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PREPARATION OF POLYMER COMPOSITES FROM POLYPROPYLENE AND SAWDUST

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ในงานวิจัยนี้ได้เตรียมวัสดุเชิงประกอบระหว่างพอลิโพรพิลีน/ขี้เลื่อย ซึ่งมีขี้เลื่อยและขี้เลื่อยที่ถูกปรับปรุงพื้นผิว 10-50 เปอร์เซ็นต์โดยน้ำหนัก ด้วยลูกกลิ้งแบบคู่แล้วจึงขึ้นรูปด้วยเครื่องอัดพลาสติกแบบไฮโดรลิก และทำการศึกษาผลของปริมาณขี้เลื่อย และสารปรับปรุงพื้นผิวต่อสมบัติเชิงกลของวัสดุเชิงประกอบระหว่างพอลิโพรพิลีน/ขี้เลื่อย พบว่าการเติมขี้เลื่อยในพอลิโพรพิลีนสามารถเพิ่มค่ามอดูลัส และค่าความแข็งได้ แต่ขี้เลื่อยนี้ทำให้ค่าความต้านทานแรงดึง ค่าการยืดตัวเมื่อขาด และค่าความต้านทานแรงกระแทกลดลง อย่างไรก็ตามลักษณะพื้นผิวของวัสดุเชิงประกอบชนิดนี้แสดงถึงความไม่เข้ากันและการยึดติดระหว่างเนื้อพลาสติกและขี้เลื่อยที่ไม่ดี ดังนั้นทำปฏิกิริยาเอสเทอริฟิเคชันด้วยบิวทิริลคลอไรด์ โดเดคคาโนอิลคลอไรด์ และสเตียโรอิลคลอไรด์เพื่อปรับปรุงพื้นผิวของขี้เลื่อยก่อนผสมกับเมทริกซ์ PP ปริมาณเอสเทอริฟิเคชันที่เหมาะสมในการเตรียมวัสดุเชิงประกอบคือ 50 เปอร์เซ็นต์โดยน้ำหนัก ซึ่งส่งผลให้มีสมบัติเชิงกลที่สูงที่สุด ผลที่ได้แสดงให้เห็นถึงสมบัติเชิงกลของวัสดุเชิงประกอบที่มีขี้เลื่อยชนิดบิวทิเรเท็ดมีค่าดีกว่าชนิดที่มีขี้เลื่อยที่ไม่ผ่านการทำเป็นเอสเทอร์ ในทำนองเดียวกันโดเดคคาโนอิลคลอไรด์และสเตียโรอิลคลอไรด์ช่วยส่งเสริมความเข้ากันระหว่างขี้เลื่อยและพอลิโพรพิลีน แม้ว่าความแข็งแรงของวัสดุเชิงประกอบที่มีขี้เลื่อยชนิดโดเดคคาโนเอเท็ดและขี้เลื่อยชนิดสเตียโรเอเท็ดจะต่ำกว่าวัสดุเชิงประกอบที่มีขี้เลื่อยชนิดบิวทิเรเท็ด การบำบัดพื้นผิวนี้เพิ่มความสามารถในการยืดและความต้านทานแรงกระแทกของวัสดุเชิงประกอบ

สาขาวิชา ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์ ลายมือชื่อนิสิต..
ปีการศึกษา 2547 ลายมือชื่ออาจารย์ที่ปรึกษา.................................

4572288923 : MAJOR PETROCHEMISTRY AND POLYMER SCIENCE
KEY WORD : COMPOSITES / COMPATIBILIZATION / PLASTICIZATION / MECHANICAL PROPERTIES

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In this work, polypropylene (PP) /sawdust composites containing 10-50% by weight of sawdust and surface-modified sawdust were prepared by two roll mill followed by compression molding and the effect of sawdust content and surface-modifying agents on mechanical properties of the PP/sawdust composites were studied. It was found that sawdust in PP increased the stiffness and hardness while the tensile strength, elongation at break and impact strength decreased. However, the surface morphology of this type of composite revealed incompatibility and poor interfacial adhesion between the sawdust and PP. Thus, the esterification reaction using butyryl chloride, dodecanoyl chloride and stearoyl chloride were adopted to modify surface of the sawdust prior to mix with the PP matrix. The optimum of amount of ester was 50% which led to the highest mechanical properties. Experimental results revealed that the mechanical properties of the composite with butyrated sawdust was better than the ones with unesterified sawdust. Likewise, the dodecanoyl chloride and stearoyl chloride helped promoting the compatibility between the sawdust and PP. Although, comparing to the composite with butyrated sawdust, the strength of the composites with dodecanoated sawdust and stearoated sawdust were lowered, this surface treatment increased the elongation at break and impact strength of the composites.

Field of study Petrochemistry and Polymer Science Student's signature……………….

Academic year 2004 Advisor's signature………………

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CONTENTS

Page

Page

Page

LIST OF TABLES

Table **Page**

LIST OF FIGURES

Figure **Page**

Figure **Page**

ABBREVIATIONS

LDPE	Low density polyethylene
HDPE	High density polyethylene
PP	Polypropylene
PE	Polyethylene
PET	Poly (ethylene terephthalate)
PVC	Poly (vinyl chloride)
HIPS	High impact polystyrene
ABS	Acrylonitrile-butadiene-styrene terpolymer
PS	Polystyrene
MAN	maleic anhydride
MAPP	maleic anhydride-polypropylene
d.s.	degree of substitution
FTIR	Fourier Transform Infrared Spectroscopy
SEM	Scanning Electron Microscopy
CRT	Cathode ray tube

DSC	Differential Scanning Calorimeter
T_m	melting temperature
MFI	melt flow index
s	second
min	minute
h	hour
% wt	percent weight
°C	degree Celsius
°F	degree Fahrenheit
T	temperature
μm	micrometer
MPa	mega pascal
GPa	giga pascal
lbf/in^2	pound-force per square inch
ft-lb/inch	foot-pound per inch
psi	pounds per square inch
g	gram

J	joule
mm	millimeter
cm	centimeter
lb	pound
h	hour
kg	kilogram
kg/cm^2	kilogram per square centimeter
%T	percentage transmittance
$\overline{M}_w$	the weight average molecular weight
$\overline{M}_n$	the number average molecular weight
MWD	the molecular weight distribution
M	the molecular weight
w	weight

CHAPTER I

INTRODUCTION

In recent years, reinforced thermoplastics and composites with different fillers have been considered to give many advantages. These composites have light weight, reasonable strength, stiffness and low cost. For these reason, attempts have also been made to find suitable reinforcing fillers. Conventionally inorganic fillers, for example asbestos, alumina, mica have been used. However, they can cause some damages to the equipments during processing. On the other hand, organic reinforcing fillers, in particular natural 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. Thus, cellulose fibers are attractive alternatives for as a filler thermoplastics. Fiber of cotton, sawdust, flax, jute, ramie, sisal, abaca, pineapple, kanaf or bamboo are the most common filler used for polymer composites [1]. Replacing the expensive synthetic fibers with these natural fibers is not only reduce the amount of waste, but also reduce the cost of composites.

In particular, sawdust is an attractive filler for thermoplastic composites because it is available from a wood manufacturing, have high stiffness, low density, non-abrasive, renewable and cheap [2]. A great deal of interest has been generated in the use of the sawdust as a filler in thermoplastic composites such as in polypropylene. Polypropylene (PP) possesses outstanding properties such as low density, good flex life, good surface hardness, very good abrasion resistance, and recyclable [2] and has been used in many application such as automotive interior panels, furniture, paneling for boats, railroad car, campers, building interior, etc.

However, the main problem in preparation of this composites is the incompatibility between the hydrophilic sawdust 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, the poor interfacial bonding between the hydrophilic sawdust and the hydrophobic polymer matrix generally leads to a lower mechanical properties. The interfacial bonding can be improved by chemical modification of the surface of cellulose fibers using various coupling agents and compatibilizers. Modification of surface for increasing interaction between the fiber and matrix.

1.2 Objectives of the Research Work

1) To prepare surface-esterified sawdust as fillers using acid chlorides.

2) To prepare polymer composites from polypropylene and surface-esterified sawdust

3) To study the effects of surface-esterified sawdust content on the mechanical properties of polypropylene composite.

4) To study the mechanical properties of sawdust composite and surface-esterified sawdust composites and the fracture surface of the composites.

1.3 Scope of the Research Work

In this study, the composites were prepared from sawdust and surface-esterified sawdust as filler and polypropylene with various amount 10 to 50% wt of filler. In order to enhance the compatibility between sawdust and polypropylene, sawdust were surface esterified with acid chloride, including butyryl chloride, dodecanoyl chloride and stearoyl chloride. The blending of surface-esterified sawdust and polypropylene were mixed by a two roll mill. After compounding, the composite sheet was removed from the two roll mill followed by compression molding. The effects of filler contents, surface modification were evaluated in terms of mechanical properties, thermal properties, and morphological properties.

CHAPTER II

THEORY AND LITERATURE REVIEW

2.1 Composite Materials

Composite material can be defined as a macroscopic combination of two or more distinct materials, having a recognizable interface between them. However, because composites are usually used for their structural properties, the definition can be restricted to include only those materials that contain a reinforcement (such as fibers or particles) supported by a binder (matrix) material. The constituents can be organic, inorganic or metallic (synthetic and naturally occurring) in the from of particles, rods, fibers, plates, foams, etc. For a given application, such physically uncorrelated parameters as strength, density, electrical properties, and cost. Furthermore, the composite may be the only effective vehicle for exploiting the unique properties of certain special materials [3-4].

2.1.1 Classification of Composite Materials

Composites can be classified in many manners. One simple classification scheme is to separate them according to reinforcement forms [3-5].

2.1.1.1 Particulate-Reinforced Composites

Particulate-reinforced composites consist of particles dispersed in a matrix. This type is considered to be a “particle” if all of its dimensions are roughly equal. Particulates may have any shapes, configurations, or sizes. They may be powder, beads, rods, crystalline, or amorphic. They may be metallic, ceramic, manmade, or natural materials. Concrete and wood particleboard are two familiar examples of particulate composites. Pieces of ceramic particles are placed in a metallic flakes have been added to improve electrical properties and provide some degree of radiation shielding in polymer composites.

Generally, particles in polymer usually extend rather than reinforce the material. These are usually referred to as “filled” systems. Because filler particles are included for the aim of cost reduction rather than reinforcement, these composites are not generally considered to be particulate composites. Nonetheless, in some cases the filler will also reinforce the matrix material [3-6].

2.1.1.2 Fiber-Reinforced Composites

Fiber-reinforced composites are composed of reinforced fibers in a matrix. They contain reinforcements having lengths greater than their cross-sectional dimensions. They can be further divided into those containing discontinuous and continuous fibers. In discontinuous fibers case, the bond between the fibers and the matrix is broken at the fiber’s ends, and thus carry less stress than at the middle part of the fiber while, continuous fibers can carry stresses along its length [3-7].

2.1.1.3 Laminar Composites

Laminar composites are composed of layers of materials held together by matrix binder, sandwich and honeycomb component as well as the term high-pressure laminates are included. Complicating the definition of a composite as having both continuous and discontinuous phases is the fact that in a laminar composite, neither of these phases may be regarded as truly continuous in these dimensions [3-7].

2.1.2 Theory of the Action of Fillers And Reinforcements

The action of active filler can be attributed to several mechanisms. Some fillers from chemical bond with the material to be reinforced. For example, carbon black produces crosslinking in elastomers by means of radical reaction [7].

Other fillers act mainly through the volume they take up. The chain molecules of the polymer to be reinforced cannot assume all the conformational positions that are basically possible. Moreover, it can be assumed that in certain zones around the filler particles the polymeric phase differs in structure and properties from the polymer matrix. The polymer segments attached to filler surfaces by primary or secondary valence bonds in turn cause a certain immobilization of adjacent segments and circumstances permitting, an orientation of the polymer matrix. The increase in glass transition temperatures observed in filled polymers, resulting from the limitations of mobility in the filler/polymer boundary zone, can be regarded as conformation of this theoretical concept.

The zone directly of filler surface, whose structure would appear to be ordered, thus causes a stiffening of the material as a whole. Lower deformability and higher strength are also due to this composite nature. Uniform distribution of fillers is especially important, so that as many polymer chains as possible can be bound to the free filler surface. The free surface energy and the polarity of the bond between the filler and the matrix are important factors in this regard.

Another mode of action of active fillers from the fact that when the polymer molecules are subjected to mechanical stress with absorption of energy, they can slide off the filler surface. The impact energy can therefore be more uniformly distributed and impact strength increased as, for example, in the unplasticized PVC/calcium-carbonate system. In some cases, microcraze formation that destroys the impact energy at the filler/polymer interface is also facilitated.

2.1.3 Properties of Filled and Reinforced Plastic

The extensive range of fillers used nowadays indicates the main objectives which are to lower cost of molding compounds and to selective modification of the properties of a specific plastic. Inert fillers or extender fillers increase the bulk and lower the price, active fillers produce specific improvements in certain mechanical or physical properties and are thus also know as reinforcing fillers [7].

The use of extender fillers can result in the following changes in the properties of thermoplastics: increase in density; increase in modulus of elasticity, as well as in compressive and flexural strength (stiffening); lower shrinkage; increase in hardness and improvement in surface quality; increase in heat deflection temperature and lowering of the temperature dependence of the mechanical properties, there being generally no improvement in mechanical and physical properties compared with unfilled polymers; and cost reduction.

Reinforcing fillers, on the other hand, produce the following improvement in thermoplastics: increase in tensile strength and tensile stress at break, as well as in compressive and shear strengths; increase in modulus of elasticity and stiffness of the composite material; increase in heat deflection temperature and lowering of the temperature dependence of the mechanical values; lower shrinkage; improvement in creep behavior and bend-creep modulus, reduction in the viscoelastic yield under load; and there is also a partial improvement in impact strength.

2.2 Matrix

Matrix is an essentially homogeneous resin or polymer material in which the fiber system of composite is embedded. Both thermoplastic and thermoset resin may be used. The purpose of the composite matrix is to bind the fiber together by virtue of its cohesive and adhesive characteristics, to together by virtue of its cohesive and adhesive characteristics, to transfer load to and between fiber and to protect them from environments and handling. Nonetheless, the matrix resin provides many essential functions. In addition to those mentioned above, the matrix keeps the reinforcing in the proper orientation and position so that they can carry the intended loads, distribute the loads more or less even among the fiber, provide resistance to crack propagation and damage, and provide all of the interlaminar shear strength of the composite. Moreover, the matrix generally determines the overall service temperature limitations of the composite, and may also control its environmental resistance [8].

2.2.1 Polypropylene

Polypropylene (PP), a thermoplastic polymer which entered to commercial production in 1957, was the first of stereoisomer polymer. Polypropylene differs form polyethylene because there is a methyl group attached to every other carbon atom, which stiffens the chain. Unless the methyl groups are arranged in one position relative to the chain, the polymer does not crystallize until the stereospecific catalysts were developed (independently) by Natta and Ziegler. Crystallinity is responsible for the stiffness and solvent resistance of the commercial plastic. The most valuable property of polypropylene is versatility. It can be tailored to many fabrication methods and applications. Some properties that are usually considered inherent advantages of polypropylene are: low specific gravity (density); excellent chemical resistance; high melting point (relative to volume plastics); good stiffness/toughness balance; adaptability to many concerting methods; great range of special purpose grades; excellent dielectric properties; and low cost (especially per unit volume).

Although polypropylene has many useful properties, it is not intrinsically tough, especially below its glass transition temperature. However, its impact resistance can be improved by adding elastomer, usually ethylene/propylene rubbers at 5 to 25% [5,6,8,10].

2.2.2 Manufacture of Polypropylene Homopolymer

For the preparation of polypropylene, the C_3 fraction (propylene and propane) is the basic material and is produced by cracking of petroleum products such as natural gas or light oils. The C_3 fraction may be separated form the other gases without undue difficulty by fractional distillation.

The separation of propylene from propane of the distillation plant. For polymer preparation, impurities such as water and methylacetylene must be carefully removed. A typical catalyst system may be prepared by reacting titanium trichloride with aluminum tributyl or aluminum diethyl monochloride in naphtha under nitrogen globe to form a slurry consisting of about 10% catalyst and 90% naphtha. The properties of the polymer are strongly dependent on the catalyst composition and its particle shape and size.

Polypropylene is transferred into the polymerization vessel under pressure while the catalyst solution and the reaction diluents (usually naphtha) are metered in separately. In batch processes, it is carried out at temperatures of about 60^{o}C for approximately 1-4 hours. In a typical process an 80-85% conversion to polymer is obtained. Since the reaction is carried out well below the polymer melting point the process involves a form of suspension rather than solution polymerization. The polymer molecular weight can be controlled in a various ways, for example by the use of hydrogen as a chain transfer agent or by variations in the molar ratio of catalyst components, the polymerization temperature, the monomer pressure or the catalyst concentration. At this stage of the process, the following materials are present in the polymerization vessel: Isotactic polymer; atactic polymer; solvent; monomer; and catalyst.

