 |
| 20% pulp | 2.020 | 2.039 | 1.994 | 2.002 | 1.986 | 2.01 | 0.02 |
| 5% esterified pulp | 0.881 | 0.863 | 0.883 | 0.905 | 0.889 | 0.88 | 0.02 |
| 10% esterified pulp | 0.866 | 0.847 | 0.813 | 0.829 | 0.834 | 0.84 | 0.02 |
| 15% esterified pulp | 0.744 | 0.797 | 0.756 | 0.740 | 0.764 | 0.76 | 0.02 |
| 20% esterified pulp | 0.681 | 0.656 | 0.661 | 0.658 | 0.668 | 0.66 | 0.01 |
| 5% pulp + 10% MAPP | 1.423 | 1.438 | 1.398 | 1.394 | 1.399 | 1.41 | 0.02 |
| 10% pulp + 10% MAPP | 1.576 | 1.578 | 1.563 | 1.577 | 1.553 | 1.57 | 0.01 |
| 15% pulp + 10% MAPP | 1.747 | 1.737 | 1.751 | 1.748 | 1.739 | 1.75 | 0.02 |
| 20% pulp + 10% MAPP | 1.958 | 1.904 | 1.941 | 1.917 | 2.004 | 1.94 | 0.04 |
| 10% pulp + 2% MAPP | 1.592 | 1.606 | 1.546 | 1.555 | 1.547 | 1.57 | 0.03 |
| 10% pulp + 5% MAPP | 1.593 | 1.559 | 1.552 | 1.543 | 1.532 | 1.56 | 0.02 |
| 10% pulp + 20% MAPP | 1.560 | 1.531 | 1.520 | 1.547 | 1.541 | 1.54 | 0.02 |

**Table B5** Flexural Strength at Maximum (MPa) of the Polypropylene / Newspaper Pulp Composites

| Flexural Strength at Maximum | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sample | Trial No. | | | | | Mean | SD |
| | 1 | 2 | 3 | 4 | 5 | | |
| PP | 43.30 | 43.54 | 43.68 | 44.53 | 44.07 | 43.82 | 0.48 |
| 5% pulp | 48.42 | 47.96 | 48.72 | 48.44 | 47.71 | 48.25 | 0.41 |
| 10% pulp | 48.23 | 48.48 | 48.72 | 48.70 | 48.14 | 48.45 | 0.26 |
| 15% pulp | 49.65 | 49.42 | 49.41 | 49.44 | 49.77 | 49.54 | 0.16 |
| 20% pulp | 50.67 | 51.01 | 50.59 | 51.10 | 51.21 | 50.92 | 0.27 |
| 5% esterified pulp | 35.92 | 35.74 | 36.50 | 35.87 | 35.93 | 35.99 | 0.29 |
| 10% esterified pulp | 34.55 | 33.91 | 33.46 | 33.92 | 34.44 | 34.06 | 0.44 |
| 15% esterified pulp | 31.23 | 31.61 | 30.58 | 29.52 | 30.83 | 30.75 | 0.79 |
| 20% esterified pulp | 28.67 | 28.28 | 28.46 | 27.28 | 27.36 | 28.01 | 0.65 |
| 5% pulp + 10% MAPP | 49.39 | 49.41 | 49.29 | 48.93 | 49.18 | 49.24 | 0.20 |
| 10% pulp + 10% MAPP | 51.55 | 51.81 | 51.32 | 51.40 | 50.90 | 51.40 | 0.33 |
| 15% pulp + 10% MAPP | 53.94 | 53.93 | 54.05 | 53.69 | 53.81 | 53.82 | 0.17 |
| 20% pulp + 10% MAPP | 58.19 | 57.43 | 57.24 | 57.70 | 58.45 | 57.80 | 0.51 |
| 10% pulp + 2% MAPP | 49.88 | 49.97 | 49.11 | 49.15 | 49.15 | 49.54 | 0.43 |
| 10% pulp + 5% MAPP | 50.92 | 50.35 | 50.22 | 49.99 | 49.86 | 50.27 | 0.41 |
| 10% pulp + 20% MAPP | 52.60 | 52.20 | 51.80 | 52.43 | 52.53 | 52.31 | 0.32 |

**Table B6** Impact Strength (KJ/$m^2$) of the Polypropylene / Newspaper Pulp Composites

| Impact Strength | | | | | | | |
|---|---|---|---|---|---|---|---|
| Sample | Trial No. | | | | | Mean | SD |
| | 1 | 2 | 3 | 4 | 5 | | |
| PP | 2.6 | 3.0 | 2.8 | 2.7 | 3.0 | 2.82 | 0.18 |
| 5% pulp | 3.0 | 3.0 | 3.1 | 2.9 | 3.0 | 3.00 | 0.71 |
| 10% pulp | 2.9 | 2.9 | 2.8 | 2.7 | 3.0 | 2.86 | 0.11 |
| 15% pulp | 3.1 | 3.0 | 3.0 | 2.6 | 2.7 | 2.88 | 0.13 |
| 20% pulp | 2.8 | 2.9 | 2.9 | 2.7 | 2.6 | 2.78 | 0.13 |
| 5% esterified pulp | 2.6 | 2.8 | 2.7 | 2.5 | 2.7 | 2.66 | 0.11 |
| 10% esterified pulp | 2.6 | 2.5 | 2.4 | 2.3 | 2.6 | 2.48 | 0.13 |
| 15% esterified pulp | 2.5 | 2.7 | 2.4 | 2.7 | 2.1 | 2.48 | 0.25 |
| 20% esterified pulp | 2.0 | 2.6 | 2.7 | 2.4 | 2.3 | 2.40 | 0.27 |
| 5% pulp + 10% MAPP | 3.1 | 3.3 | 3.3 | 2.9 | 2.9 | 3.10 | 0.20 |
| 10% pulp + 10% MAPP | 3.0 | 2.9 | 2.9 | 3.0 | 2.7 | 2.90 | 0.12 |
| 15% pulp + 10% MAPP | 2.5 | 2.6 | 2.7 | 2.6 | 2.6 | 2.60 | 0.07 |
| 20% pulp + 10% MAPP | 2.9 | 2.4 | 2.5 | 2.6 | 2.4 | 2.56 | 0.22 |
| 10% pulp + 2% MAPP | 2.7 | 2.9 | 2.5 | 2.6 | 2.7 | 2.68 | 0.15 |
| 10% pulp + 5% MAPP | 2.9 | 2.8 | 2.9 | 2.7 | 2.6 | 2.78 | 0.13 |
| 10% pulp + 20% MAPP | 3.0 | 3.3 | 2.9 | 3.0 | 3.3 | 3.10 | 0.19 |