The first step in separating these ingredients involves the transfer of the reaction mixture to a drum to remove the unreacted monomer which is purified (where necessary) and recycled. The residual slurry is centrifuged to remove the bulk of the solvent together with most of the atactic material which is soluble in the naphtha. The remaining material is then treated with an agent which decomposes the catalyst and dissolves the residue. A typical agent is methanol containing a trace of hydrochloric acid. The solution of residues in the methanol is removed by a centrifuging operation and the polymer is washed and dried at about 80^{o}C. At this stage, the polymer may be blended with antioxidants, extruded and cut into pellets. There are a number of variations in this basic process, many of which involve extra processes to reduce the atactic content of the polymer. There have also been a number of quite substantial changes in the method of polymerization over the years. For example newer catalyst system, such as those containing magnesium compounds, give an appreciable improvement in the yield of isotactic material and this and appreciable improvement in the yield of isotactic material and this enables the washing stage to be dispensed with. Furthermore whilst the suspension process (in hydrocarbon) continues to predominate gas phase polymerizations, and polymerization in liquid propylene are now being used. Thermal and chemical after treatments have also been developed to reduce the width of the molecular mass distribution [11].

2.2.3 Classification of Polypropylene Polymer

2.2.3.1 Polypropylene Homopolymer

Polypropylene is synthesized by placing propylene monomer under controlled conditions of heat and pressure in the presence of organometallic, stereospecific catalysts (Ziegler-Natta type). Depending on the catalyst and polymerization process used, the molecular structure of the resulting polymer consist of three different types of stereochemical configurations in varying amounts. These are referred to an isotactic, syndiotacic, and atactic, for which their structures are shown in Figure 2.1 [12].

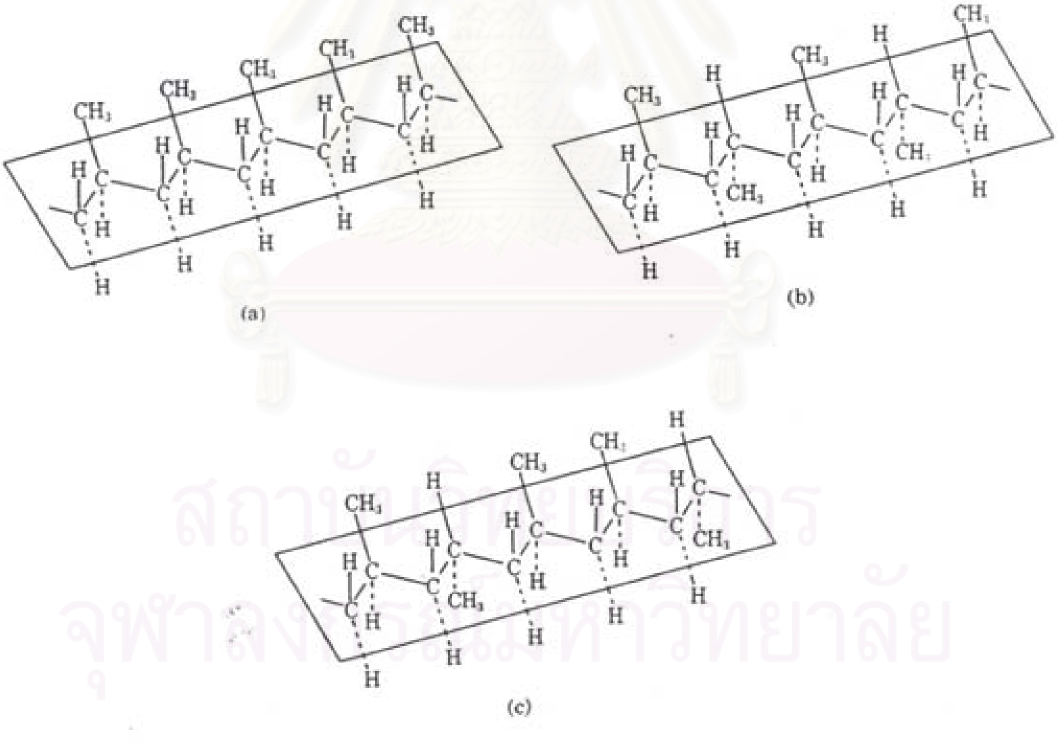


Figure 2.1 Polypropylene structures.
(a) isotactic (b) syndiotactic (c) atactic

In isotactic polypropylene (the most common commercial form), the methyl groups are all on the same side of the polymer backbone, providing a structure which readily allows crystal formation. The crystalline nature of the isotactic form gives it good solvent and heat resistances. Catalyst technology implemented during the last decade, which minimizes the formation of the non-isotactic isomers, has eliminated the need for separation of the less-valued atactic fraction, thus reducing the number of processing steps. The two processes primarily used of produce polypropylene are a vapor phase and a slurry in liquid propylene.

By comparison with high density polyethylene and low density polyethylene, polypropylene homopolymer has lower densities, significantly higher melting temperatures, and a higher flexural modulus, i.e., stiffness. These property distinctions lead to differences in end-uses. Stiffness and ease of orientation make polypropylene homopolymers suitable for numerous fiber and stretched tape applications, while their higher heat resistance makes them useful in rigid, autoclavable containers and in molded parts for appliances and autos.

Variables that have primary influence on the processing and physical properties of polypropylene homopolymer include molecular weight (normally expressed in term of flow rate), molecular weight distribution (MWD), stereospecificity, and additives. The average molecular weight ranges from about 200,000 to 600,000. The MWD is usually expressed as ratio of the weight average molecular weight of the polymer ($\overline{M}_w$) to the number average weight of the polymer ($\overline{M}_w$), or $\overline{M}_w/\overline{M}_n$. This relationship is also known as the polydispersity index. The MWD of a significant effect on its processability and end-use properties. A polypropylene composition having a broad MWD is more shear-sensitive than one with a narrow MWD. As a result, broad MWD materials process more readily in injection molding applications. MWD is a function of both the catalyst system and the polymerization process.

Polypropylene homopolymers are used in a variety of processes to produce a wide range of products. Extrusion is the largest market, with textile fibers and filaments the largest segment within the market. Polypropylene has long been a major raw material for making fibers because of its colorability, wear, and chemical resistances; and its favorable economics. Injection moulding, the next largest market for homopolymer, includes containers and closures, automotive applications, housewears, toys, and many other consumer and industrial end-uses.

2.2.3.2 Polypropylene Copolymer

Polypropylene copolymer preparation, isotactic polypropylene homopolymer is made by polymerizing propylene in the presence of Ziegler-Natta catalyst systems. The ethylene/propylene rubber fraction is either synthesized in the presence of homopolymer in a second, gas-phase reactor or is purchased beforehand and then blended with the homopolymer in the extruder. The resulting impact polypropylene copolymer is palletized and sold as such.

Impact polypropylene copolymer, one of the lightest thermoplastics, has a density less than 1, and is less expensive per pound than PET, HIPS, and ABS. Based on specific volume, the cost per cubic unit of impact polypropylene is less than these resins and PVC. Only HDPE is competitive by this measure. The effect of the elastomer is that amorphous rubber particles distributed throughout the semicrystalline homopolymeric matrix provide stress concentration point at the interface, which initiate local deformation instead of allowing cracks to propagate. So, impact polypropylene copolymer has excellent notched impact energy; izod impact strength range from 1.5 to 15 ft-lb/inch, and also excellent in Gardner impact properties at low temperatures; Gardner impact strength at $-40^{\circ}F$ range from 15 to over 300 inch-pound. Furthermore, it is highly resistant to chemicals and environmental stress cracking. The rubber fraction that lended polypropylene its impact resistance does, however, decrease stiffness and lower the heat distortion temperature of impact polypropylene relative to the homopolymer.

The chief commercial application of impact polypropylene is injection molding of articles used in automotive applications, housewears, and appliances.

The impact resistance, low density, colorability and processability of impact polypropylene make it ideal for such applications. More applications for extruded sheeting made from impact polypropylene copolymers, extruded sheets can be thermoformed into large, thick parts. Good examples are fender and trunk liners in the automotive industry. Sheet extruded from impact polypropylene also can be used in stamping processes in which small, odd-shaped parts are stamped from a large sheet. Some properties of isotactic polypropylene and polypropylene copolymer are compared in Table 2.1 [13].

Table 2.1 Some Mechanical and Thermal Properties of Commercial Polypropylenes.

Properties	Test method	Homopolymers			Copolymers	
Melt flow index	(a)	3.0	0.7	0.2	3.0	0.2
Tensile strength						
(lbf/in^2)	(b)	5000	4400	4200	4200	3700
(MPa)		30	34	29	29	25
Elongation at break (%)	(b)	350	115	175	40	240
Flexural modulus						
(x 1000 lbf/in^2)	-	190	170	160	187	150
(MPa)		1310	1170	1100	1290	1030
Brittleness temperature	ICE/ASTM					
(^{o}C)	D476	+15	0	0	-15	-20
Vicat softening point	BS 2782					
(^{o}C)		145-150	148	148	148	147
Rockwell hardness						
(R-scale)	-	95	90	90	95	88.5
Impact strength						
(ft-lbf)	(c)	10	25	34	34	42.5
(J)		13.5	34	46	46	57.5

(a) Standard polyethylene grader: load 2.16 kg at 230^{o}C.

(b) Straining rate 18 in/min.

(c) Falling weight test on 14 in diameter molded bowls at 20^{o}C.

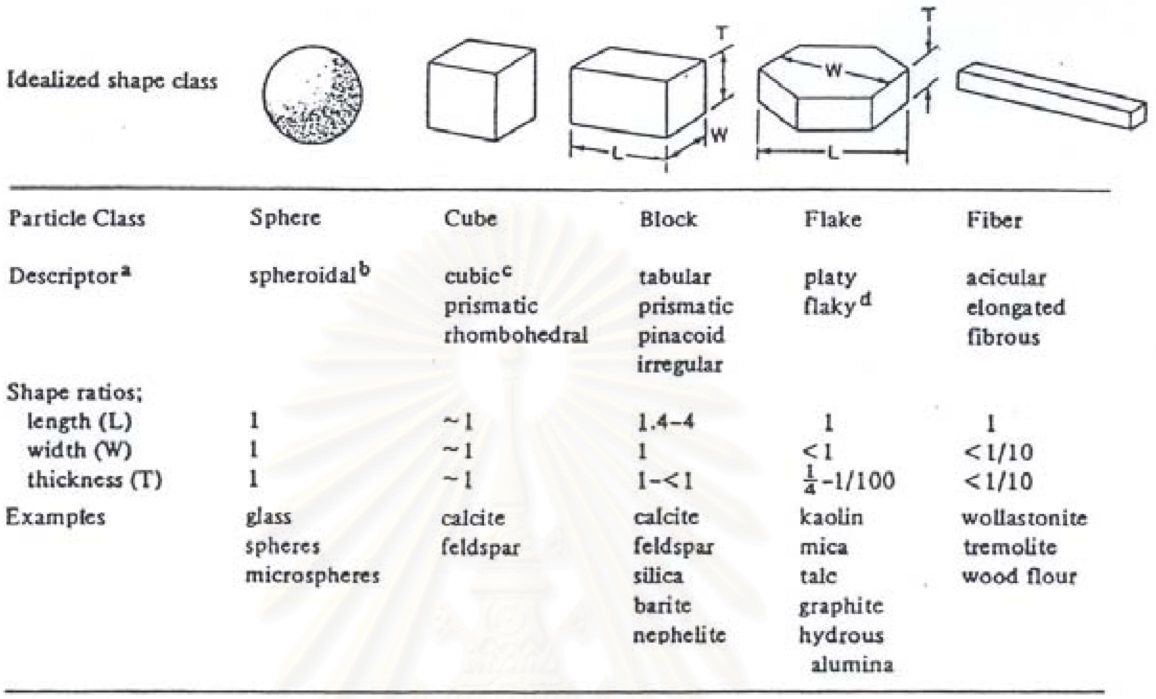
2.3 Fillers

A filler is a finely divided solid that is added to a liquid semisolid, or solid composition to modify the composition's properties and reduce its cost. Fillers are usually classified according to their source, function, composite, or morphology (see Table 2.2) [14]. However, none of these classification schemes is entirely adequate owing to overlap and ambiguity of their categories. Filler can constitute either a major or a minor part of a composition. The structure of the filler particles can range from irregular masses to precise geometrical forms such as spheres, polyhedrons, or short fiber as shown in Table 2.3 [15]. An understanding of physical properties of filler and associated functions is most important in applying filler technology. Mineral fillers represent over 80% of the filler marker primarily because of their low cost.

Table 2.2 Classification of Fillers

Method of classification	Examples
Source	Natural (mineral), synthetic
Function	Pacification, reinforcement
Composition	Carbonate, silicate, lignin
Morphology	Hollow, sphere, fiber, platelet

Table 2.3 Particle Characteristics



Idealized shape class					
Particle Class	Sphere	Cube	Block	Flake	Fiber
Descriptor[a]	spheroidal[b]	cubic[c] prismatic rhombohedral	tabular prismatic pinacoid irregular	platy flaky[d]	acicular elongated fibrous
Shape ratios;					
length (L)	1	~1	1.4–4	1	1
width (W)	1	~1	1	<1	<1/10
thickness (T)	1	~1	1–<1	$\frac{1}{4}$–1/100	<1/10
Examples	glass spheres microspheres	calcite feldspar	calcite feldspar silica barite nephelite	kaolin mica talc graphite hydrous alumina	wollastonite tremolite wood flour

[a] Preferred to particle class since this is based on relative surface area. First descriptor is preferred.

[b] In the sence that a spheroid approaches a true sphere.

[c] Generally distorted cubes; more nearly prismatic.

[d] Generally having the natural of hexagonal platelets, as illustrated.

In the plastics industry, the term filler refers to particulate materials that are added to plastic resins relatively large (over 5%) volume loadings. At present, the performance specifications for most compounded plastic products are less strict that for other filled products, such as elastomers and paints, and cost reduction is the primary objective. Hence, plastic compounders tend to compound with the objective of optimizing properties at minimum cost rather than maximizing properties at optimum cost. Table 2.4 lists typical plastic fillers and their uses [16].

Table 2.4 Typical Plastic Fillers and Their Uses

Filler	Specific Gravity	Typical compatible Resins	Uses
Alumina trihydrate	2.4	Polyesters	fire resistant filler
Carbon black	0.2-2.3	Epoxies	electrical goods
Calcium carbonate			
mineral	2.7	most resins	tile, molded goods
precipitated	2.6	most resins	pipe, putty
Clays	2.6	most resins	flooring tile
Feldspar	2.6	Thermoplastics	plastisols
Metal	2.5-11.5	Epoxies	radiation shields, solders
Mica	2.82	most resins	sheet molded goods
Polymers			
solid spheres	1.1-1.3	most resins	molded goods
hollow spheres	0.2-0.5	Thermosets	molded goods
Silica			
diatomite	2.0-2.4	Polyethylene	films
novaculite	2.65	Thermosets	electrical goods
quartz flour	2.65	Thermosets	molded goods
tripolite	2.65	Thermosets	molded goods
wet process	1.9-2.2	Thermoplastics	sheet, films
vitreous	2.18	Epoxies	electrical goods
Silicate glass			
solid spheres	2.5	most resins	molded goods
hollow spheres	0.22	Thermosets	molded goods
flakes	2.01	Thermosets	electrical goods
Talc	2.7-2.9	PVC, polyalkenes	Extruded and molded goods
Wood and shell flour	0.19-1.6	most resins	molded goods

2.3.1 Organic Fillers

Initially, these additives were of natural origin, and were abundantly available at low cost. Most of them, like wood flour, cotton, and vegetable fibers, are fibrous in structure, and are composed largely of cellulose, with lesser amounts of lignin and other compounds. However, some are not fibrous in nature, and some are of animal origin. At present, synthetic organic materials, chiefly fibers, are also being used as plastic additive, principally for reinforcement of physical properties. Like fillers and reinforcements generally, the organic material additives affect many properties of the compounds into which they are incorporated. The natural materials are generally less which they are incorporated. The natural materials are generally less expensive than the resins with which they are compounded, and this is the most an important reason for their use. However, both natural and synthetic organic additives have important functional effects, including improvement in processability and desirable modification of the final compound. Organic fillers are shown in Table 2.5. The more important specifications of the common organic fillers are generalized as shown in Table 2.6 [17].

Table 2.5 Organic Material that have been used as Fillers for Plastics.

NATURAL MATERIALS

- Wood flour
- Soft woods
  - Pine. ponderosa
  - Pine, white
  - Norway fir
  - Douglas fir
  - Spruce
  - Redwood
- Hard woods
  - Ash
  - Beech
  - Birch
  - Maple
  - Oak
- Bark, fir
- Sawdust, shavings, chips
- Sawdust, rubber-coated

- Vegetable fibers
  - Hemp
  - Coconut (coir fiber)
  - Jute
  - Ramie
  - Sisal

- Shell fiber
  - Almond shell
  - Apricot pit shell
  - Brazil nut shell
  - Candle nut shell
  - Coconut nut shell
  - Filbert shell
  - Peanut shell
  - Pecan shell
  - Walnut shell

- Cotton fibers
  - Cotton flock
  - Cotton fabric, chopped
  - Cotton cord, chopped
  - Cotton linters
  - Cotton seed hulls
  - Cotton seed fibers
  - Cellulose fibers

- Miscellaneous materials
  - Beer hops, spent
  - Coal, anthracite fines
  - Coca bean material
  - Coke
  - Cork, granulated
  - Corn, cobs
  - Citrus pulp, dried
  - Flax shives
  - Furfural process residues
  - Hemp hurds
  - Keratin
  - Chicken feathers
  - Cattle hooves
  - Hog bristles
  - Leather
  - Milkweed products
  - Peat moss
  - Soybean meal
  - Starch, corn, potato, rice
  - Wheat straw
  - Wool fibers

Table 2.5 (continued) Organic Material that have been used as Fillers for Plastics.

SYNTHETIC MATERIALS
Regenerated cellulose
Rayon fabric
Cellophane, finely cut
Polyacrylonitrile fibers
Polyamide, aliphatic (nylon) fibers
Polyamide, aromatic (aramid) fibers
Polyester fibers
Polytetrafluoroethylene fibers
Polyvinyl alcohol fibers
Rubber dust, hard
Rubber dust, vulcanized

Table 2.6 Properties of Common Organic Fillers

Detail	Wood flour	Cotton flock, Chopped cotton fabric	Cellulose flock	Sisal flock
Ash content	0.3%	0.5-1.5%	0.15%	0.3% max.
Acetone sol.	8.5% max.	2.0-3.0%	-	-
Oil absorption (cm^3/10 grams)	15-30	20-30	-	-
Ether extract	5.0% max.	2.0% max.	0.24%	0.5-1.5%
%Insolubles	0.0%	1.5-2.5%	0.0%	0.0%
Color	softwood (light cream) hardwood (light tan)	bleached (white colored)	bleached (white) unbleached (tan)	Light tan
Appearance	fibrous	fibrous/macerated	fibrous	fibrous
Moisture	5.0-8.0%	5.0-8.0%	5.0-8.0%	12.0% max.
Bulk density (ml/50 grams)	softwood (190-260)	180-300	135-400	140-330

Table 2.6 (continued) Properties of Common Organic Fillers

Detail	**Wood flour**	**Cotton flock, Chopped cotton fabric**	**Cellulose flock**	**Sisal flock**
	hardwood (160-200)			
Weight/cu ft	softwood (6-10 lb) hardwood (11-16 lb)	7-11 lb	5-18 lb	4-16 lb
Particle size	5-140 mesh	10-200 mesh	10-200 mesh (10-100 mesh) Precision cut. (1/32-1 inch)	Random cut

2.3.2 Wood Flour

Wood flour is a finely ground wood, dried wood product, fibrous in structure, that acts as reinforcing material for plastics. It is made mostly from softwood, chiefly pine and spruce, but hardwood maple or ash flour are used where no wood resin content is desired. Woods containing essential oils, such as cedar, are not suitable. Wood flour is made from sawdust, chip and shavings by grinding in a buhrstone mill, and has the appearance of wheat flour. Wood flour is composed largely of cellulose in content. Cellulose structure can be shown below.

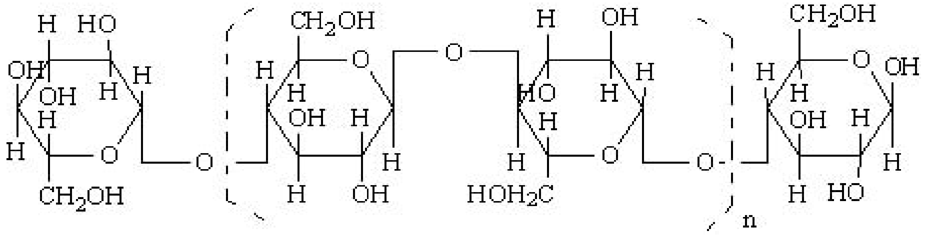


Figure 2.3 Structure of cellulose.

Compared to inorganic fillers, cellulose fillers offer many advantages [13-15]

a) Lower cost.
b) Little damage during processing.
c) Lower abrasion of processing equipment.
d) Thermoformability into shaped products.
e) No health hazard.
f) Lower density.
g) Abundant renewable resource.
h) Biodegradable in nature.

Particle sizes commonly used for plastics fillers are 40, 60 and 80 mesh, with sizes as fine as 140 mesh available. Wood flour may absorb some resins or gums when mixed with some plastics, and mineral fillers may also be combined to vary the properties of the molded product. Wood flour is already being employed in thermoplastic on an industrial scale. Its use results in the following advantages: cheap filler; improved shrinkage behavior; increase in modulus of elasticity and stiffness, fall less rapidly at elevated temperatures; and tensile strength and tensile stress at break are scarcely affected.

2.3.3 Natural Fibers Fillers Polymer Composites

In view of the amount of natural fibers, natural fibers polymer composites are attractive ways to improve the properties of polymer over 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 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.

2.4 Modification of Natural Fillers

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.

2.4.1 Physical Methods for Surface Modification of Natural Fibers

Reinforcing fibers can be modified by physical methods, such as stretching, calendaring, 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.

2.4.2 Chemical Methods for Surface Modification of Natural Fibers

Chemical treatments such as dewaxing (defatting), dilignification, bleaching, acetylation, and esterification 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 [17].

Esterification like simple alcohols, the hydroxyl groups of cellulose can be esterified by reaction with acids or other acylation agents.

Chemical modification 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. 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 [17].

Table 2.3 Chemical Treatments Used for Modification of Natural Fibers [17]

Fiber	**Chemical Treatment**	**Coupling Agent**
Wood flour	Succinic acid, styrene, urea-formaldehyde, *m*-phynylene bismalemide, acetic anhydride, maleic anhydride, itaconic anhydride, polyisocyanate, linoleic acid, oxalic acid,	Maleated PP, Acrylic acid Graft PP, Silane, Zirconate, Titanate
Jute	Phenol-formaldehyde, malamine-formaldehyde, Cardonol-formaldehyde	
Sisal	NaOH, isocyanate, sodium alginate, *n*-substitutec mathacrylamide	
Pineapple	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 an another method of the surface treatment that can be used for lowering the interfacial tension and strees transfer across the inter face, 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.

2.5 Cellulose Filled Polypropylene

Cellulose materials are good candidates to use as fillers in polymers, especially with their recent importance in recycling. There are many different types of materials available, such as wood flour, recycled newspaper, nut shells, and starch. These materials have several advantages, including low cost, low density, low abrasiveness, and they are a renewable resource. However, they do have a number of disadvantages, such as low thermal stability, high moisture adsorption, and poor interfacial adhesion. Despite these problems, there are a number of products available in the marketplace. One of the most visible is plastic lumber. Most plastic lumber is made using polyethylene as the base resin and contains up to 50% wood. Much of the time, both resin and wood feedstocks come from recycled sourced.

2.6 Plasticizers

Plasticizers are added to plastics to improve flow and, therefore, processability and to reduce the brittleness of the product. This is achieved by lowering the glass transition temperature below; room temperature, thus achieving a change in properties from those of a hard, brittle, glasslike solid to those of a soft, flexible tough material. An example is the plasticization of poly (vinyl chloride) and vinyl chloride-acetate copolymers. Similar changes is properties can, of course, be brought about by altering the molecular structure of the polymer (e.g., by copolymerization, sometimes called internal plasticization)

The basic requirements which must be met by a plasticizer are compatibility and permanence. The plasticizer must be miscible with the polymer. This implies a similarity in the intermolecular forces active in the two components, and explains why compatibility is difficult to achieve with a non vapor pressure and a low diffusion rate of the plasticizer within the polymer, both of which are obtained by the use of high-molecular-weight plasticizers.

The efficiency of the plasticizer in bringing about the desired changes in properties is important in determining the proportion in which the plasticizer must be added to the resin. Plasticizer efficiency may be evaluated, by a number of different semiempirical tests. Some of these measure the amount of nonsolvent needed to cause phase separation when added to polymer plasticizer solutions (dilution ratio), the viscosity of dilute solutions of the polymer in the plasticizer, polymer-solvent interaction constants measured on these solutions, the depression of the glass transition temperature, the melt viscosity of the plasticized polymer, the electrical or mechanical properties of the plasticized polymer, or the; molecular size and shape or viscosity of the plasticizer itself. Not all these needless to say, rate plasticizer candidates in the same order. The selection of a particular plasticizer still depends to a large extent upon empirical results rather than theoretical predictions.

The following types of plasticizers are in common use:

1 Phthalate esters, accounting for over half of the total volume of plasticizers used.
2 Phosphate esters, chiefly tricresyl phosphate, valued primarily for their flameproofing characteristics.
3 Adipates, azelates, oleates, and sebacates, used chiefly in vinyl resins for improving low-temperature flexibility.
4 Epoxy plasticizers, produced by reacting hydrogen peroxide with unsaturated vegetable oils and fatty acids.
5 Fatty acid esters from natural sources, used primarily as extenders to reduce cost (secondary plasticizers)
6 Glycol derivatives, employed mainly as lubricants and mold-release agents, and as plasticizers for poly (vinyl alcohol)
7 Sulfonamides, used to plasticize cellulose esters, phenolic and amino
8 Hydrocarbons and hydrocarbon derivative, serving assecondary plasticizers. [18-20].

2.7 Polymer Processing

2.7.1 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 subject 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 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 can be folded to the side. By cutting and folding many times from both sides, good distribution and dispersion are achieved [18,23].

2.7.2 Compression Molding

Molding processes are those in which a finely divided plastic is forced by the application of heat and pressure to flow into, fill and conform to the shape of a cavity (mold). One of the oldest methods of polymer processing is compression molding. Here the polymer is put between stationary and movable members of a mold. The mold is closed and heat and pressure are applied so that the material becomes plastic, flows to fill the mold, and becomes a homogeneous mass. The necessary pressure and temperature vary considerably depending upon the thermal and rheological properties of the polymer. For a typical compression-molding material they may be near $150^{o}C$ and 1000-3000 psi. A slight excess of material is usually placed in the mold to insure its being completely filled. The rest of the polymer is squeezed out between the mating surfaces of the mold in a thin, a easily removed film known as flash.

If a thermoplastic material is being molded, the mold is cooled, the pressure released, and the molded article removed. If a thermosetting material is used, the mold need not be cooled at the end of the molding operation or cycle, as the polymer will have set up and can no longer flow or distort [23-24].

2.8 Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM) is a microscope that uses electrons rather than light to form an image. There are many advantages to using the SEM instead of a light microscope.

The SEM has a large depth of field, which allows a large amount of the sample to be in focus at one time. The SEM also produces images of high resolution, which means that closely spaced features can be examined at a high magnification. Preparation of the samples is relatively easy since most SEM on require the sample to be conductive. The combination of higher magnification, larger depth of focus, greater resolution and ease of sample observation makes the SEM one of the most heavily used instruments in research areas today.

A beam of electrons is generated in the electron gun, located at the top of the column, which is pictured to the left. This beam is attracted through the anode. Condensed by a condenser lens, and focused as a very tine point on the sample by the objective lens. The scan coils are energized (by varying the voltage produced by the scan generator) and create a magnetic field which deflects the beam back and forth in a controlled pattern. The varying voltage is also applied to the coils around the neck of the Cathode-ray tube (CRT) which produces a pattern of light deflected back and forth on the surface of the CRT. The pattern of deflection of the electron beam is the same as the pattern of deflection of the spot of light on the CRT.

The electron beam hits the sample producing secondary electron from the sample. These electrons are collected by a secondary detector of a backscatter detector converted to a voltage and amplified. The amplified voltage is applied to the grid of the CRT and causes the intensity of the spot of light to change. The image consists of thousands of spots of varying intensity on the face of a CRT the correspond to the topography of the sample.

2.8.1 Specimen Preparation

Three requirements for preparing samples for a regular SEM

1) Remove all water, solvents, of other materials that could vaporize while in the vacuum.

2) Firmly mount all the samples.

3) Non-metallic samples, such as bugs, plants, fingernails, and ceramics, should be coated so they are electrically conductive. Metallic sample can be placed directly into the SEM [21].

2.9 Literature Review

The use of cellulose and lignocellulose composites appears to gain on importance, at least, judging from the increasing number of research works in this area. The applications of such materials range from simple filling to more elabolate structures like laminates and chemically modified system. Despite the large number of literature references, systematic studies of the various aspects of this area appear to be relatively rare. This is also the case with cellulose and various types of lignocellulosic materials used as fillers for thermoplastics. In this literature survey, the work of polymer filled with natural fillers and reinforcements is summarized as follows:

In 1995 Thiebaud and Borredon [25] studied a method for wood esterification using fatty-acid chlorides in the absence of organic solvents. The experimental conditions being optimal (nitrogen flow rate, temperature and reaction time, quantity of fatty-acid chloride), there was an increase in weight of 87% and a 60% ester content for the sample esterified with octanoyl chloride. Improvement in the thermoplastic properties of wood following esterification was demonstrated.

In 1995 Sagar and Merrill [26] studied the properties of starch esters for their possible application as environmentally degradable thermoplastics. The rheological, thermal, and mechanical properties of a series of fatty-acid esters of high-amylose (as well as the effect of adding plasticizer on some selected properties). The ester group acts like an internal plasticizer, with an increase in the size of the fatty-acid chain, resulting in greater internal plasticization. This is reflected in the rheological and thermal measurement as well as in the mechanical properties. Overall, larger ester groups and the addition of external plasticizer make these starch-based materials more processable and more ductile. However, comparing their properties and cost to commodity thermoplastics leads us to believe that their commercial applications are likely to be limited, at least in the near future.

In 1997 Thiebaud et al. [27] studied a new esterification method using wood sawdust and fatty-acid chlorides. The esterified wood materials showed high hydrophobicity properties which increased with using longer fatty-acid chlorides. The thermalstability of wood was improved after chemical modification.

In 1997 Thieaud et al. [28] studied properties of fatty-acid esters of starch, starch octanoates OCST1.8 and OCST2.7 with degrees of substitution (d.s) of 1.8 and 2.7, respectively, and dodecanoate DODST2.7 (d.s = 2.7), by esterification of native starch with fatty acid chlorides. These starch esters were mixed with low density polyethylene (LDPE). Water and moisture absorption, thermal and mechanical properties, and biodegradation were investigated as a function of blend composites. The DODST2.7/LDPE blends showed, in general, better thermal stability and higher elongation, but lower tensile strength and water absorption, than did corresponding OCST/LDPE blends. The addition of starch esters to LDPE led to a very slow rate of biodegradation of these blends.

In 1999 Aburto et al. [29] studied a series of starch and amylose esters with different degrees of substitution and side-chain length. The esters were prepared by acylation of the polysaccharide with the appropriate acid chloride, such as octanoic, dodecanoic, and octadecanic. After preparation, the resulting esters were characterized by elemental analysis, ^{1}H nuclear magnetic resonance (^{1}H-NMR), fourier transform infrared (FTIR), differential scanning (DSC), thermogravimetric analysis (TGA), contact angle, and water uptake measurements. Their mechanical properties and, in particular, the tensile strength and elongation at break depend on the side-chain length. The extent of their biodegradability, after exposure to activated sludge, was assessed by weight loss measurements and scanning electron microscopy (SEM). It was found that these new materials biodegradable, and the biodegradation rate decreases with increasing degree of esterification.

In 2000 Wu et al. [30] studied the effect of fiber surface pretreatment on the interfacial strength and mechanical properties of wood fiber-polypropylene (WF/PP) composites. The results demonstrate that fiber surface conditions significantly influence the fiber-matrix interfacial bond, which, in turn determines the mechanical properties of the composites. The WF/PP composite containing fibers pretreated with an acid-silane aqueous solution exhibits the highest tensile properties among the materials studied. This observation was a direct result of the strong interfacial caused by the acid/water condition used in the fiber pretreatment. Evidence from coupling chemistry, rheological and electron microscopic studied support the above conclusion. When SEBS-g-MA copolymer was used, a synergistic toughening effect between the wood fiber and the copolymer was observed. The V-notch Charpy impact strength of the WF/PP composite. The synergistic toughening mechanisms were discussed with respect to the interfacial bond strength, fiber-matrix debonding, and matrix plastic deformation.