# Appendix C : Water Absorption

**Table C1** Weight of the Composites without MAPP at Different Time

| Weight (g) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (hr.) | | | | | | | | | | | | | | |
| Sample | Trial No. | 0 | 2 | 4 | 6 | 8 | 10 | 24 | 48 | 72 | 96 | 120 | 144 | 168 |
| PP | 1 | 5.9538 | 5.9539 | 5.9538 | 5.9539 | 5.9542 | 5.9543 | 5.9546 | 5.9554 | 5.9555 | 5.9555 | 5.9555 | 5.956 | 5.956 |
| | 2 | 5.9437 | 5.9437 | 5.9437 | 5.9439 | 5.9439 | 5.9439 | 5.9437 | 5.9439 | 5.9441 | 5.9441 | 5.9441 | 5.9441 | 5.9441 |
| | 3 | 5.9615 | 5.9616 | 5.9616 | 5.9616 | 5.9617 | 5.9619 | 5.9624 | 5.9624 | 5.9628 | 5.9627 | 5.9627 | 5.9627 | 5.9627 |
| | 4 | 5.9542 | 5.9542 | 5.9543 | 5.9543 | 5.9543 | 5.9543 | 5.9543 | 5.9547 | 5.9548 | 5.955 | 5.955 | 5.955 | 5.955 |
| | 5 | 5.9656 | 5.9658 | 5.9658 | 5.9658 | 5.9658 | 5.9659 | 5.9658 | 5.9659 | 5.9659 | 5.9665 | 5.9665 | 5.9665 | 5.9665 |
| 5%pulp | 1 | 6.1222 | 6.1235 | 6.1235 | 6.1247 | 6.1248 | 6.1249 | 6.1251 | 6.1251 | 6.1291 | 6.1293 | 6.1298 | 6.1203 | 6.1203 |
| | 2 | 6.1044 | 6.1079 | 6.1079 | 6.1081 | 6.1083 | 6.1086 | 6.1092 | 6.1095 | 6.1128 | 6.1135 | 6.114 | 6.1145 | 6.1145 |
| | 3 | 6.1383 | 6.142 | 6.142 | 6.1422 | 6.1422 | 6.1422 | 6.1425 | 6.1427 | 6.1462 | 6.1464 | 6.1468 | 6.1468 | 6.1468 |
| | 4 | 6.1214 | 6.1239 | 6.124 | 6.1244 | 6.1244 | 6.1244 | 6.1247 | 6.1259 | 6.1293 | 6.1296 | 6.1301 | 6.1303 | 6.1303 |
| | 5 | 6.1312 | 6.1333 | 6.1332 | 6.1334 | 6.1335 | 6.1337 | 6.1339 | 6.1343 | 6.1389 | 6.1394 | 6.1394 | 6.1394 | 6.1394 |
| 10%pulp | 1 | 6.2358 | 6.2391 | 6.2395 | 6.2401 | 6.2404 | 6.2407 | 6.2409 | 6.2412 | 6.243 | 6.2491 | 6.2493 | 6.2493 | 6.22493 |
| | 2 | 6.2581 | 6.2609 | 6.261 | 6.2618 | 6.262 | 6.2625 | 6.2628 | 6.2633 | 6.2658 | 6.2711 | 6.2714 | 6.2715 | 6.2715 |
| | 3 | 6.2576 | 6.2617 | 6.2622 | 6.2626 | 6.2626 | 6.2627 | 6.2629 | 6.2636 | 6.2671 | 6.2702 | 6.2702 | 6.2702 | 6.2702 |
| | 4 | 6.2484 | 6.2517 | 6.2517 | 6.2517 | 6.2525 | 6.253 | 6.2534 | 6.2539 | 6.258 | 6.2613 | 6.2609 | 6.2609 | 6.2609 |
| | 5 | 6.2169 | 6.2169 | 6.2181 | 6.2232 | 6.2232 | 6.2232 | 6.2232 | 6.2231 | 6.2275 | 6.2303 | 6.2307 | 6.2307 | 6.2307 |
| 15%pulp | 1 | 6.4205 | 6.4241 | 6.425 | 6.4264 | 6.4284 | 6.429 | 6.4295 | 6.4311 | 6.4352 | 6.4396 | 6.441 | 6.4411 | 6.4411 |
| | 2 | 6.4056 | 6.4088 | 6.4099 | 6.4112 | 6.4121 | 6.4137 | 6.4142 | 6.4163 | 6.4201 | 6.4254 | 6.4267 | 6.4267 | 6.4267 |
| | 3 | 6.3952 | 6.3993 | 6.3998 | 6.4005 | 6.402 | 6.4034 | 6.4038 | 6.4095 | 6.4108 | 6.4147 | 6.4157 | 6.4157 | 6.4157 |
| | 4 | 6.4381 | 6.4418 | 6.4421 | 6.4429 | 6.4441 | 6.446 | 6.4461 | 6.4498 | 6.4534 | 6.4575 | 6.4585 | 6.4585 | 6.4585 |
| | 5 | 6.4245 | 6.4284 | 6.4293 | 6.4305 | 6.4314 | 6.4322 | 6.4322 | 6.4375 | 6.4401 | 6.4437 | 6.4455 | 6.4456 | 6.4456 |
| 20%pulp | 1 | 6.529 | 6.5353 | 6.5353 | 6.5354 | 6.5371 | 6.5387 | 6.5399 | 6.5438 | 6.547 | 6.5523 | 6.5547 | 6.5547 | 6.5549 |
| | 2 | 6.5675 | 6.5708 | 6.5709 | 6.5715 | 6.5732 | 6.5754 | 6.5757 | 6.584 | 6.5884 | 6.5906 | 6.5914 | 6.5914 | 6.5914 |
| | 3 | 6.602 | 6.6068 | 6.6073 | 6.6083 | 6.6001 | 6.6124 | 6.6124 | 6.6186 | 6.6204 | 6.6257 | 6.628 | 6.628 | 6.6281 |
| | 4 | 6.545 | 6.55 | 6.5502 | 6.5508 | 6.553 | 6.5555 | 6.5561 | 6.5601 | 6.5661 | 6.5708 | 6.5711 | 6.5713 | 6.5714 |
| | 5 | 6.5383 | 6.5444 | 6.546 | 6.5475 | 6.5479 | 6.5489 | 6.549 | 6.5532 | 6.5594 | 6.5651 | 6.5658 | 6.566 | 6.5661 |

**Table C2** Water Absorption of the Composites without MAPP at different Time

| Water Absorption (%) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (hr.) | | | | | | | | | | | | | | |
| Sample | Trial No. | 0 | 2 | 4 | 6 | 8 | 10 | 24 | 48 | 72 | 96 | 120 | 144 | 168 |
| PP | 1 | 0.0000 | 0.0017 | 0.0000 | 0.0017 | 0.0067 | 0.0084 | 0.0134 | 0.0269 | 0.0286 | 0.0286 | 0.0286 | 0.0370 | 0.0370 |
| | 2 | 0.0000 | 0.0000 | 0.0000 | 0.0034 | 0.0034 | 0.0034 | 0.0000 | 0.0034 | 0.0067 | 0.0067 | 0.0067 | 0.0067 | 0.0067 |
| | 3 | 0.0000 | 0.0017 | 0.0017 | 0.0017 | 0.0034 | 0.0067 | 0.0151 | 0.0151 | 0.0218 | 0.0201 | 0.0201 | 0.0201 | 0.0201 |
| | 4 | 0.0000 | 0.0000 | 0.0017 | 0.0017 | 0.0017 | 0.0017 | 0.0017 | 0.0084 | 0.0101 | 0.0134 | 0.0134 | 0.0134 | 0.0134 |
| | 5 | 0.0000 | 0.0034 | 0.0034 | 0.0034 | 0.0034 | 0.0050 | 0.0034 | 0.0050 | 0.0050 | 0.0151 | 0.0151 | 0.0151 | 0.0151 |
| 5%pulp | 1 | 0.0000 | 0.0212 | 0.0212 | 0.0408 | 0.0425 | 0.0441 | 0.0474 | 0.0474 | 0.1127 | 0.1160 | 0.1241 | -0.0310 | -0.0310 |
| | 2 | 0.0000 | 0.0573 | 0.0573 | 0.0606 | 0.0639 | 0.0688 | 0.0786 | 0.0835 | 0.1376 | 0.1491 | 0.1573 | 0.1655 | 0.1655 |
| | 3 | 0.0000 | 0.0603 | 0.0603 | 0.0635 | 0.0635 | 0.0635 | 0.0684 | 0.0717 | 0.1287 | 0.1320 | 0.1385 | 0.1385 | 0.1385 |
| | 4 | 0.0000 | 0.0408 | 0.0425 | 0.0490 | 0.0490 | 0.0490 | 0.0539 | 0.0735 | 0.1291 | 0.1340 | 0.1421 | 0.1454 | 0.1454 |
| | 5 | 0.0000 | 0.0343 | 0.0326 | 0.0359 | 0.0375 | 0.0408 | 0.0440 | 0.0506 | 0.1256 | 0.1337 | 0.1337 | 0.1337 | 0.1337 |
| 10%pulp | 1 | 0.0000 | 0.0529 | 0.0593 | 0.0690 | 0.0738 | 0.0786 | 0.0818 | 0.0866 | 0.1155 | 0.2133 | 0.2165 | 0.2165 | -0.1743 |
| | 2 | 0.0000 | 0.0447 | 0.0463 | 0.0591 | 0.0623 | 0.0703 | 0.0751 | 0.0831 | 0.1230 | 0.2077 | 0.2125 | 0.2141 | 0.2141 |
| | 3 | 0.0000 | 0.0655 | 0.0735 | 0.0799 | 0.0799 | 0.0815 | 0.0847 | 0.0959 | 0.1518 | 0.2014 | 0.2014 | 0.2014 | 0.2014 |
| | 4 | 0.0000 | 0.0528 | 0.0528 | 0.0528 | 0.0656 | 0.0736 | 0.0800 | 0.0880 | 0.1536 | 0.2065 | 0.2001 | 0.2001 | 0.2001 |
| | 5 | 0.0000 | 0.0000 | 0.0193 | 0.1013 | 0.1013 | 0.1013 | 0.1013 | 0.0997 | 0.1705 | 0.2155 | 0.2220 | 0.2220 | 0.2220 |
| 15%pulp | 1 | 0.0000 | 0.0561 | 0.0701 | 0.0919 | 0.1230 | 0.1324 | 0.1402 | 0.1651 | 0.2290 | 0.2975 | 0.3193 | 0.3208 | 0.3208 |
| | 2 | 0.0000 | 0.0500 | 0.0671 | 0.0874 | 0.1015 | 0.1265 | 0.1343 | 0.1670 | 0.2264 | 0.3091 | 0.3294 | 0.3294 | 0.3294 |
| | 3 | 0.0000 | 0.0641 | 0.0719 | 0.0829 | 0.1063 | 0.1282 | 0.1345 | 0.2236 | 0.2439 | 0.3049 | 0.3206 | 0.3206 | 0.3206 |
| | 4 | 0.0000 | 0.0575 | 0.0621 | 0.0746 | 0.0932 | 0.1227 | 0.1243 | 0.1817 | 0.2376 | 0.3013 | 0.3169 | 0.3169 | 0.3169 |
| | 5 | 0.0000 | 0.0607 | 0.0747 | 0.0934 | 0.1074 | 0.1199 | 0.1199 | 0.2024 | 0.2428 | 0.2989 | 0.3269 | 0.3284 | 0.3284 |
| 20%pulp | 1 | 0.0000 | 0.0965 | 0.0965 | 0.0980 | 0.1241 | 0.1486 | 0.1669 | 0.2267 | 0.2757 | 0.3569 | 0.3936 | 0.3936 | 0.3967 |
| | 2 | 0.0000 | 0.0502 | 0.0518 | 0.0609 | 0.0868 | 0.1203 | 0.1249 | 0.2512 | 0.3182 | 0.3517 | 0.3639 | 0.3639 | 0.3639 |
| | 3 | 0.0000 | 0.0727 | 0.0803 | 0.0954 | -0.0288 | 0.1575 | 0.1575 | 0.2514 | 0.2787 | 0.3590 | 0.3938 | 0.3938 | 0.3953 |
| | 4 | 0.0000 | 0.0764 | 0.0794 | 0.0886 | 0.1222 | 0.1604 | 0.1696 | 0.2307 | 0.3224 | 0.3942 | 0.3988 | 0.4018 | 0.4034 |
| | 5 | 0.0000 | 0.0933 | 0.1178 | 0.1407 | 0.1468 | 0.1621 | 0.1637 | 0.2279 | 0.3227 | 0.4099 | 0.4206 | 0.4237 | 0.4252 |

**Table C3** Average Water Absorption of the Composites without MAPP at Different Time

| | | Water Absorption (%) | | | |
|---|---|---|---|---|---|
| | | | Mean | | |
| Time (hr.) | PP | 5%pulp | 10%pulp | 15%pulp | 20%pulp |
| 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 0.0013 | 0.0428 | 0.0432 | 0.0577 | 0.0778 |
| 4 | 0.0013 | 0.0428 | 0.0503 | 0.0692 | 0.0852 |
| 6 | 0.0024 | 0.0500 | 0.0724 | 0.0860 | 0.0967 |
| 8 | 0.0037 | 0.0513 | 0.0766 | 0.1063 | 0.0902 |
| 10 | 0.0050 | 0.0532 | 0.0811 | 0.1259 | 0.1300 |
| 24 | 0.0067 | 0.0585 | 0.0846 | 0.1306 | 0.1565 |
| 48 | 0.0118 | 0.0653 | 0.0907 | 0.1880 | 0.2376 |
| 72 | 0.0144 | 0.1267 | 0.1429 | 0.2359 | 0.3227 |
| 96 | 0.0168 | 0.1329 | 0.2089 | 0.3023 | 0.4099 |
| 120 | 0.0168 | 0.1391 | 0.2105 | 0.3226 | 0.3941 |
| 144 | 0.0185 | 0.1104 | 0.2108 | 0.3232 | 0.3954 |
| 168 | 0.0185 | 0.1104 | 0.2200 | 0.3232 | 0.3969 |