In 2002 Basu et al. [31] studied properties of amylose (AM) and/or dodecanoyl ester of amylose (DODAM), and their blend with polypropylene (PP). Biodegradability increased with increases in AM/DODAM content. It was found to be dependent on DODAM content and was at a maximum in blends containing 40% AM+DODAM. Blends with no DODAM or 2.5% DODAM showed almost no adherence of the phases. Dispersion of AM improved in blends with 5% DODAM, and it showed satisfactory adherence to PP also. The tensile strength, elongation at break, and Izod impact strength decreased with increasing AM content. However, in blends with both AM and DODAM, all these properties, especially the elongation at break, showed improvements. The same trend was observed for melt flow index (MFI).

In 2003 Nunez et al [2] studied the mechanical performance of different wood flour/polypropylene (PP) composites with interface modifications. Wood flour was incorporated into the matrix after esterification with maleic anhydride (MAN) or without any modification but with the addition of a compatibilizing agent [maleic anhydride-polypropylene copolymer (PPMAN)] to modify the polymer-filler interaction. Composites were prepared by injection molding with different concentrations of wood flour. Mechanical properties improved either by the wood flour chemical modification or by the use of PPMAN. However, both compatibilization methods were successful in improving the dispersion of the wood flour in the PP matrix. Creep behavior of composite samples was improved by the addition of PPMAN, whereas the composites prepared from MAN-treated wood flour showed larger deformations than composites made with untreated particles.

In 2004 Hritov et al. [32] studied the effect of grafting level of maleic anhydride (MA) in the maleated polypropylene (PPMA) on the fracture, deformation mechanisms, and mechanical properties of polypropylene (PP) wood flour composites. Tensile strength, elongation at break, and impact strength are noticeably improved with addition of interfacial modifiers as maximum values of the examined mechanical properties were detected when concentration of MA in the compatibilizer was 1 wt%. To explore the microstructure and deformation mechanisms, scanning electron microscopy was employed. It was found that low concentrations of MA up to 1 wt% led to the creation of a thin and irregular polymer layer assisted formation of fibrillated plastic deformation zone around the wood particle, while the bulk PP matrix experienced voiding and brittle fracture. Higher concentrations of MA fetch to stronger interaction between PP and wood flour, the reason for brittle fracture and reduced ductility of the matrix.

CHAPTER III

EXPERIMENTS

3.1 Materials, Equipments, Glasswares, and Apparatus

3.1.1 Materials

Polypropylene (POLENE 2300 NC) supplied by Thai Petrochemical Industry Public Co., Ltd. Its melt flow index and density are 2.16 g/10 min and 0.910 g/cm^3, respectively.

Sawdust were used as a filler, and provided by Chareonpan Wood. Ltd., Part.

Methanol, commercial grade from ACS, was purified by distillation at atmospheric pressure before use.

Ethanol, commercial grade from ACS, was purified by distillation at atmospheric pressure before use.

Hexane, commercial grade from ACS, was purified by distillation at atmospheric pressure before use.

Other analytical grade chemicals, as shown in Table 3.1 were used without further purification.

Table 3.1 Chemicals

Chemicals	Source
Butyryl chloride	Fluka, Buchs, Switzerland
Dodecanoyl chloride (lauroyl chloride)	Fluka, Buchs, Switzerland
Stearoyl chloride	Fluka, Buchs, Switzerland
Toluene	Merck, Darmstadt, Germany
Hydrochloric acid, HCl	BDH, Poole, England
Sodium hydroxide, NaOH	Merck, Hohenbrunn, Germany

3.1.2 Glasswares

Three-necked round bottom flask, condenser, mechanical stirrer, hot plate thermometer, magnetic stirrer, erlenmayer flask, desiccator, reduced pressure filtering system, 50, 60, 100, and 120-mesh aluminium screen, analytical balance, oven, and general laboratory glasswares and equipments.

3.1.3 Apparatus and 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.

1) Two roll mill: Model LRM 150, Lab Tech. Engineering Co., Ltd.
2) Compression molding: Model LP 20, Lab Tech. Engineering Co., Ltd.
3) Universal testing machine: Model LLOYD LR 5 K
4) Impact testing machine: Model Gotech, Gt-7045
5) Hardness tester: Model Indentec, 4150 AK
6) Scanning electron microscope: Model JEOL–JSM–6400
7) Test sieve: Model Retsch
8) Drying oven: Model Sanyo
9) Fourier transform infrared spectrometer: Model Nicolot Impact 410
10) Differential Scanning Calorimeter: Model METTLER TOLEDO DSC 822

3.2 Experimental

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

3.2.1 Preparation of Sawdust

Sawdust of *Shorea obtuse* wall was obtained from the wood manufacture. The coarse sawdust that was further sieved into required particle size at smaller than 120 mesh (140 μm) was used in all experiments. The particle size of sawdust was determined by test sieve. In making such an analysis, a set of standard screens was arranged serially in a stack, with the smallest mesh (120 mesh) at the bottom and larger mesh (100, 60, and 50 mesh) on the top. Weighed sawdust was placed on the top screen and the stack was shaken mechanically for about 15 min. The particle retained on each screen were removed and weighed. After the preparation, the sawdust was dried in an oven at 105°C overnight prior to use. The dried sawdust was then divided into two sets. The first set was blended with polypropylene alone and the second set of sawdust was modified by an esterification reaction, as described in section 3.2.2, before blending with polypropylene.

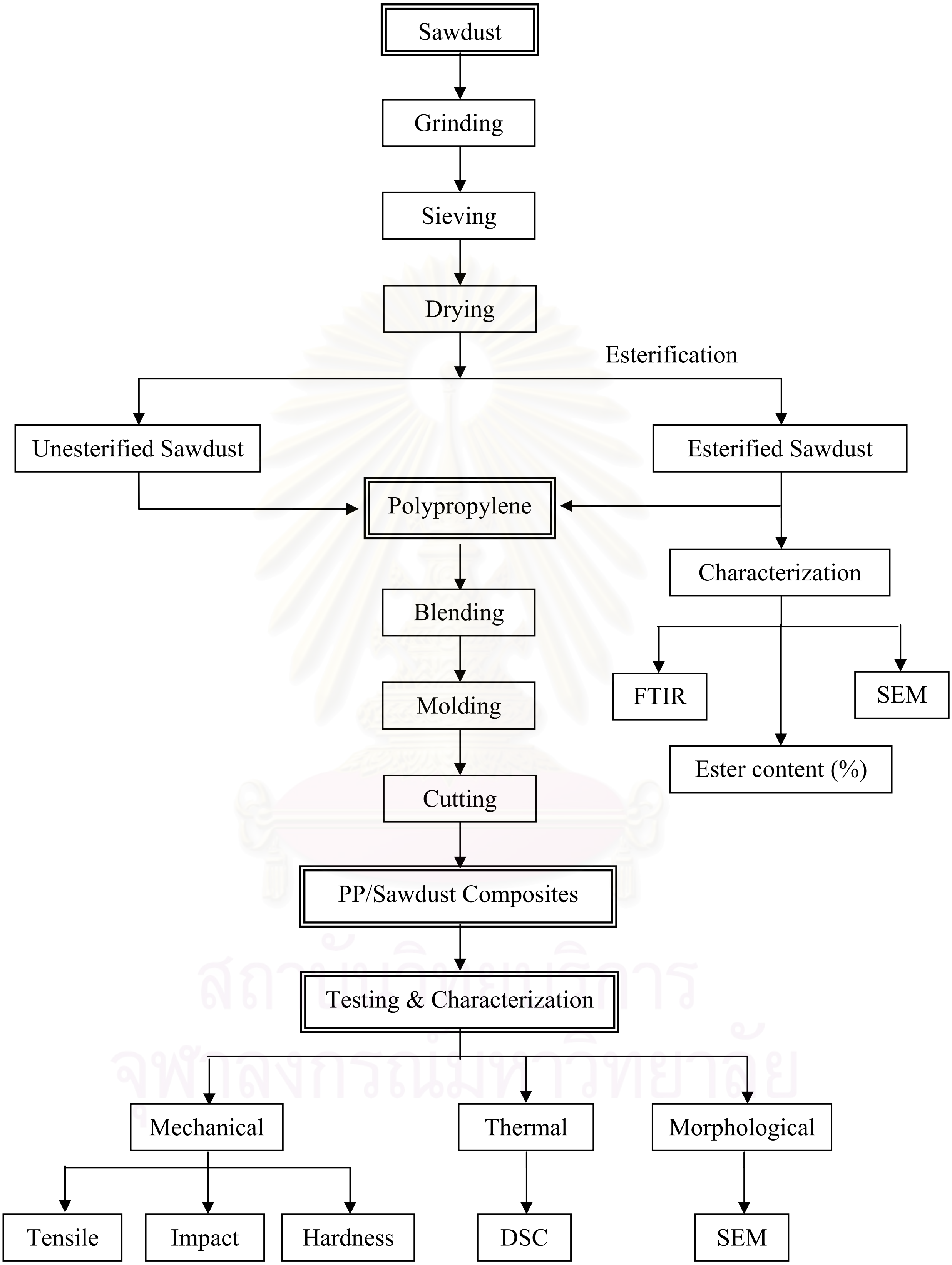


Figure 3.1 The flow chart of the entire procedure process.

3.2.2 Esterification of Sawdust

This method was adopted from Thiebaud's method [23]. The procedure of esterification was as follows. Firstly, the sawdust was dried overnight in an oven at 105°C to remove its moisture. The dried sawdust (20 g) was placed in a three–necked flask, equipped with a condenser and a argon-gas bubbling system. In order to trap the hydrogen chloride formed, a wash bottle containing an aqueous sodium hydroxide solution was placed at the outlet of the condenser. Subsequently, 100 ml of toluene as solvent, catalytic amount of triethylamine and the required amount of acid chlorides were added. By changing the amount of chloride, it was possible to prepare esters with different ester content (%). The experimental conditions for the esterification reaction as shown in Table 3.2. The reaction was heated at reflux temperature for 4 hours. Upon completion of the reaction, the esterified sawdust was filtered and washed with hexane (100 ml) and then soxhlet-extracted using methanol for 6 hours in order to remove the excess of acid chloride and by-products. Finally, the esterified sawdust was dried at 105°C for 24 hours.

Table 3.2 Conditions for Sawdust Esterification

Batch	Samples	Alkyl chain	Amount of acid chloride	Solvents
1	Butyrated sawdust	C_4	0.05 mol	Non-solvent
2				Dichloromethane
3				Toluene
4	Dodecanoated sawdust	C_{12}	0.05 mol	Non-solvent
5				Dichloromethane
6				Toluene
7	Stearoated sawdust	C_{18}	0.05 mol	Non-solvent
8				Dichloromethane
9				Toluene
10	Butyrated sawdust	C_4	0.02 mol	Toluene
11			0.05 mol	
12			0.075 mol	
13	Butyrated sawdust	C_4	0.05 mol	Toluene
14	Dodecanoated sawdust	C_{12}	0.075 mol	Toluene
15	Stearoated sawdust	C_{18}	0.12 mol	Toluene

3.2.3 Effect of Solvents on the Esterification Reaction

3.2.3.1 The same experiment procedure as described in Section 3.2.2 was carried out, except for the mol of acid chloride was fixed at 0.05 mol, but the solvent changed from toluene to dichloromethane.

3.2.3.2 The same experiment procedure as described in Section 3.2.3.1 has been done, without solvents.

3.2.4 Preparation of the Polypropylene/Sawdust Composites.

The sawdust was prepared into four sets including, unesterified sawdust, butyrated sawdust, dodecanoated sawdust and stearoated sawdust for esterification reaction prior to mixed with polypropylene. The blending of polypropylene and sawdust were homogenized on two roll mill for 10 min. The temperatures of the mixing rolls were maintained constantly at 170°C for the front roll and 175°C for the back roll. Sawdust content at 10, 20, 30, 40, and 50% by weight were prepared by adding polypropylene after melting and the mixing for 10 min. During the mixing period, a brass scraping knife and a sawdust–scrapper were necessary for manual mixing so as to increase good homogeneity in all directions. Finally, the mixture was removed out of two roll mill and folded to a square shape. All compositions tabulated in Table 3.3 were prepared.

Each sawdust–polypropylene mixture was placed in a mold whose dimension was 150 mm x 160 mm x 3 mm. Then, it was preheated on the heating part for about 10 min. Compression molding of the composite was done at 190°C. The molding time was 11 min and the pressure used was 160 kg/cm^2. Finally, the compressed sheet was transferred to the cooling part and cooled for 11 min with the constant pressure at 160 kg/cm^2 during the process. The sheet composite was cut to the standard specimens for mechanical property tests according to the ASTM test method, including ASTM D 638, ASTM D256, and ASTM D 785.

Table 3.3 Compositions of the Composites

Batch	PP (g)	Unesterified sawdust (g)	Esterified sawdust (g)			Ester content (%)
			C_4	C_{12}	C_{18}	
1	100	-	-	-	-	-
2	90	10	-	-	-	-
3	80	20	-	-	-	-
4	70	30	-	-	-	-
5	60	40	-	-	-	-
6	50	50	-	-	-	-
7	90	-	10	-	-	50
8	80	-	20	-	-	50
9	70	-	30	-	-	50
10	60	-	40	-	-	50
11	50	-	50	-	-	50
12	90	-	-	10	-	50
13	80	-	-	20	-	50
14	70	-	-	30	-	50
15	60	-	-	40	-	50
16	50	-	-	50	-	50
17	90	-	-	-	10	50
18	80	-	-	-	20	50
19	70	-	-	-	30	50
20	60	-	-	-	40	50
21	50	-	-	-	50	50
22	80	-	20	-	-	0
23	80	-	20	-	-	20
24	80	-	20	-	-	80

3.3 Characterization of the Esterified Sawdust.

3.3.1 Determination of the Ester Content (%) [26]

3.3.1.1 A mixture of 1 g of esterified sawdust (accurately weighed), 2 g of sodium hydroxide and 100 ml of ethanol were added into the round bottom flask. The reaction mixture was stirred at 75°C for 3 hours and then left to cool down to room temperature. The excess sodium hydroxide was titrated with a 0.5 M hydrochloric acid solution with phenolphthalein as the indicator.

3.3.1.2 The same experiment procedure as described in Section 3.3.1.1 was carried out by replacing the esterified sawdust with sawdust as a background.

The ester content (%) was determined as follows:

Ester content (%)

$$=\{[(V_{NaOH} \times C_{NaOH}) - (V_{HCl} \times C_{HCl})] - [(V_{NB} \times C_{NB}) - (V_{HB} \times C_{HB})]\} \times \frac{M}{10 \times W}$$

V_{NaOH} : Volume of sodium hydroxide solution added to sample (ml).
V_{NB} : Volume of sodium hydroxide solution added to background (ml).
C_{NaOH} : Concentration of sodium hydroxide solution added to sample (M).
C_{NB} : Concentration of sodium hydroxide solution added to background (M).
V_{HCl} : Volume of hydrochloric acid solution added to sample
at the end point of titration (ml).
V_{HB} : Volume of hydrochloric acid solution added to background (ml).
at the end point of titration (ml).
C_{HCl} : Concentration of hydrochloric acid solution added to sample (M).
C_{HB} : Concentration of hydrochloric acid solution added to background (M).
M : Molar mass of grafted acyl radical (g/mol).
W : Weight of sample (g).

3.3.2 Identification of Function Groups of the Surface-Esterified Sawdust

The function groups of the unesterified and esterified sawdust were investigated by Fourier Transform Infrared Spectroscopy (FTIR), Nicolet Impact 410, using KBr pellet. Each spectrum was recorded at a resolution of 4 cm^{-1} , with total of 32 scans and a frequency range of 4000–400 cm^{-1}.

3.3.3 Determination of Surface Morphology of the Surface-Esterified Sawdust

Scanning Electron Microscope (SEM), JEOL-JSM-6400 was used to study the sawdust surface. The surface of the sample was coated with gold before being scanned.

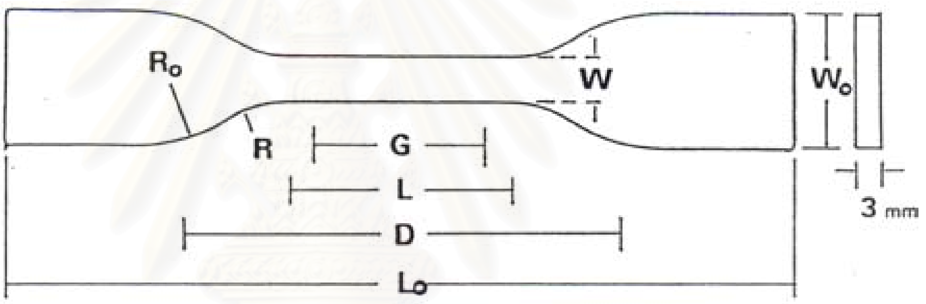
3.4 Characterization of Polypropylene/Sawdust Composites.