**Table C4** Weight of the Composites with 10% MAPP at Different Time

| Weight (g) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (hr.) | | | | | | | | | | | | | | |
| Sample | Trial No. | 0 | 2 | 4 | 6 | 8 | 10 | 24 | 48 | 72 | 96 | 120 | 144 | 168 |
| 5%pulp | 1 | 6.1695 | 6.1720 | 6.1722 | 6.1724 | 6.1725 | 6.1727 | 6.1728 | 6.1730 | 6.1733 | 6.1753 | 6.1756 | 6.1757 | 6.1757 |
| | 2 | 6.1648 | 6.1676 | 6.1678 | 6.1681 | 6.1682 | 6.1686 | 6.1688 | 6.1690 | 6.1691 | 6.1697 | 6.1700 | 6.1702 | 6.1702 |
| | 3 | 6.1670 | 6.1703 | 6.1704 | 6.1705 | 6.1708 | 6.1709 | 6.1714 | 6.1714 | 6.1714 | 6.1781 | 6.1723 | 6.1723 | 6.1723 |
| | 4 | 6.1423 | 6.1467 | 6.1468 | 6.1469 | 6.1469 | 6.1465 | 6.1469 | 6.1470 | 6.1471 | 6.1479 | 6.1481 | 6.1481 | 6.1481 |
| | 5 | 6.1360 | 6.1385 | 6.1368 | 6.1387 | 6.1387 | 6.1387 | 6.1387 | 6.1387 | 6.1393 | 6.1399 | 6.1403 | 6.1405 | 6.1405 |
| 10%pulp | 1 | 6.2804 | 6.2826 | 6.2828 | 6.2830 | 6.2835 | 6.2842 | 6.2853 | 6.2859 | 6.2869 | 6.2876 | 6.2878 | 6.2879 | 6.2879 |
| | 2 | 6.2755 | 6.2786 | 6.2970 | 6.2793 | 6.2796 | 6.2804 | 6.2806 | 6.2816 | 6.2824 | 6.2833 | 6.2835 | 6.2836 | 6.2836 |
| | 3 | 6.2631 | 6.2656 | 6.2656 | 6.2668 | 6.2668 | 6.2673 | 6.2679 | 6.2683 | 6.2695 | 6.2708 | 6.2708 | 6.2710 | 6.2710 |
| | 4 | 6.2527 | 6.2559 | 6.2561 | 6.2565 | 6.2569 | 6.2577 | 6.2580 | 6.2582 | 6.2589 | 6.2604 | 6.2606 | 6.2607 | 6.2607 |
| | 5 | 6.2683 | 6.2715 | 6.2715 | 6.2720 | 6.2721 | 6.2723 | 6.2743 | 6.2755 | 6.2751 | 6.2754 | 6.2755 | 6.2755 | 6.2755 |
| 15%pulp | 1 | 6.4486 | 6.4519 | 6.4524 | 6.4528 | 6.4544 | 6.4572 | 6.4573 | 6.4574 | 6.4576 | 6.4602 | 6.4605 | 6.4606 | 6.4607 |
| | 2 | 6.4308 | 6.4343 | 6.4351 | 6.4362 | 6.4371 | 6.4381 | 6.4382 | 6.4392 | 6.4406 | 6.4419 | 6.4423 | 6.4423 | 6.4423 |
| | 3 | 6.4480 | 6.4517 | 6.4525 | 6.4538 | 6.4542 | 6.4559 | 6.4560 | 6.4571 | 6.4582 | 6.4598 | 6.4600 | 6.4602 | 6.4602 |
| | 4 | 6.4680 | 6.4716 | 6.4720 | 6.4734 | 6.4745 | 6.4761 | 6.4773 | 6.4773 | 6.4780 | 6.4795 | 6.4806 | 6.4804 | 6.4804 |
| | 5 | 6.4780 | 6.4813 | 6.4820 | 6.4825 | 6.4835 | 6.4850 | 6.4859 | 6.4865 | 6.4871 | 6.4895 | 6.4903 | 6.4906 | 6.4906 |
| 20%pulp | 1 | 6.5664 | 6.5704 | 6.5719 | 6.5738 | 6.5741 | 6.5754 | 6.5766 | 6.5774 | 6.5788 | 6.5820 | 6.5822 | 6.5823 | 6.5823 |
| | 2 | 6.5740 | 6.5772 | 6.5796 | 6.5821 | 6.5826 | 6.5833 | 6.5842 | 6.5845 | 6.5853 | 6.5891 | 6.5895 | 6.5897 | 6.5898 |
| | 3 | 6.6015 | 6.6065 | 6.6069 | 6.6079 | 6.6094 | 6.6117 | 6.6129 | 6.6139 | 6.6153 | 6.6179 | 6.6196 | 6.6196 | 6.6196 |
| | 4 | 6.6103 | 6.6154 | 6.6155 | 6.6159 | 6.6178 | 6.6196 | 6.6201 | 6.6217 | 6.6231 | 6.6260 | 6.6278 | 6.6280 | 6.6281 |
| | 5 | 6.6167 | 6.6207 | 6.6214 | 6.6231 | 6.6240 | 6.6258 | 6.6274 | 6.6284 | 6.6298 | 6.6322 | 6.6350 | 6.6352 | 6.6354 |

**Table C5** Water Absorption of the Composites with 10% MAPP at Different Time

| | | Water Absorption (%) | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Time (hr.) | | | | | | | | | | |
| Sample | Trial No. | 0 | 2 | 4 | 6 | 8 | 10 | 24 | 48 | 72 | 96 | 120 |
| 5%pulp | 1 | 0.0000 | 0.0405 | 0.0438 | 0.0470 | 0.0486 | 0.0519 | 0.0535 | 0.0567 | 0.0616 | 0.0940 | 0.0989 |
| | 2 | 0.0000 | 0.0454 | 0.0487 | 0.0535 | 0.0552 | 0.0616 | 0.0649 | 0.0681 | 0.0698 | 0.0795 | 0.0843 |
| | 3 | 0.0000 | 0.0535 | 0.0551 | 0.0568 | 0.0616 | 0.0632 | 0.0713 | 0.0713 | 0.0713 | 0.1800 | 0.0859 |
| | 4 | 0.0000 | 0.0716 | 0.0733 | 0.0749 | 0.0749 | 0.0684 | 0.0749 | 0.0765 | 0.0781 | 0.0912 | 0.0944 |
| | 5 | 0.0000 | 0.0407 | 0.0130 | 0.0440 | 0.0440 | 0.0440 | 0.0440 | 0.0440 | 0.0538 | 0.0636 | 0.0701 |
| 10%pulp | 1 | 0.0000 | 0.0350 | 0.0382 | 0.0414 | 0.0494 | 0.0605 | 0.0780 | 0.0876 | 0.1035 | 0.1146 | 0.1178 |
| | 2 | 0.0000 | 0.0494 | 0.3426 | 0.0606 | 0.0653 | 0.0781 | 0.0813 | 0.0972 | 0.1100 | 0.1243 | 0.1275 |
| | 3 | 0.0000 | 0.0399 | 0.0399 | 0.0591 | 0.0591 | 0.0671 | 0.0766 | 0.0830 | 0.1022 | 0.1229 | 0.1229 |
| | 4 | 0.0000 | 0.0512 | 0.0544 | 0.0608 | 0.0672 | 0.0800 | 0.0848 | 0.0880 | 0.0992 | 0.1231 | 0.1263 |
| | 5 | 0.0000 | 0.0511 | 0.0511 | 0.0590 | 0.0606 | 0.0638 | 0.0957 | 0.1149 | 0.1085 | 0.1133 | 0.1149 |
| 15%pulp | 1 | 0.0000 | 0.0512 | 0.0589 | 0.0651 | 0.0899 | 0.1334 | 0.1349 | 0.1365 | 0.1396 | 0.1799 | 0.1845 |
| | 2 | 0.0000 | 0.0544 | 0.0669 | 0.0840 | 0.0980 | 0.1135 | 0.1151 | 0.1306 | 0.1524 | 0.1726 | 0.1788 |
| | 3 | 0.0000 | 0.0574 | 0.0698 | 0.0900 | 0.0965 | 0.1225 | 0.1241 | 0.1411 | 0.1582 | 0.1830 | 0.1861 |
| | 4 | 0.0000 | 0.0557 | 0.0618 | 0.0835 | 0.1005 | 0.1252 | 0.1438 | 0.1438 | 0.1546 | 0.1778 | 0.1948 |
| | 5 | 0.0000 | 0.0509 | 0.0617 | 0.0695 | 0.0849 | 0.1081 | 0.1220 | 0.1312 | 0.1405 | 0.1775 | 0.1899 |
| 20%pulp | 1 | 0.0000 | 0.0609 | 0.0838 | 0.1127 | 0.1173 | 0.1371 | 0.1553 | 0.1675 | 0.1888 | 0.2376 | 0.2406 |
| | 2 | 0.0000 | 0.0487 | 0.0852 | 0.1232 | 0.1308 | 0.1415 | 0.1552 | 0.1597 | 0.1719 | 0.2297 | 0.2358 |
| | 3 | 0.0000 | 0.0757 | 0.0818 | 0.0969 | 0.1197 | 0.1545 | 0.1727 | 0.1878 | 0.2090 | 0.2484 | 0.2742 |
| | 4 | 0.0000 | 0.0772 | 0.0787 | 0.0847 | 0.1135 | 0.1407 | 0.1483 | 0.1725 | 0.1936 | 0.2375 | 0.2647 |
| | 5 | 0.0000 | 0.0605 | 0.0710 | 0.0967 | 0.1103 | 0.1375 | 0.1617 | 0.1768 | 0.1980 | 0.2343 | 0.2766 |

**Table C6** Average Water Absorption of the Composites with 10%MAPP at Different Time

| Water Absorption (%) | | | | | |
|---|---|---|---|---|---|
| Mean | | | | | |
| Time (hr.) | PP | 5%pulp | 10%pulp | 15%pulp | 20%pulp |
| 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 0.0013 | 0.0504 | 0.0453 | 0.0539 | 0.0646 |
| 4 | 0.0013 | 0.0468 | 0.1052 | 0.0638 | 0.0801 |
| 6 | 0.0024 | 0.0552 | 0.0562 | 0.0784 | 0.1029 |
| 8 | 0.0037 | 0.0569 | 0.0603 | 0.0940 | 0.1183 |
| 10 | 0.0050 | 0.0578 | 0.0699 | 0.1205 | 0.1423 |
| 24 | 0.0067 | 0.0617 | 0.0833 | 0.1280 | 0.1586 |
| 48 | 0.0118 | 0.0633 | 0.0941 | 0.1366 | 0.1729 |
| 72 | 0.0144 | 0.0669 | 0.1047 | 0.1490 | 0.1923 |
| 96 | 0.0168 | 0.0700 | 0.1197 | 0.1782 | 0.2375 |
| 120 | 0.0168 | 0.0867 | 0.1219 | 0.1868 | 0.2584 |
| 144 | 0.0185 | 0.0884 | 0.1235 | 0.1881 | 0.2605 |
| 168 | 0.0185 | 0.0884 | 0.1235 | 0.1884 | 0.2617 |