3.4.1 Mechanical Properties

Mechanical properties of the composites were measured by following the ASTM test method:

*3.4.1.1 ASTM D638-02***:** standard test method for tensile properties.

The test specimens (type IV) dimension was presented in Figure 3.2.



W : 6 mm Wo : 19 mm G : 25 mm R : 14 mm

L : 33 mm Lo : 115 mm D : 65 mm Ro : 25 mm

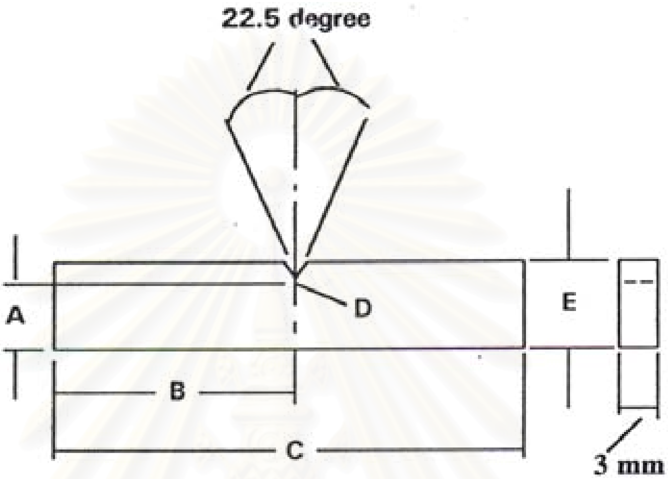
Figure 3.2 Schematic of tensile test specimen (type IV)

The tensile testing condition were as follows:

Temperature: 25°C
Relative humidity: 60%
Speed of testing: 500 mm/min
Distance between grips: 64 mm
Gage length: 25 mm

3.4.1.2 ASTM D256-02: standard test method for impact resistance.

The test specimens dimension for Charpy impact test is show in Figure 3.3.



A : 10.16±0.05 mm

B : 31.8±1.0 mm

C : 12.70±0.15 mm

C : 63.50±2.0 mm

D : 0.25±0.05 mm

Figure 3.3 Schematic of charpy impact type test specimen.

The machine parameters and testing conditions of the impact test were listed below:

Temperature:	25°C
Relative humidity:	60%
Pendulum capacity:	11.0 J
Depth of specimen:	10.16 mm

3.4.1.3 ASTM 785-03: standard test method for Rockwell hardness (R scale).

For the assignment of the specimen for hardness testing, the test specimen should be of at least 6 mm in thickness. The surface of the specimen should be flat and parallel over a sufficient area to permit the presser foot to contact the specimen. For materials having hardness values above 50 Rockwell hardness (R scale), the thickness of the specimen should be of at least 6 mm and measurements should not be made closer than 6 mm to any edge.

According to the thickness, the test specimen in this experiment were composed of plied pieces to obtain the necessary thickness. The Rockwell hardness was used in this experiment. The condition in this testing were shown as follows:

Temperature: 25°C
Relative humidity: 50 %
Number of pieces plied: 2 pieces
Relative humidity: 60%

All of the properties measured, at least five hardness were tested on materials to obtain a reliable average and standard deviation.

3.4.2 Morphological Study

Scanning Electron Microscope (SEM), JEOL-JSM-6400 at acceleration voltage of 15 KV was used to study the tensile fractured surface of the composites in order to understand the failure mechanism of the composites in the presence of sawdust. 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.

3.4.3 Thermal Properties

For Differential Scanning Calorimeter (DSC), METTLER TOLEDO DSC 822 measurements, samples were placed in sealed aluminum cells, using a quantity of ~2 mg for each sample. The same temperature history was applied to all samples: first heating from -20°C to 300°C at a heating rate of 10°C/min under nitrogen atmosphere, followed by quenching the sample to -20°C to remove any previous thermal history, and finally heating to 300°C at a scanning rate of 10°C/min. From these thermograms the melting temperature (T_m) and the glass transition temperature (T_g) were determined.

CHAPTER IV

RESULTS AND DISCUSSION

4.1 Preparation of Surface-Esterified Sawdusts

4.1.1 Effect of Solvents on the Ester Content (%)

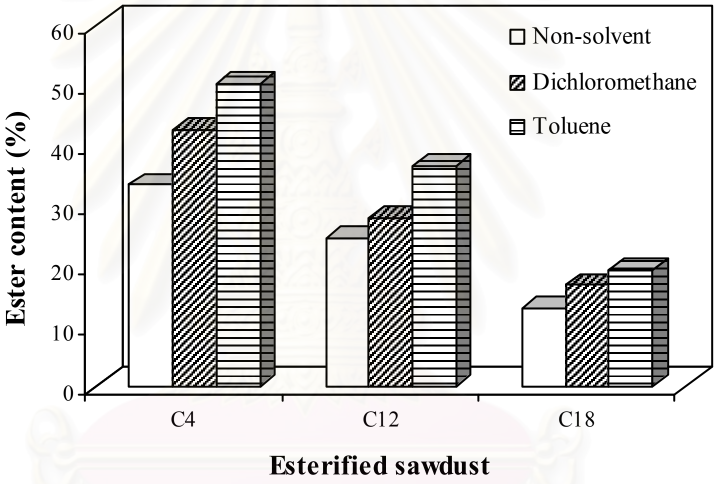
Surface of *Shorea obtuse* wall sawdust was esterified with three acid chloride, including butyryl chloride, dodecanoyl chloride and stearoyl chloride in the presence of solvents and in absence of solvents followed by determining the ester content of surface-esterified sawdust. The results of the ester content of sawdust treated with 0.05 mole of acid chloride were summarized in Table 4.1 and Figure 4.1. It was found that the reaction in the presence of toluene gave the highest ester content.

As can be seen in Table 4.1 and Figure 4.1, the ester content (%) of the surface-esterified sawdust was increased from non-solvent, dichloromethane and toluene, respectively. In addition, the organic solvent used, it was simpler to use and more economic. Moreover, it facilitates the treatment of the reaction medium to cover the products.

Table 4.1 Effect of Solvents on the Ester Content (%)

Sample	Ester content (%)		
	Non-solvent	Dichloromethane	Toluene
Butyrated sawdust	33.56 (3.54)	42.74 (1.47)	50.38 (1.86)
Dodecanoated sawdust	24.63 (3.43)	28.05 (0.55)	36.71 (4.35)
Stearoated sawdust	12.88 (0.97)	16.80 (2.83)	19.39 (2.55)

Values in parentheses are standard deviations (S.D).



C_4 : Butyrated sawdust C_{12} : Dodecanoated sawdust C_{18} : Stearoated sawdust

Figure 4.1 Effect of solvents on the ester content (%).

The ester content (%) of the surface-esterified sawdust : butyrated sawdust with ester content (%) was 50.38%, dodecanoated sawdust with ester content (%) was 36.71% and stearoated sawdust ester content (%) was 19.39%.

In order to study the surface chemistry, FTIR was used to determine the chemical structure and functional groups of sawdust and surface-esterified sawdusts with butyryl chloride, dodecanoyl chloride and stearoyl chloride. The results were illusteated in Figures 4.3-4.4.

In the spectrum of sawdust, it showed the broad absorption of O-H stretching vibration at 3000-3600 cm^{-1}, a C=C stretching vibration at 1635 cm^{-1} and the C-O stretching vibration at 1020-1190 cm^{-1}.

Because the esterification reaction on hydroxyl groups of cellulose with acid chlorides (as shown in Figure 4.2), the hydroxyl peak intensity of the surface-esterified sawdusts were decreased and the strong carbonyl stretching vibration appeared at ~1746 cm^{-1}. Additionally higher absorption of C-H stretching vibration of the methyl/methylene groups of long-chain hydrocarbon radical observed in the esterified sawdust at 2800-2950 cm^{-1} and the absorption increased also with increasing carbon chain length of the acyl radical. Thus the intensity of the stearoated sawdust at 2800-2950 cm^{-1} region was greatest, compared to the dodecaonated and butyrated sawdust.

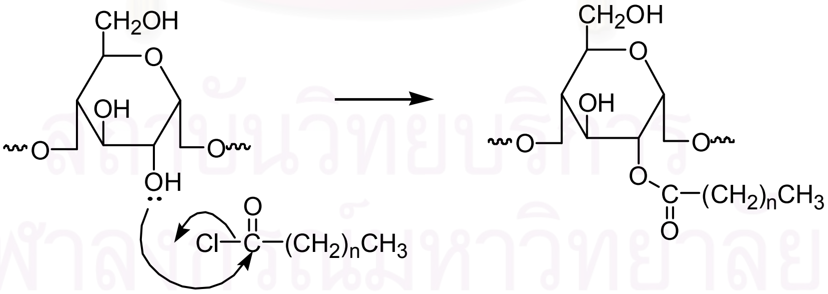
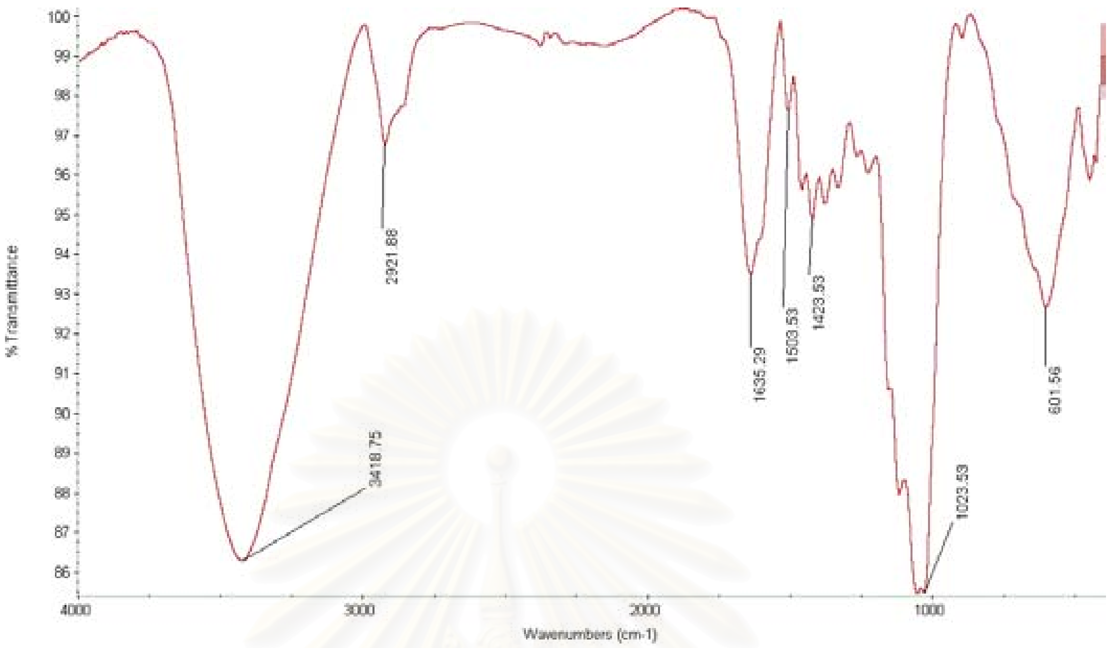
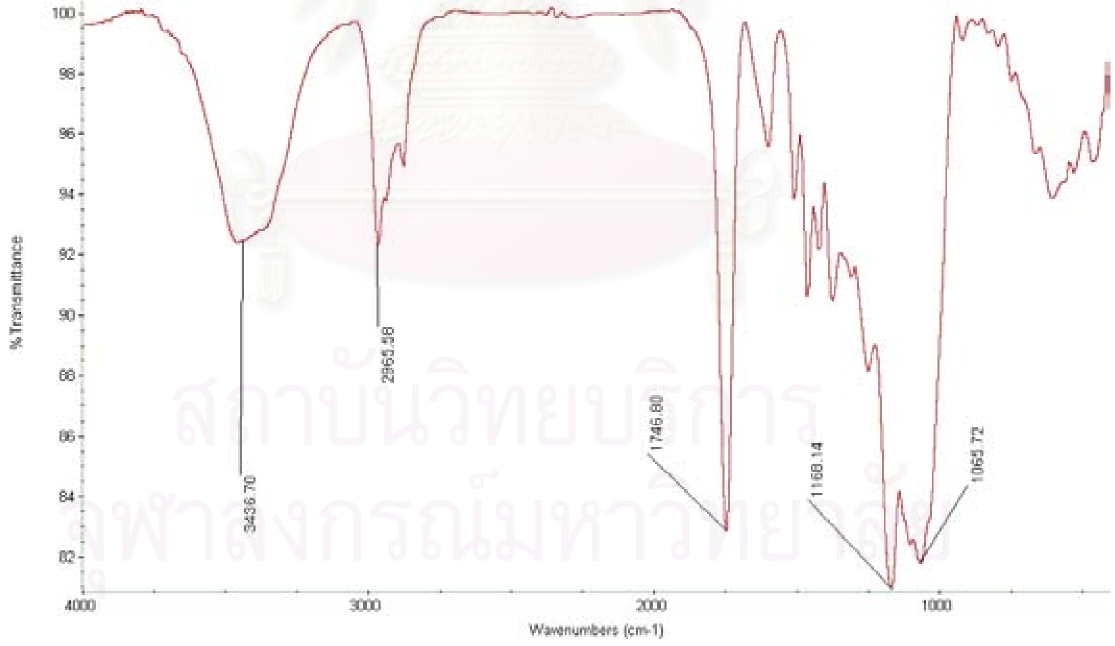


Figure 4.2 Esterification reaction of sawdust and acid chloride.

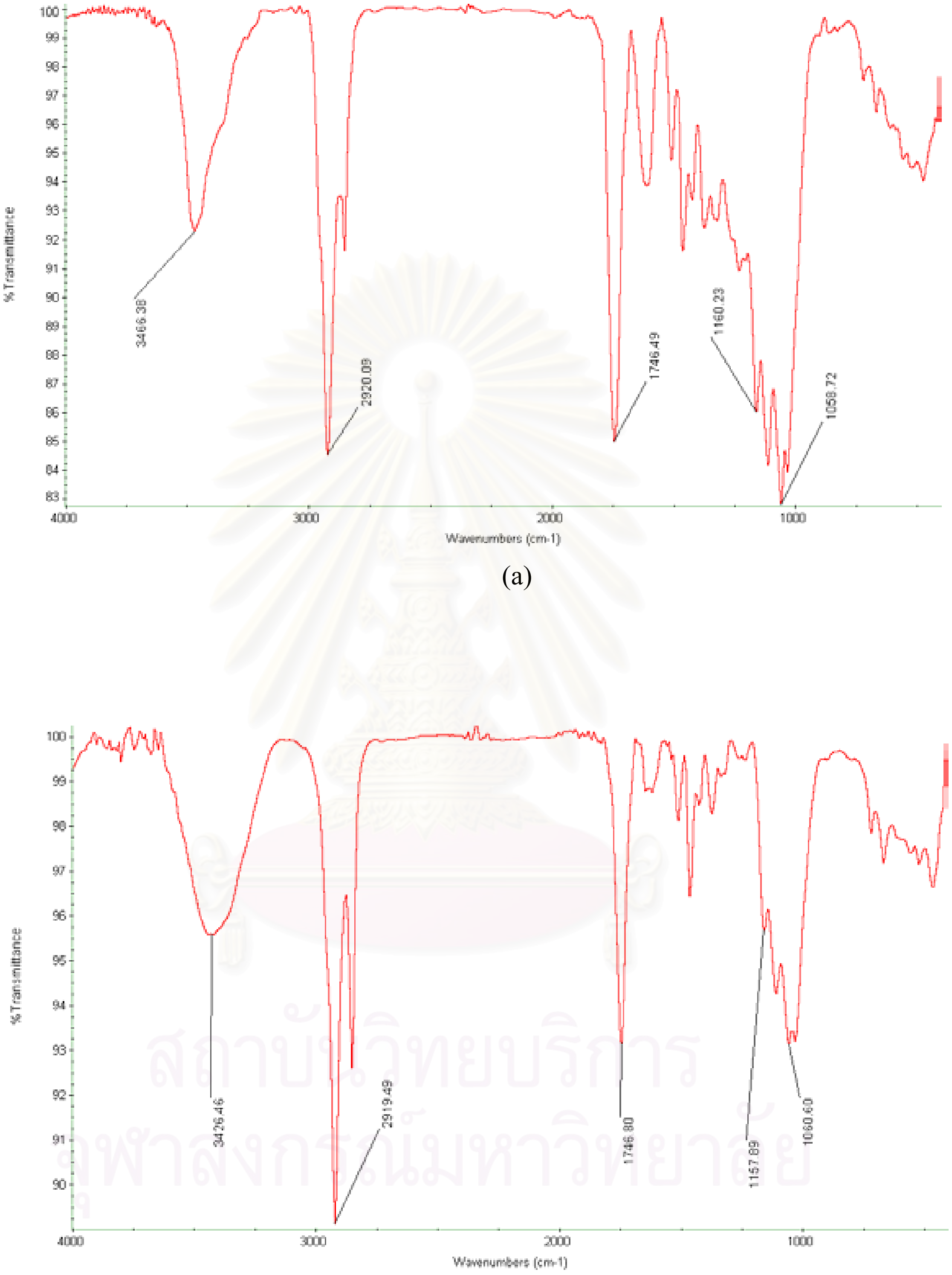


(a)



(b)

Figure 4.3 FTIR spectra of sawdust at 50 % ester content. (a) unesterified sawdust, (b) butyrated sawdust.