**Table C7** Weight of the Composites with MAPP at 10% pulp and at Different Time

| Weight (g) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (hr.) | | | | | | | | | | | | | | |
| Sample | Trial No. | 0 | 2 | 4 | 6 | 8 | 10 | 24 | 48 | 72 | 96 | 120 | 144 | 168 |
| 2%MAPP | 1 | 6.3246 | 6.3274 | 6.3280 | 6.3281 | 6.3296 | 6.3305 | 6.3309 | 6.3310 | 6.3314 | 6.3317 | 6.3330 | 6.3332 | 6.3332 |
| | 2 | 6.3144 | 6.3179 | 6.3180 | 6.3183 | 6.3196 | 6.3203 | 6.3206 | 6.3208 | 6.3208 | 6.3212 | 6.3236 | 6.3240 | 6.3240 |
| | 3 | 6.3070 | 6.3119 | 6.3120 | 6.3128 | 6.3130 | 6.3163 | 6.3140 | 6.3140 | 6.3142 | 6.3147 | 6.3164 | 6.3166 | 6.3162 |
| | 4 | 6.3210 | 6.3255 | 6.3260 | 6.3265 | 6.3270 | 6.3277 | 6.3278 | 6.3280 | 6.3284 | 6.3293 | 6.3304 | 6.3304 | 6.3305 |
| | 5 | 6.3065 | 6.3095 | 6.3100 | 6.3106 | 6.3116 | 6.3122 | 6.3129 | 6.3130 | 6.3130 | 6.3134 | 6.3152 | 6.3154 | 6.3156 |
| 5%MAPP | 1 | 6.2947 | 6.2979 | 6.2984 | 6.2999 | 6.3001 | 6.3003 | 6.3001 | 6.3005 | 6.3010 | 6.3016 | 6.3029 | 6.3030 | 6.3030 |
| | 2 | 6.3094 | 6.3139 | 6.3142 | 6.3146 | 6.3150 | 6.3152 | 6.3154 | 6.3156 | 6.3160 | 6.3172 | 6.3172 | 6.3172 | 6.3172 |
| | 3 | 6.2982 | 6.3009 | 6.3012 | 6.3014 | 6.3024 | 6.3044 | 6.3050 | 6.3050 | 6.3050 | 6.3055 | 6.3068 | 6.3070 | 6.3070 |
| | 4 | 6.3145 | 6.3166 | 6.3172 | 6.3180 | 6.3195 | 6.3198 | 6.3205 | 6.3208 | 6.3210 | 6.3213 | 6.3226 | 6.3230 | 6.3230 |
| | 5 | 6.3155 | 6.3184 | 6.3188 | 6.3190 | 6.3200 | 6.3214 | 6.3213 | 6.3214 | 6.3215 | 6.3226 | 6.3225 | 6.3224 | 6.3225 |
| 20%MAPP | 1 | 6.2779 | 6.2807 | 6.2810 | 6.2816 | 6.2820 | 6.2830 | 6.2834 | 6.2842 | 6.2844 | 6.2853 | 6.2870 | 6.2872 | 6.2873 |
| | 2 | 6.2837 | 6.2883 | 6.2882 | 6.2883 | 6.2882 | 6.2885 | 6.2890 | 6.2891 | 6.2898 | 6.2904 | 6.2917 | 6.2920 | 6.2921 |
| | 3 | 6.2946 | 6.2973 | 6.2971 | 6.2971 | 6.2981 | 6.2995 | 6.3001 | 6.3004 | 6.3011 | 6.3011 | 6.3029 | 6.3030 | 6.3030 |
| | 4 | 6.2836 | 6.2860 | 6.2870 | 6.2863 | 6.2874 | 6.2880 | 6.2891 | 6.2891 | 6.2895 | 6.2900 | 6.2908 | 6.2912 | 6.2914 |
| | 5 | 6.2867 | 6.2875 | 6.2878 | 6.2885 | 6.2892 | 6.2909 | 6.2923 | 6.2923 | 6.2925 | 6.2926 | 6.2935 | 6.2937 | 6.2936 |

**Table C8** Water Absorption of the Composites with MAPP at 10% pulp and at Different Time

| Water Absorption (%) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (hr.) | | | | | | | | | | | | | | |
| Sample | Trial No. | 0 | 2 | 4 | 6 | 8 | 10 | 24 | 48 | 72 | 96 | 120 | 144 | 168 |
| 2%MAPP | 1 | 0 | 0.0443 | 0.0538 | 0.0553 | 0.0791 | 0.0933 | 0.0996 | 0.1012 | 0.1075 | 0.1123 | 0.1328 | 0.1360 | 0.1360 |
| | 2 | 0 | 0.0554 | 0.0570 | 0.0618 | 0.0824 | 0.0934 | 0.0982 | 0.1014 | 0.1014 | 0.1077 | 0.1457 | 0.1520 | 0.1520 |
| | 3 | 0 | 0.0777 | 0.0793 | 0.0920 | 0.0951 | 0.1475 | 0.1110 | 0.1110 | 0.1142 | 0.1221 | 0.1490 | 0.1522 | 0.1459 |
| | 4 | 0 | 0.0712 | 0.0791 | 0.0870 | 0.0949 | 0.1060 | 0.1076 | 0.1107 | 0.1171 | 0.1313 | 0.1487 | 0.1487 | 0.1503 |
| | 5 | 0 | 0.0476 | 0.0555 | 0.0650 | 0.0809 | 0.0904 | 0.1015 | 0.1031 | 0.1031 | 0.1094 | 0.1380 | 0.1411 | 0.1443 |
| 5%MAPP | 1 | 0 | 0.0508 | 0.0588 | 0.0826 | 0.0858 | 0.0890 | 0.0858 | 0.0921 | 0.1001 | 0.1096 | 0.1303 | 0.1319 | 0.1319 |
| | 2 | 0 | 0.0713 | 0.0764 | 0.0824 | 0.0888 | 0.0919 | 0.0951 | 0.0983 | 0.1046 | 0.1236 | 0.1236 | 0.1236 | 0.1236 |
| | 3 | 0 | 0.0429 | 0.0476 | 0.0508 | 0.0667 | 0.0984 | 0.1080 | 0.1080 | 0.1080 | 0.1159 | 0.1365 | 0.1397 | 0.1397 |
| | 4 | 0 | 0.0333 | 0.0428 | 0.0554 | 0.0792 | 0.0839 | 0.0950 | 0.0998 | 0.1029 | 0.1077 | 0.1283 | 0.1346 | 0.1346 |
| | 5 | 0 | 0.0459 | 0.0523 | 0.0554 | 0.0713 | 0.0934 | 0.0918 | 0.0934 | 0.0950 | 0.1124 | 0.1108 | 0.1093 | 0.1108 |
| 20%MAPP | 1 | 0 | 0.0446 | 0.0494 | 0.0589 | 0.0653 | 0.0812 | 0.0876 | 0.1004 | 0.1035 | 0.1179 | 0.1450 | 0.1481 | 0.1497 |
| | 2 | 0 | 0.0732 | 0.0716 | 0.0732 | 0.0716 | 0.0764 | 0.0843 | 0.0859 | 0.0971 | 0.1066 | 0.1273 | 0.1321 | 0.1337 |
| | 3 | 0 | 0.0429 | 0.0397 | 0.0397 | 0.0556 | 0.0778 | 0.0874 | 0.0921 | 0.1033 | 0.1033 | 0.1319 | 0.1334 | 0.1334 |
| | 4 | 0 | 0.0382 | 0.0541 | 0.0430 | 0.0605 | 0.0700 | 0.0875 | 0.0875 | 0.0939 | 0.1019 | 0.1146 | 0.1209 | 0.1241 |
| | 5 | 0 | 0.0127 | 0.0175 | 0.0286 | 0.0398 | 0.0668 | 0.0891 | 0.0891 | 0.0923 | 0.0938 | 0.1082 | 0.1113 | 0.1098 |

**Table C9** Average Water Absorption of the Composites with MAPP at 10% pulp and at Different Time

| Water Absorption (%) | | | | | |
|---|---|---|---|---|---|
| Mean | | | | | |
| Time (hr.) | 0%MAPP | 2%MAPP | 5%MAPP | 10%MAPP | 20%MAPP |
| 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 0.0432 | 0.0592 | 0.0488 | 0.0453 | 0.0423 |
| 4 | 0.0503 | 0.0649 | 0.0556 | 0.0523 | 0.0465 |
| 6 | 0.0724 | 0.0722 | 0.0653 | 0.0562 | 0.0487 |
| 8 | 0.0766 | 0.0865 | 0.0783 | 0.0603 | 0.0586 |
| 10 | 0.0811 | 0.1061 | 0.0913 | 0.0699 | 0.0745 |
| 24 | 0.0846 | 0.1036 | 0.0951 | 0.0833 | 0.0872 |
| 48 | 0.0907 | 0.1055 | 0.0983 | 0.0941 | 0.0910 |
| 72 | 0.1429 | 0.1086 | 0.1021 | 0.1047 | 0.0980 |
| 96 | 0.2089 | 0.1166 | 0.1139 | 0.1197 | 0.1047 |
| 120 | 0.2105 | 0.1428 | 0.1259 | 0.1219 | 0.1254 |
| 144 | 0.2108 | 0.1460 | 0.1278 | 0.1235 | 0.1292 |
| 168 | 0.2110 | 0.1457 | 0.1281 | 0.1235 | 0.1301 |

**Table C10** Weight of the Composites with Esterified Pulp at Different Time

| Weight (g) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (hr.) | | | | | | | | | | | | | | |
| Sample | Trial No. | 0 | 2 | 4 | 6 | 8 | 10 | 24 | 48 | 72 | 96 | 120 | 144 | 168 |
| 5%pulp | 1 | 6.0667 | 6.0679 | 6.0674 | 6.0672 | 6.0669 | 6.0669 | 6.0670 | 6.0671 | 6.0674 | 6.0683 | 6.0685 | 6.0684 | 6.0685 |
| | 2 | 6.0719 | 6.0725 | 6.0730 | 6.0722 | 6.0728 | 6.0732 | 6.0728 | 6.0729 | 6.0729 | 6.0740 | 6.0745 | 6.0745 | 6.0747 |
| | 3 | 6.0851 | 6.0865 | 6.0865 | 6.0862 | 6.0863 | 6.0862 | 6.0864 | 6.0863 | 6.0863 | 6.0875 | 6.0876 | 6.0876 | 6.0876 |
| | 4 | 6.1078 | 6.1085 | 6.1094 | 6.1082 | 6.1082 | 6.1080 | 6.1090 | 6.1088 | 6.1088 | 6.1102 | 6.1100 | 6.1100 | 6.1100 |
| | 5 | 6.0717 | 6.0737 | 6.0730 | 6.0721 | 6.0721 | 6.0721 | 6.0723 | 6.0723 | 6.0723 | 6.0727 | 6.0727 | 6.0726 | 6.0727 |
| 10%pulp | 1 | 6.2710 | 6.2723 | 6.2725 | 6.2727 | 6.2727 | 6.2723 | 6.2729 | 6.2729 | 6.2730 | 6.2737 | 6.2738 | 6.2740 | 6.2741 |
| | 2 | 6.2707 | 6.2715 | 6.2716 | 6.2717 | 6.2719 | 6.2720 | 6.2724 | 6.2724 | 6.2725 | 6.2737 | 6.2738 | 6.2738 | 6.2740 |
| | 3 | 6.2941 | 6.2948 | 6.2952 | 6.2952 | 6.2955 | 6.2957 | 6.2957 | 6.2957 | 6.2956 | 6.2962 | 6.2964 | 6.2965 | 6.2966 |
| | 4 | 6.2951 | 6.2952 | 6.2953 | 6.2954 | 6.2955 | 6.2956 | 6.2963 | 6.2963 | 6.2969 | 6.2974 | 6.2974 | 6.2976 | 6.2977 |
| | 5 | 6.2760 | 6.2783 | 6.2784 | 6.2785 | 6.2784 | 6.2785 | 6.2785 | 6.2784 | 6.2787 | 6.2796 | 6.2797 | 6.2798 | 6.2800 |
| 15%pulp | 1 | 6.1500 | 6.1505 | 6.1510 | 6.1519 | 6.1522 | 6.1528 | 6.1525 | 6.1526 | 6.1526 | 6.1537 | 6.1537 | 6.1537 | 6.1537 |
| | 2 | 6.1838 | 6.1856 | 6.1840 | 6.1841 | 6.1842 | 6.1845 | 6.1842 | 6.1850 | 6.1861 | 6.1858 | 6.1859 | 6.1859 | 6.1860 |
| | 3 | 6.1669 | 6.1696 | 6.1700 | 6.1698 | 6.1696 | 6.1692 | 6.1699 | 6.1700 | 6.1702 | 6.1708 | 6.1707 | 6.1707 | 6.1708 |
| | 4 | 6.1435 | 6.1442 | 6.1450 | 6.1459 | 6.1450 | 6.1452 | 6.1456 | 6.1470 | 6.1474 | 6.1476 | 6.1478 | 6.1478 | 6.1478 |
| | 5 | 6.1762 | 6.1765 | 6.1765 | 6.1766 | 6.1769 | 6.1779 | 6.1779 | 6.1780 | 6.1786 | 6.1787 | 6.1787 | 6.1787 | 6.1788 |
| 20% pulp | 1 | 6.2080 | 6.2096 | 6.2109 | 6.2110 | 6.2112 | 6.2111 | 6.2111 | 6.2124 | 6.2126 | 6.2125 | 6.2127 | 6.2129 | 6.2130 |
| | 2 | 6.2157 | 6.2169 | 6.2179 | 6.2180 | 6.2184 | 6.2185 | 6.2190 | 6.2193 | 6.2193 | 6.2201 | 6.2203 | 6.2205 | 6.2205 |
| | 3 | 6.2582 | 6.2599 | 6.2583 | 6.2594 | 6.2600 | 6.2600 | 6.2602 | 6.2604 | 6.2608 | 6.2631 | 6.2613 | 6.2616 | 6.2616 |
| | 4 | 6.2390 | 6.2457 | 6.2412 | 6.2414 | 6.2420 | 6.2430 | 6.2429 | 6.2430 | 6.2436 | 6.2436 | 6.2438 | 6.2440 | 6.2441 |
| | 5 | 6.2451 | 6.2481 | 6.2469 | 6.2472 | 6.2474 | 6.2484 | 6.2496 | 6.2498 | 6.2500 | 6.2515 | 6.2517 | 6.2520 | 6.2521 |