(a)

(b)

Figure 4.4 FTIR spectra of sawdust at 50 % ester content. (a) dodecanoated sawdust, (b) stearoated sawdust.

4.2 Surface-Esterified Sawdust Composites and Their Mechanical Properties

Effect of the ester content of surface-butyrated sawdust on the mechanical properties of the surface-esterified sawdust/PP composite at 20% of the surface-esterified sawdust was investigated. The results were shown in Table 4.2 and Figure 4.5. Tensile strength, tensile modulus, impact strength, and hardness of the composite increased with increase of ester content ranging from 0-50 % while elongation at break composite was decreased in range of 0-50 %. The impact strength of the 80 % butyrated sawdust/PP composite was decreased from the value at 50 % butyrated sawdust/PP composite. This may cause by. impact resistance was moderately decreased with increasing the amount of ester (%) but hardness property was increased in the narrow scale.

Therefore, the optimum ester content for surface-butyrated sawdust/PP composites should be 50%.

Table 4.2 The Effect of the Ester Content (%) on Mechanical Properties of Surface-Butyrated Sawdust (20%) / PP composites

Mechanical properties	The ester content (%)			
	0%	20%	50%	80%
Tensile strength, MPa	19.89 (0.45)	20.00 (1.28)	24.10 (0.42)	24.18 (0.38)
Tensile modulus, GPa	2.68 (0.21)	2.70 (0.16)	3.15 (0.18)	3.12 (0.19)
Elongation at break,%	13.04 (0.72)	12.90 (0.42)	11.87 (0.70)	11.24 (0.35)
Impact strength, J/cm	5.07 (0.73)	5.10 (0.22)	5.69 (0.13)	5.00 (0.22)
Hardness, HRR	92.80 (0.80)	94.97 (1.68)	96.80 (0.70)	96.90 (0.43)

Values in parentheses are standard deviations (S.D).

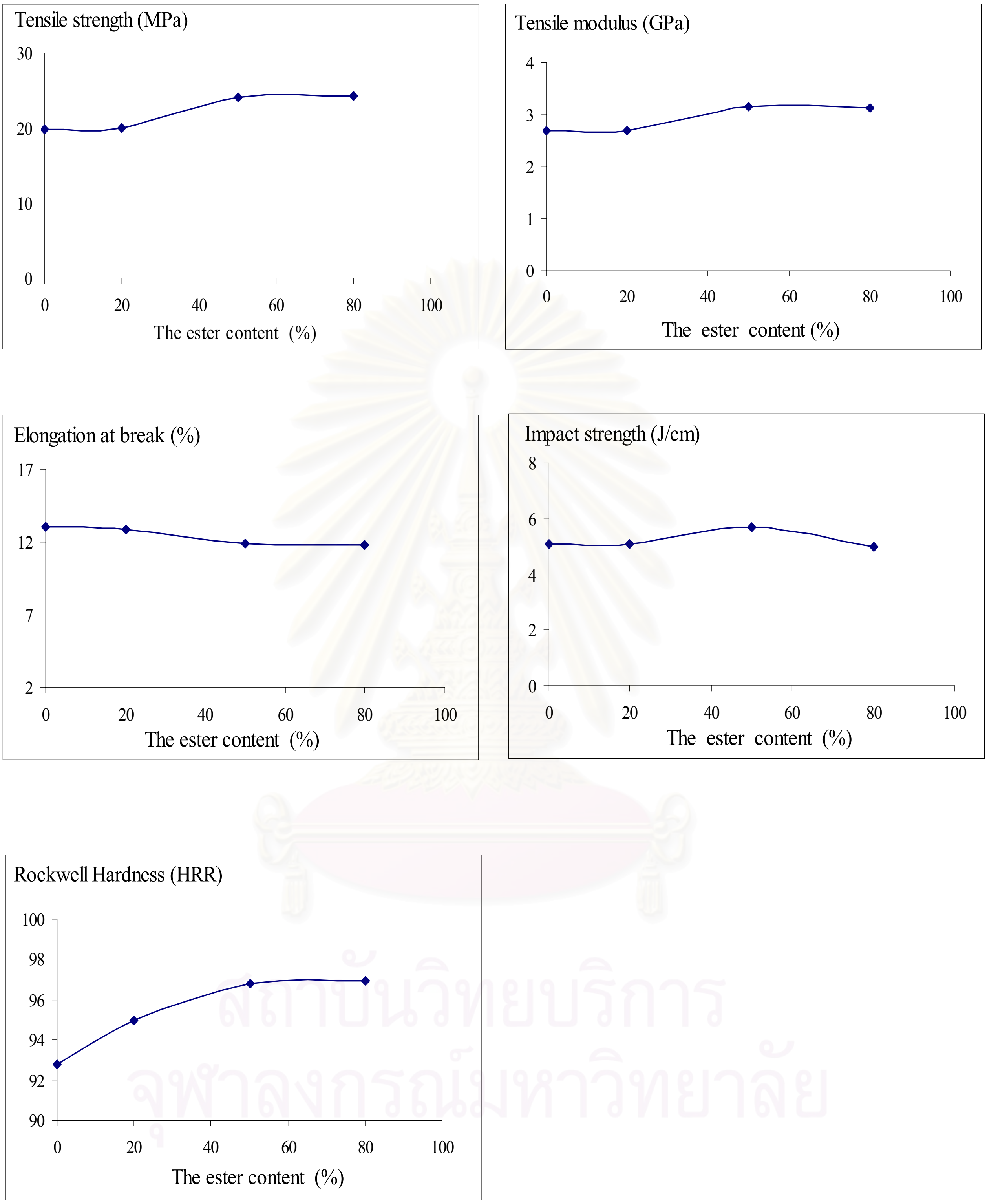


Figure 4.5 Effect of the ester content (%) on mechanical properties of the surface-butyrated sawdust (20%)/PP composite.

4.3 Mechanical Properties of Polypropylene/Sawdust Composites

4.3.1 Stress-Strain Curve of the Polypropylene/Sawdust Composites with Different Coupling Agents

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 behavior of material is useful as it provides information concerning important mechanical properties.

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

The stress-strain or load-extension curve can be readily obtained for polymer by subjecting a specimen a tensile force applied at a constant rate of testing. In Figure 4.6, stress is plotted against strain. For polypropylene curve, initially the stress is proportion 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 decrease in slope until it reaches a maximum. This is know as the yield point. Although not obviously, polypropylene has reached its yield point at about 27.15 MPa and further elongates until break. In other words plastic deformation occurs. During elastic deformation the cross sectional area of the specimen decreases uniformally as length increases.

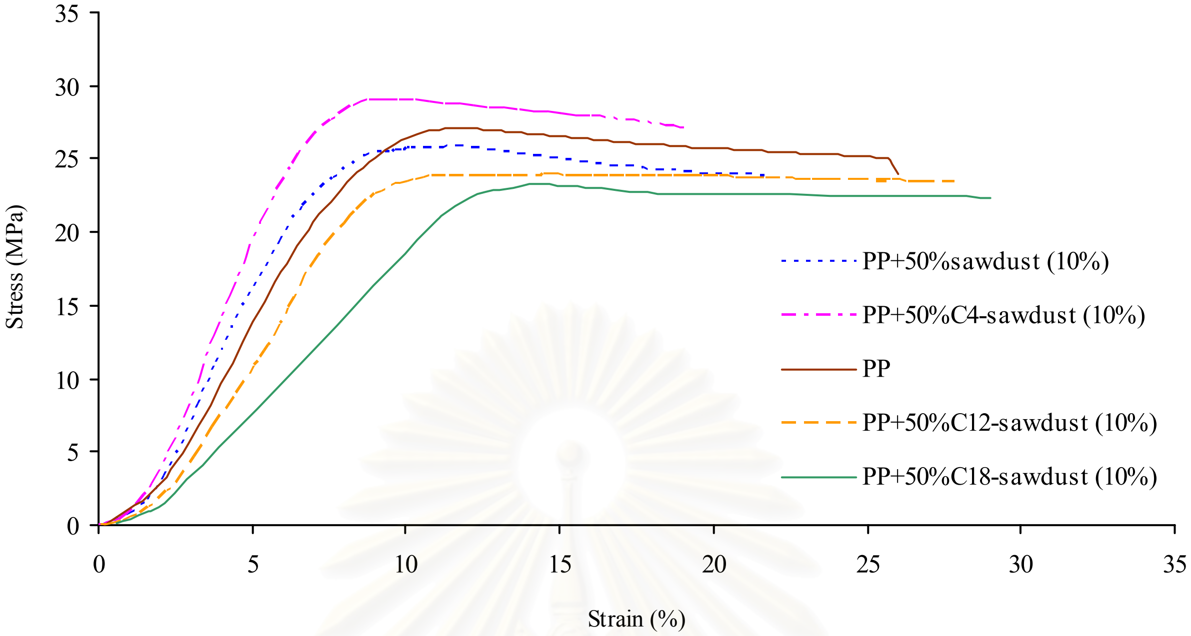


Figure 4.6 Stress-strain curve of the 50% esterified-sawdust / PP composite at various percent of sawdust.

In the case of the composite with unesterified sawdust and the composite with butyrated sawdust, it can be observed that the increase in stress or load of these composites is more faster than that of the pure polypropylene. This suggested that the stiffness of these composites is improved by the addition of sawdust. After a prolonged testing period, the stress changes to a non-linear behavior which illustrates the viscoelastic properties of the composites. The characteristic curve of these two composites are similar, but the tensile modulus and maximum stress of the composites with butyrated sawdust are higher than those of the composite with unesterified sawdust. This is because the modification of sawdust with butyryl chloride can improve compatibility and interfacial bonding between the polypropylene matrix and sawdust. The weakness of the composite with unesterified sawdust implies poor interfacial bonding between sawdust and polypropylene. After reaching their maximum stress, the plastic deformation starts to occur.

These composites fracture more rapidly than polypropylene. The elongation at break of the composite with unesterified sawdust and the composites with butyrated sawdust are about 22.14% and 19.80%, respectively.

These composites curves are different from polypropylene since the influence of sawdust that reduces the ductility and enhances the stiffness of polypropylene. From the area under the curves, polypropylene is tougher than there two composites.

For the composites with dodecanoated sawdust and stearoated sawdust, the stress-strain curve shows lower tensile modulus than the composite with unesterified sawdust and butyrated sawdust, and even lower than that of polypropylene. The increasing of stress is much slower than both composites and polypropylene. The characteristic curves of these two composites are similar, but the tensile modulus and the maximum stress for the composite with dodecanoated sawdust are higher than those for the composite stearoated sawdust. From the observation, the composite with stearoated sawdust and dodecanoated sawdust are softer than those both composites and polypropylene. This is owing to the plasticizing effect of long chain hydrocarbon of fatty acid ester groups grafted on sawdust. After the stress reaches its maximum or at the yield point of about 21.99 MPa and 20.65 MPa, respectively. The different among the composite with stearoated sawdust, the composites with dodecanoated sawdust, the composites with butyrated sawdust and the composite with unesterified sawdust is the extension or elongation at break. Among them, the elongation at break of the composite with stearoated sawdust is highest. In fact, its extension is also greater than that of the pure polypropylene.

Therefore, it can be concluded that the composite with stearoated sawdust and dodecanoated sawdust have lower tensile strength than any other composites including polypropylene. The lower values are due to the internal plasticization effect of the bulk fatty ester groups.

4.3.2 Effect of Filler Content on Mechanical Properties of Polypropylene / Sawdust Composites

The effect of surface-esterified sawdust/PP composites at 50% ester content on the mechanical properties were further investigated in the case of sawdust surface-esterified with dodecanoyl chloride and stearoyl chloride varies filler content. The results were shown in Tables 4.3-4.7 and Figures 4.7-4.11. The variation of properties with addition of sawdust filler to polypropylene, sawdust content is varied from 10-50% by weight of polypropylene.

The effect of the unesterified sawdust content on mechanical properties. Tensile strength, elongation at break and impact energy decreased while tensile modulus and hardness increased with increasing filler loading. This effect may be attributed to dewetting of the sawdust particle and the matrix that has opposite polarity. Dewetting behavior is clearly dependent on the sawdust and its surface characteristics which can be shown in the following section of the SEM. Because the sawdust does not adhere to PP, the sawdust cannot carry any load [23]. The more extender content, the higher incompatibility that exhibited a higher loss in mechanical properties.

The change of properties may also be explained by the pores in the sawdust structure. In general typical sawdust contains voids which are interconnected in a very tortuous manner so that permeation of the polymer is difficult. This reason may be led to the poor packing and dewetting characteristics.

The mechanical properties of PP/sawdust composites with different coupling agent are presented in Figures 4.7-4.11. The change at the sawdust surface due to the coupling agent plays an important role in determining the properties of the composites. This is evidenced by an improvement in mechanical properties of the PP/sawdust composites which contains butyryl chloride, dodecanoyl chloride and stearoyl chloride. However, effects of the butyrated sawdust content behave in the same trend as the unesterified sawdust content. But, in the case of effect of the dodecanoated sawdust and stearoated sawdust content a similar trend, tensile strength, tensile modulus, elongation at break, impact strength and hardness decreases with increasing filler content.

4.3.3 Comparison of Tensile Properties of the Polypropylene/Sawdust Composite with Different Coupling Agents

The comparison of tensile properties of the polypropylene filled with unesterified sawdust, butyrated sawdust, dodecanoated sawdust and stearoated sawdust are summarized in Table 4.3-4.5 and Figure 4.7-4.9.

Figure 4.7 and Table 4.3 shows the comparison of tensile strength of different composites. As observed, the tensile strength decrease with increasing sawdust content in all of the composites. For the composites with dodecanoated sawdust and stearoated sawdust, the decrease is monotonic, but for the composites with butyrated sawdust and unesterified sawdust a minimum is observed. These the composites also have better tensile strength than both composites of the same sawdust content. Tensile strength of polypropylene was decreased from 27.15 to 13.28 MPa with increment of unesterified sawdust content from 10 to 50% by weight, mainly because of worse transfer of the applied load through the interface.

The incompatibility of polypropylene and sawdust contribute to the lower tensile strength, it is well known that modification of sawdust to PP/sawdust composite increases the tensile strength of the composites. The composite with butyrated sawdust gave the highest tensile strength. At 20% sawdust content, tensile strength of the PP/unesterified sawdust and PP/butyrated sawdust composites were 18.03 and 24.10 MPa, respectively, therefore, the increase in tensile strength was 33.67%.

In the case of the composite with dodecanoated sawdust and the composite with stearoated sawdust, the decreasing in tensile strength can be attributed to the internal plasticization provided by the long chain fatty acid ester. Thus, the composite containing stearoated sawdust provided the lower tensile strength than did dodecanoated sawdust. The order of increasing tensile strength using different coupling agents is as follows:

butyrated sawdust > unesterified sawdust > dodecanoated sawdust > stearoated sawdust

Table 4.3 Tensile Strength of the Polypropylene/Sawdust Composites.

Filler content (%wt)	Tensile strength (MPa)			
	Unesterified sawdust	50% Esterified sawdust		
		C_4	C_{12}	C_{18}
0	27.15 (0.29)	-	-	-
10	24.42 (0.94)	26.89 (0.61)	21.99 (0.29)	20.65 (0.96)
20	19.89 (0.45)	24.10 (0.42)	18.00 (0.18)	16.53 (0.42)
30	17.61 (0.64)	21.35 (0.52)	15.98 (0.46)	14.00 (0.47)
40	15.67 (0.48)	17.21 (0.42)	14.01 (0.36)	12.00 (0.65)
50	13.28 (0.94)	14.21 (0.54)	12.17 (0.24)	9.98 (0.98)

Values in parentheses are standard deviations (S.D).