**Table C11** Water Absorption of the Composites with Esterified Pulp at Different Time

| Water Absorption (%) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Time (hr.) | | | | | | | | | | | | | | |
| Sample | Trial No. | 0 | 2 | 4 | 6 | 8 | 10 | 24 | 48 | 72 | 96 | 120 | 144 | 168 |
| 5% pulp | 1 | 0 | 0.0198 | 0.0115 | 0.0082 | 0.0033 | 0.0033 | 0.0049 | 0.0066 | 0.0115 | 0.0264 | 0.0297 | 0.0280 | 0.0297 |
| | 2 | 0 | 0.0099 | 0.0181 | 0.0054 | 0.0148 | 0.0214 | 0.0148 | 0.0165 | 0.0165 | 0.0346 | 0.0428 | 0.0428 | 0.0461 |
| | 3 | 0 | 0.0230 | 0.0230 | 0.0181 | 0.0197 | 0.0181 | 0.0214 | 0.0197 | 0.0197 | 0.0394 | 0.0411 | 0.0411 | 0.0411 |
| | 4 | 0 | 0.0115 | 0.0262 | 0.0065 | 0.0069 | 0.0033 | 0.0196 | 0.0164 | 0.0164 | 0.0393 | 0.0360 | 0.0360 | 0.0360 |
| | 5 | 0 | 0.0329 | 0.0214 | 0.0066 | 0.0066 | 0.0066 | 0.0099 | 0.0099 | 0.0099 | 0.0165 | 0.0165 | 0.0148 | 0.0165 |
| 10% pulp | 1 | 0 | 0.0207 | 0.0239 | 0.0271 | 0.0271 | 0.0204 | 0.0303 | 0.0303 | 0.0319 | 0.0431 | 0.0446 | 0.0478 | 0.0494 |
| | 2 | 0 | 0.0128 | 0.0144 | 0.0159 | 0.0191 | 0.0207 | 0.0271 | 0.0271 | 0.0287 | 0.0478 | 0.0494 | 0.0494 | 0.0526 |
| | 3 | 0 | 0.0111 | 0.0175 | 0.0175 | 0.0222 | 0.0254 | 0.0254 | 0.0254 | 0.0238 | 0.0334 | 0.0365 | 0.0381 | 0.0397 |
| | 4 | 0 | 0.0016 | 0.0032 | 0.0048 | 0.0064 | 0.0079 | 0.0191 | 0.0191 | 0.0286 | 0.0365 | 0.0365 | 0.0397 | 0.0413 |
| | 5 | 0 | 0.0366 | 0.0382 | 0.0398 | 0.0382 | 0.0398 | 0.0398 | 0.0382 | 0.0430 | 0.0574 | 0.0590 | 0.0605 | 0.0637 |
| 15% pulp | 1 | 0 | 0.0081 | 0.0163 | 0.0309 | 0.0358 | 0.0455 | 0.0407 | 0.0423 | 0.0423 | 0.0602 | 0.0602 | 0.0602 | 0.0602 |
| | 2 | 0 | 0.0291 | 0.0032 | 0.0049 | 0.0065 | 0.0113 | 0.0065 | 0.0194 | 0.0372 | 0.0323 | 0.0340 | 0.0340 | 0.0356 |
| | 3 | 0 | 0.0438 | 0.0503 | 0.0470 | 0.0438 | 0.0373 | 0.0486 | 0.0503 | 0.0535 | 0.0632 | 0.0616 | 0.0616 | 0.0632 |
| | 4 | 0 | 0.0114 | 0.0244 | 0.0391 | 0.0244 | 0.0277 | 0.0342 | 0.0570 | 0.0635 | 0.0667 | 0.0700 | 0.0700 | 0.0700 |
| | 5 | 0 | 0.0049 | 0.0049 | 0.0065 | 0.0113 | 0.0275 | 0.0275 | 0.0291 | 0.0389 | 0.0405 | 0.0405 | 0.0405 | 0.0421 |
| 20% pulp | 1 | 0 | 0.0258 | 0.0467 | 0.0483 | 0.0515 | 0.0499 | 0.0499 | 0.0709 | 0.0741 | 0.0725 | 0.0757 | 0.0789 | 0.0805 |
| | 2 | 0 | 0.0193 | 0.0354 | 0.0370 | 0.0434 | 0.0450 | 0.0531 | 0.0579 | 0.0579 | 0.0708 | 0.0740 | 0.0772 | 0.0772 |
| | 3 | 0 | 0.0272 | 0.0016 | 0.0192 | 0.0288 | 0.0288 | 0.0320 | 0.0352 | 0.0415 | 0.0783 | 0.0495 | 0.0543 | 0.0543 |
| | 4 | 0 | 0.1074 | 0.0353 | 0.0385 | 0.0481 | 0.0641 | 0.0625 | 0.0641 | 0.0737 | 0.0737 | 0.0769 | 0.0801 | 0.0817 |
| | 5 | 0 | 0.0480 | 0.0288 | 0.0336 | 0.0368 | 0.0528 | 0.0721 | 0.0753 | 0.0785 | 0.1025 | 0.1057 | 0.1105 | 0.1121 |

**Table C12** Average Water Absorption of the Composites with Esterified Pulp at Different Time

| Water Absorption (%) | | | | | |
|---|---|---|---|---|---|
| Mean | | | | | |
| Time (hr.) | PP | 5% | 10% | 15% | 20% |
| 0 | 0 | 0 | 0 | 0 | 0 |
| 2 | 0.0013 | 0.0050 | 0.0166 | 0.0195 | 0.0250 |
| 4 | 0.0013 | 0.0060 | 0.0194 | 0.0198 | 0.0296 |
| 6 | 0.0024 | 0.0090 | 0.0210 | 0.0257 | 0.0353 |
| 8 | 0.0037 | 0.0103 | 0.0226 | 0.0244 | 0.0417 |
| 10 | 0.0050 | 0.0105 | 0.0229 | 0.0299 | 0.0481 |
| 24 | 0.0067 | 0.0141 | 0.0283 | 0.0315 | 0.0539 |
| 48 | 0.0118 | 0.0200 | 0.0280 | 0.0396 | 0.0607 |
| 72 | 0.0144 | 0.0250 | 0.0312 | 0.0471 | 0.0652 |
| 96 | 0.0168 | 0.0312 | 0.0436 | 0.0526 | 0.0750 |
| 120 | 0.0168 | 0.0332 | 0.0452 | 0.0532 | 0.0764 |
| 144 | 0.0185 | 0.0326 | 0.0471 | 0.0532 | 0.0802 |
| 168 | 0.0185 | 0.0339 | 0.0494 | 0.0542 | 0.0812 |

# BIOGRAPHY

Miss Tassanee Puttana was born in Nakornpathom, Thailand, on January 28, 1978. She received the Bachelor of Science degree majoring in Polymer Science and Textile from the Department of Materials Science, Faculty of Science, Chulalongkorn University in 1999. Afterwards, she persued her post graduate degree at the Deparement of Materials Science in 1999. She completed the programme and obtained her Master degree in Applied Polymer Science and Textile Technology in October 2001.