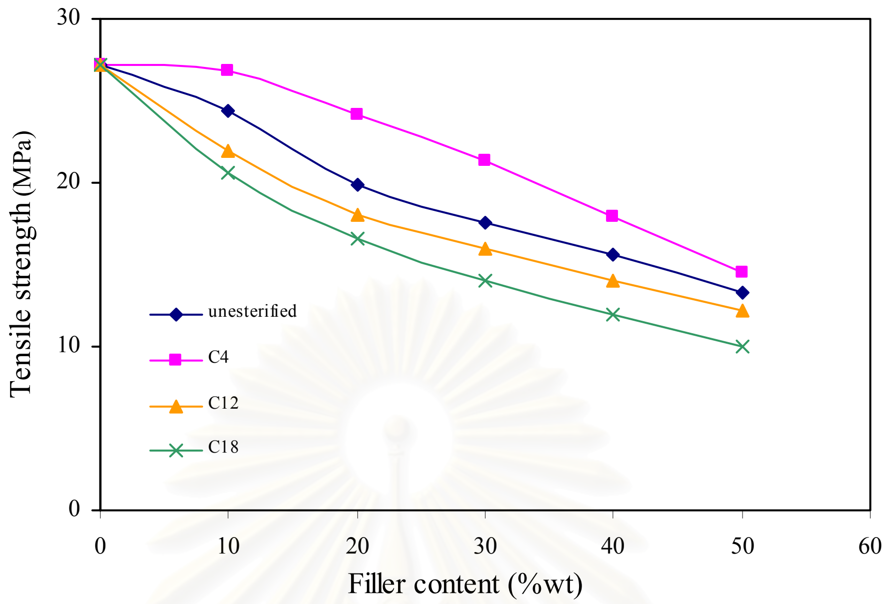


Figure 4.7 Tensile strength of the polypropylene/sawdust composites.

Figure 4.8 and Table 4.4 illustrate the comparison of tensile modulus of different composites. For the composite with unesterified sawdust and the composite with butyrated sawdust, tensile modulus increases with increasing the sawdust content. This is due to the reinforcing effect of sawdust.

In contrast, the tensile modulus of the composite with dodecanoated sawdust and the composite with stearoated sawdust decreases with increasing sawdust content. This is owing to the plasticizing effect of long chain hydrocarbon of ester groups, as shown in Figure 4.8, the decrease in tensile modulus is compensated by the increase in elongation.

Comparing between the composite with butyrated sawdust and unesterified sawdust, as would be expected the tensile modulus of the composite with butyrated sawdust is greater than that of the composite with unesterified sawdust. It is known that strong interaction can cause a stiffening effect on the polymer matrix adjacent to the filler particles interphase. Hence, it was expected that the improved interaction between the sawdust and PP due the esterification with butyryl chloride would cause an increment of the composite modulus. Overall tensile modulus of polypropylene increase 50.92% with the addition of 20% butyrated sawdust, and decreases with the addition of 20% dodecanoated sawdust and stearoated sawdust were 21.79% and 35.40%, respectively, the longer the modifier chain is, the stronger the achieved interface is. Esterification with dodecanoyl chloride and stearoyl chloride improved the compatibility (wettability) between the filler and the matrix but did not improve the strength [2]. The order of increasing tensile modulus using different coupling agents is as follows:

> butyrated sawdust > unesterified sawdust > dodecanoated sawdust > stearoated sawdust

Table 4.4 Tensile modulus of the Polypropylene/Sawdust composites.

Filler content (%wt)	Tensile modulus (GPa)			
	Unesterified sawdust	50% Esterified sawdust		
		C_4	C_{12}	C_{18}
0	2.18 (1.37)	-	-	-
10	2.21 (0.24)	2.34 (0.27)	2.12 (0.50)	1.93 (0.32)
20	2.68 (0.21)	3.15 (0.18)	1.97 (0.42)	1.84 (0.21)
30	3.14 (0.30)	3.52 (0.54)	1.61 (0.48)	1.44 (0.25)
40	3.78 (0.69)	4.06 (0.22)	1.44 (0.20)	1.24 (0.25)
50	4.12 (0.50)	4.38 (0.52)	1.26 (0.21)	0.99 (0.12)

Values in parentheses are standard deviations (S.D).

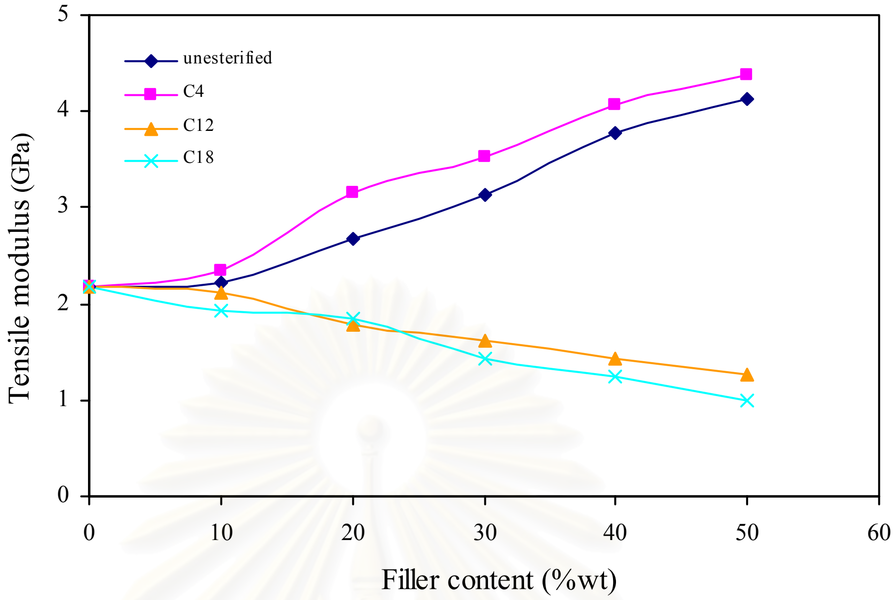


Figure 4.8 Tensile modulus of the polypropylene/sawdust composites.

Figure 4.9 and Table 4.5 illustrate the comparison of the elongation at break of different composites. The same conclusions can be reached when elongation at break of the composites decreases with increasing sawdust content from 10 to 50% by weight. As a result of filler addition, the ultimate elongation decreased as the sawdust content increased because of the decreased deformability of the matrix (restricted by the rigid particles).

At 10 to 20% sawdust content, the composites were still of the hard-ductile polymer but, at 30 to 50% sawdust content, the composites were of the hard brittle material. Thus, the elongation at break of the composites with content from 10 to 20% are higher than those of the composites with sawdust content from 30 to 50%. Obviously, at 30 to 50% sawdust content gave the lowest rate in decreasing elongation at break, while at 10 to 20% sawdust content were sharply dropped. At 10% filler content, the composite with stearoated sawdust gave the highest elongation at break of about 28%, elongation at break increases 41.41% compared to the composite with butyrated sawdust. The order of increasing the elongation at break is shown as follows:

stearoated sawdust > dodecanoated sawdust > unesterified sawdust >
butyrated sawdust

In conclusion, it can be seen that tensile strength decreases, while the elongation at break increases with increasing side-chain length of fatty acid ester. This is because sawdust with higher content of fatty acid groups becomes more plasticized and also loss its crystallinity. This can be attributed to the internal plasticization provided by the bulky side ester groups, and the higher elongation at break of stearoated sawdust is further evidence that the stearoic ester acts as a better plasticizer than the dodecanoic one . Obviously, the bulkier groups are more effective internal plasticizers.

Table 4.5 Elongation at break of the Polypropylene/Sawdust composites.

Filler content (%wt)	Elongation at break (%)			
	Unesterified sawdust	Esterified sawdust		
		C_4	C_{12}	C_{18}
0	26.00 (1.37)	-	-	-
10	22.14 (1.10)	19.80 (0.56)	26.39 (0.37)	28.00 (0.64)
20	13.04 (0.72)	11.87 (0.70)	14.20 (0.30)	15.17 (0.56)
30	8.41 (0.82)	7.44 (0.67)	6.83 (0.23)	9.32 (0.96)
40	5.80 (1.98)	4.91 (0.52)	6.22 (0.14)	7.01 (0.69)
50	4.23 (0.61)	3.32 (0.52)	4.87 (1.10)	5.53 (0.46)

Values in parentheses are standard deviations (S.D).

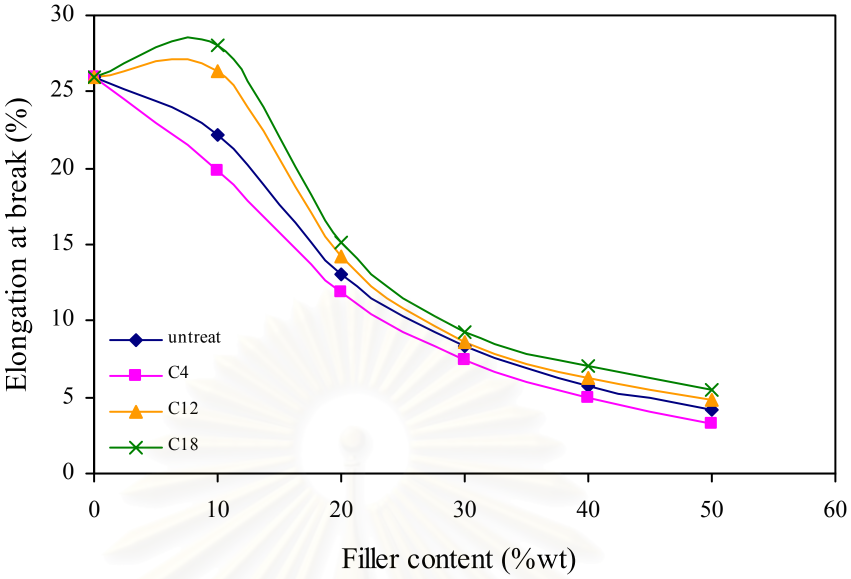


Figure 4.9 Elongation at break of the polypropylene/sawdust composites.

4.3.4 Comparison of Impact Property of the Polypropylene/Sawdust Composites with Different Coupling Agents

The comparison of impact strength of the PP filled with unesterified sawdust, butyrated sawdust, dodecanoated sawdust and stearoated sawdust are summarized in Table 4.6 and Figure 4.10.

Impact strength of all the composites was decreased with the rise in filler content as presented in Figure 4.10. The impact strength initially exceeded that of the neat PP because of the additional mechanisms of energy absorption effective during fracture in the filled systems. However, the impact strength of reinforced PP decreased with increasing sawdust content, whereas stiffness simultaneously increased. Although impact strength usually decreases with increasing amount of filler, quite frequently a maximum is observed at a low (< 15% volume) filler content. The maximum is most probably the combined result of different competitive micromechanical deformation processes influenced by polymer-filler interactions and particle-particle interaction. As the concentration of sawdust increased, the material became more rigid, and the impact strength was reduced, there was a change from ductile to more brittle fracture behavior because of the restrictive presence of the rigid particles.

The hardening of the interlayer led to an increase in modulus, but reduced the impact strength of the composites. Thus, the composite with butyrated sawdust shows lower impact strength than the composite with dodecanoated and stearoated sawdust.

The composite with stearoated sawdust at all sawdust content shows the highest impact strength. Similar to the elongation at break previously discussed, the plasticizing effect from stearoated sawdust (long chain fatty acid ester) plays an important role in decreasing all the strength of polypropylene/sawdust composites. At 10% filler content, impact strength of the composite with stearoated sawdust and unesterified sawdust were 6.52 and 5.8 J/cm, respectively. The slight increase in impact strength was 10.70%. The order of increasing the elongation at break is shown as follows:

stearoated sawdust > dodecanoated sawdust > butyrated sawdust
unesterified sawdust

Table 4.6 Impact Strength of the Polypropylene/Sawdust composites.

Filler content (%wt)	Impact strength (J/cm)			
	Unesterified sawdust	50% Esterified sawdust		
		C_4	C_{12}	C_{18}
0	3.97 (0.32)	-	-	-
10	5.89 (0.65)	6.02 (0.08)	6.41 (0.39)	6.52 (0.24)
20	5.07 (0.73)	5.69 (0.13)	6.01 (0.26)	6.04 (0.16)
30	4.24 (0.86)	4.70 (0.45)	5.19 (0.22)	5.34 (0.41)
40	3.67 (0.38)	4.08 (0.22)	4.25 (0.24)	4.41 (0.51)
50	3.00 (0.67)	3.19 (0.20)	3.76 (0.13)	4.02 (0.13)

Values in parentheses are standard deviations (S.D).

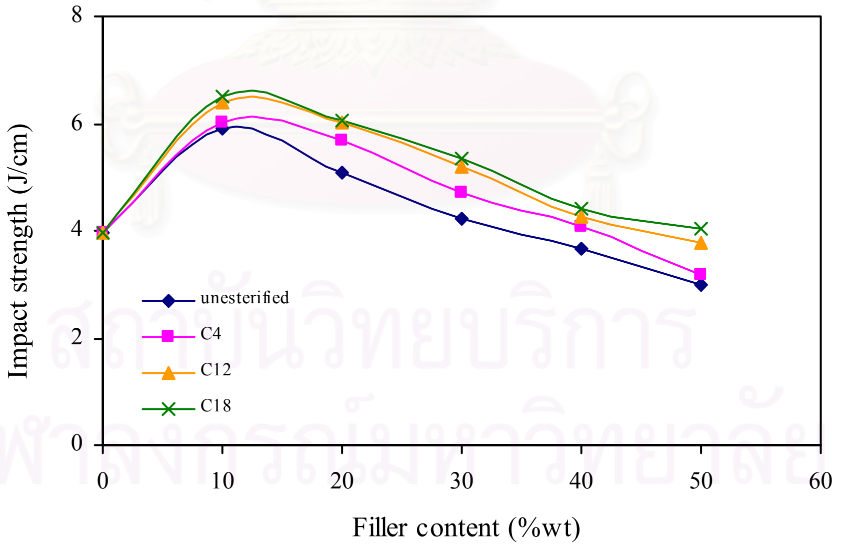


Figure 4.10 Impact strength of the polypropylene/sawdust composites.

4.3.5 Comparison of Hardness Property of the PP/Sawdust Composites with Different Coupling Agents

The comparison of hardness property of the PP filled with unesterified, butyrated sawdust, dodecanoated sawdust and stearoated sawdust are summarized in Figure 4.11 and Table 4.7.

In the case of the composite with butyrated sawdust and the composite with unesterified sawdust, the composite with butyrated sawdust was greater than that of the composite with unesterified sawdust. This is because the butyryl chloride can improve compatibility and interfacial strength between the polypropylene and sawdust, resulting in hardening of the composite and the hardness increased with the filler content.

In contrast, the hardness of the composite with dodecanoated sawdust and stearoated sawdust lower than the composite with butyrated sawdust and unesterified sawdust, and even lower than that of polypropylene. From the observation, the composite with dodecanoated sawdust and stearoated sawdust are softer than all the composites. This is owing to the plasticizing effect of long chain hydrocarbon of dodecanoyl chloride and stearoyl chloride. Obviously, as shown in Figure 4.11 and Table 4.7, the hardness decreased with increasing sawdust content. In this case, the esterified sawdust with dodecanoyl chloride and stearoyl chloride do not function as a reinforce filler, but a plasticizer for polypropylene. The order of hardness values is as follows:

butyrated sawdust > unesterified sawdust > dodecanoated sawdust > stearoated sawdust

Table 4.7 Rockwell Hardness of the Polypropylene/Sawdust Composites.

Filler content (%wt)	Rockwell hardness (HRR)			
	Unesterified sawdust	50% Esterified sawdust		
		C_4	C_{12}	C_{18}
0	86.80 (2.38)	-	-	-
10	90.10 (2.07)	94.50 (1.92)	85.60 (2.31)	77.60 (6.85)
20	92.80 (0.80)	96.80 (0.70)	80.40 (4.73)	73.20 (4.09)
30	95.00 (0.76)	97.20 (0.63)	79.20 (1.82)	67.40 (2.20)
40	96.60 (0.67)	99.50 (0.90)	75.00 (3.66)	64.30 (3.53)
50	98.50 (1.37)	103.10 (1.50)	74.70 (1.20)	60.90 (2.11)

Values in parentheses are standard deviations (S.D).

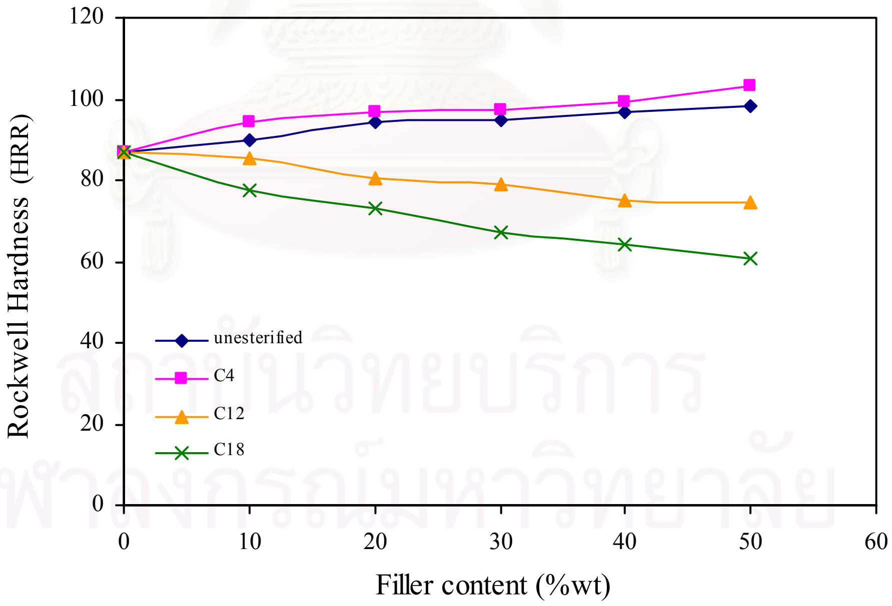


Figure 4.11 Rockwell hardness of the polypropylene/sawdust composites.

4.3.6 Effect of Surface Modification on Mechanical Properties

Surface modification of sawdust is very necessary due to the incompatibility between the polypropylene matrix and sawdust which contributing to the unsatisfactory mechanical properties. In this part, mechanical properties of the composites with butyrated sawdust are compared with that of the composite with dodecanoated sawdust and stearoated sawdust.

In conclusion, the improvement of compatibility between polypropylene and sawdust with butyryl chloride, dodecanoyl chloride and stearoyl chloride are similar. As shown in Figures 4.11-4.15, butyrated sawdust helps improving the tensile and hardness properties of PP/sawdust composite. Since butyryl chlorides enhances the compatibility between polypropylene and sawdust, the tensile strength and stiffness of this composite are higher than that of the composite with unesterified sawdust. In contrast, the surface modification of sawdust with dodecanoyl chloride and stearoyl chloride cannot improve the tensile strength and stiffness, but the elongation at break and impact property of the composite. From Figure 4.6 the stress-strain behavior illustrates that the dodecanoated sawdust and stearoated sawdust composites are soft and ductile. This behavior could be explained by the increase in the free volume of the polymer, which is caused by the introduction of bulky flexible side-chain groups. The internal plasticization due to the esterification is so effective that the composites are soft and ductile.

4.4 Morphological Study of Polypropylene/Sawdust Composites

The scanning electron microscope (SEM) was employed to investigate the fracture surface of the samples from the uniaxial tensile tests. The SEM micrographs of the unsterifired sawdust and esterified sawdust are shown in Figure 4.12 (a)-(d)

In comparison, the surface of esterified sawdust however is rougher than that of unesterified sawdust, as confirmed by higher magnification of SEM micrographs. As presented in Figure 4.12 (b)-(d), the surface of esterified sawdust, butyrated sawdust (a), dodecanoated sawdust (b) and stearoated sawdust (c), exhibit very rough and distinct surface, as opposed to the smoother surface of the unesterified sawdust as shown in Figure 4.12 (a). This is owing to cellulose in sawdust has the opportunity of forming significant hydrogen bonding. The resulting high intermolecular forces, result in its high degree of crystallinity. On the other hand, chemical reaction can disrupt the regularity of the crystallites. The chemical reaction begins in the amorphous region of the cellulose, since the reagent cannot diffuse inhibit crystalline region. Thus it reacts first at the chain ends on the surface of the crystallites. This results in the opening of some of the hydrogen-bonded cellulose chains, thus producing the formation of amorphous cellulose. The acid chloride then diffuses into these new amorphous regions to react with accessible hydroxyl groups and consequently generate more amorphous cellulose.

However, the particle surface of sawdust showed a very similar appearance if they were esterified with butyryl chloride, dodecanoyl chloride and stearoyl chloride.

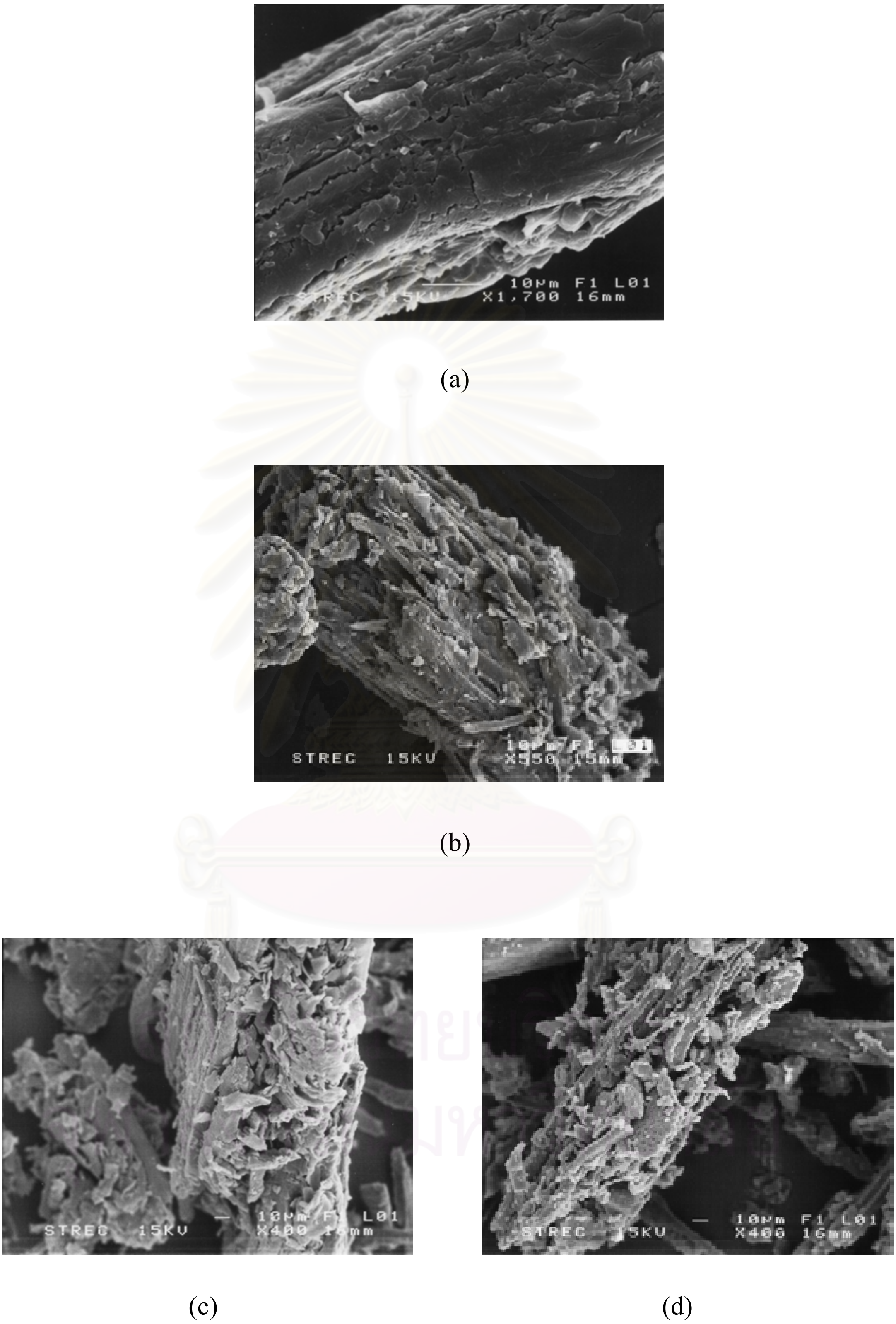
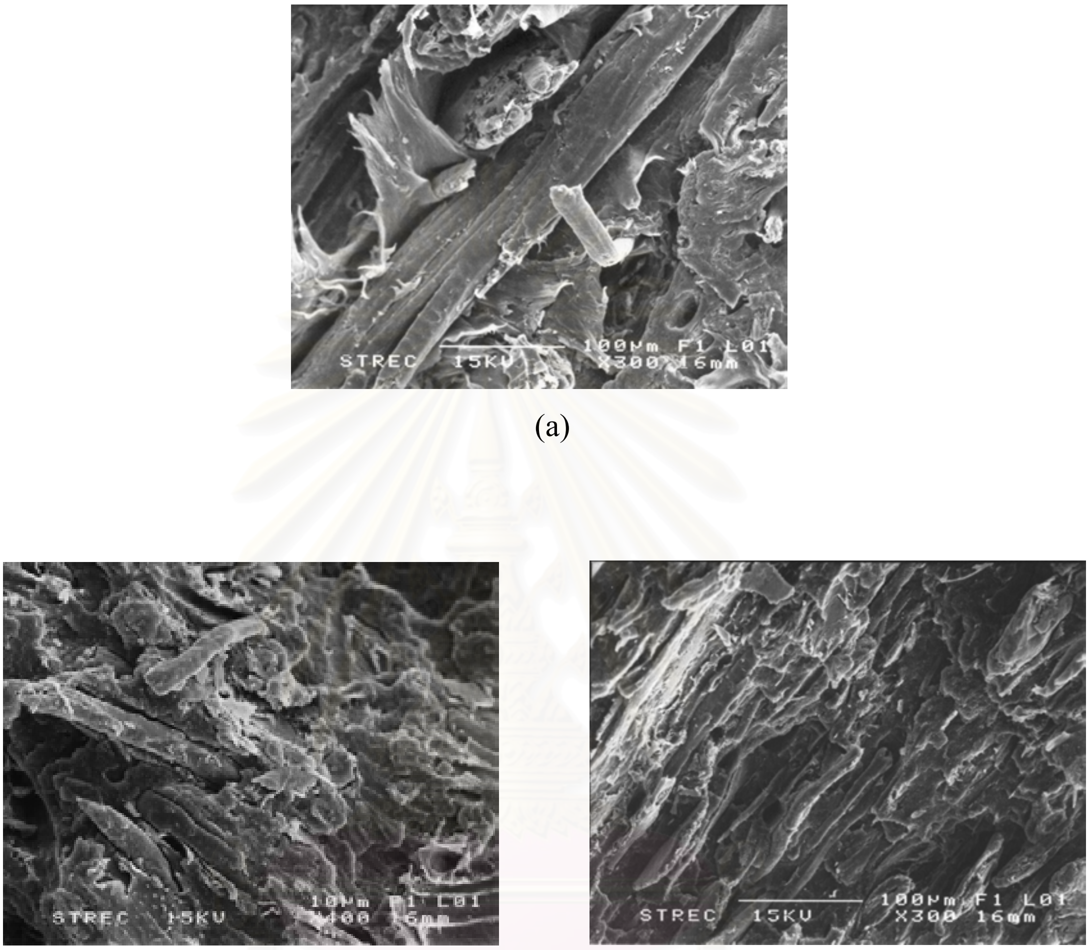


Figure 4.12 SEM micrographs of the sawdust surface in (a) unesterified, (b) C_4, (c) C_{12} and (d) C_{18}.

The SEM micrographs of the tensile fractured surface of the composite with unesterified were shown in Figure 4.13 (a)-(c). As shown in Figure 4.13 due to a number of the hydrogen bonds formed between the sawdust (cellulose) and the difference in character between the hydrophilic sawdust and hydrophobic polypropylene matrix, the sawdust tends to agglomerate and becomes unevenly distributed throughout the matrix.

These micrographs reveal poor wetting of sawdust by the polypropylene matrix. Without effective wetting of the fiber, strong interfacial adhesion cannot exist. Lack of interfacial interaction leads to a separation between the matrix and sawdust. In other words, fracture will occur at the interface of sawdust and polypropylene. As shown in Figure 4.13 sawdust is 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 sawdust.



(a)

(b)

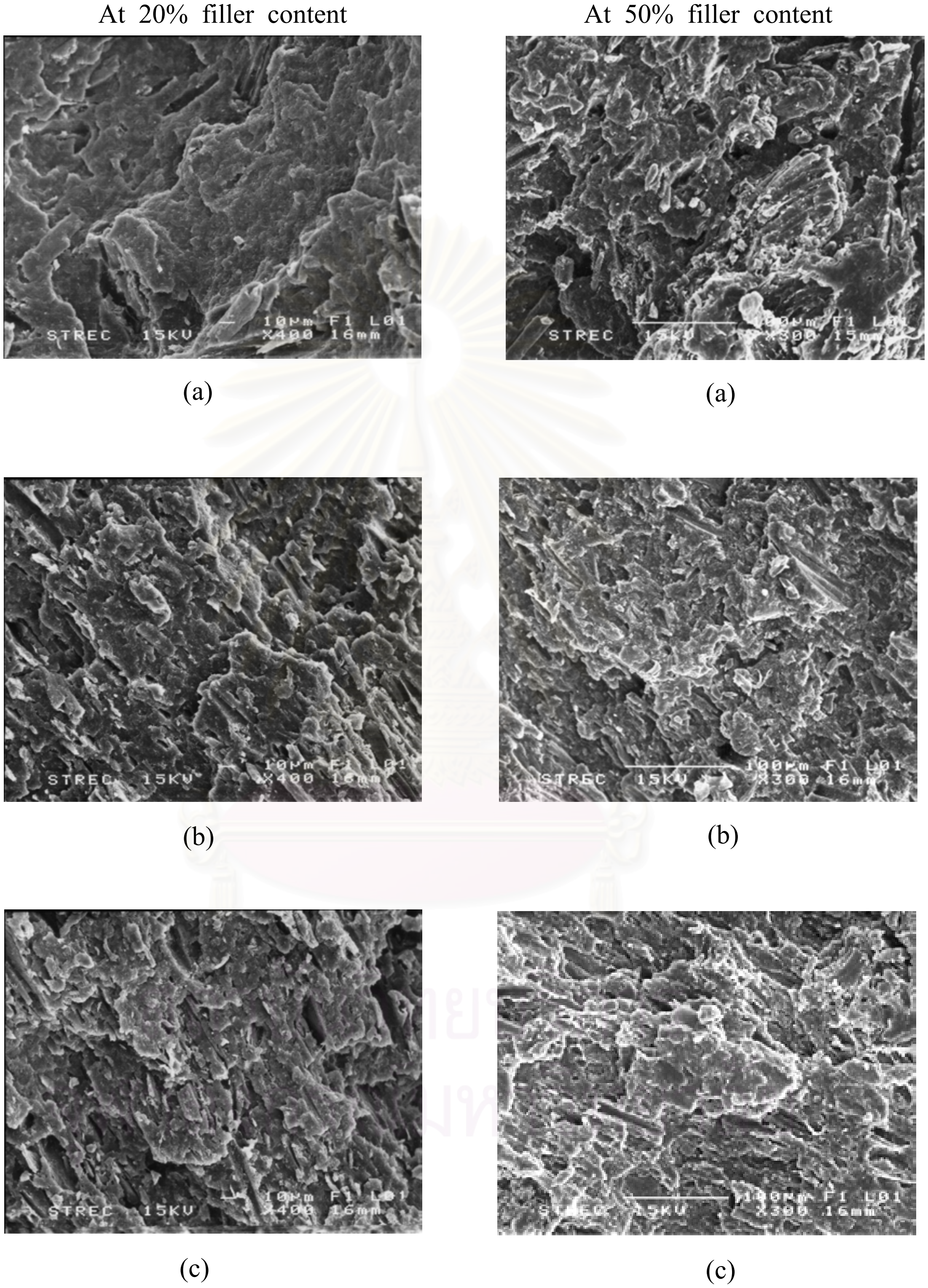
(c)

Figure 4.13 SEM micrographs of tensile fracture surfaces for the composite with (a) 10%, (b) 20% and (c) 50% unesterified sawdust, showing hole and fiber pull-out.

SEM micrographs for the composites with esterified sawdust (butyrated sawdust, dodecanoated sawdust and stearoated sawdust) are similar in Figure 4.14 (a)-(c). In contrast to the composite with unesterified sawdust, the same results are observed of all three coupling agents that the esterified sawdust do not agglomerate within the matrix. The sawdust shows better dispersion with improving adhesion to the matrix. A good compatibility and enhanced wettability between the two phases is evidenced by a number of firmly embedded sawdust that cannot be pulled out during the fracture process. In contrast to the sharp interface of uncompatibilized composite. As shown in Figure 4.14 (a)-(c), the entire sawdust is covered by a layer of polypropylene matrix that has been pulled out together with sawdust.

Another distinct difference is that there is no trace of holes or fiber-pulled out from the matrix, unlike the composite with unesterified sawdust, more uniform fractured surface is observed. These results imply that the interfacial bond strength of the polypropylene/sawdust composite can be improved by the modification of surface of sawdust, as confirmed by the enhanced mechanical properties. All the composites with esterified sawdust are similar.

In conclusion, in order to obtain composite with satisfactory mechanical properties, good adhesion of fibers in the matrix, effective wetting of fibers by matrix, and good interfacial adhesion are required. Therefore, if unesterified sawdust is used, poor wetting will occur. This is owing to the large difference in surface energy between sawdust and polypropylene matrix. By the esterification reaction, their surface energy is lower to a level much closer to the surface energy of the matrix. Thus better wetting is obtained.



At 20% filler content

At 50% filler content

(a) (a)

(b) (b)

(c) (c)

Figure 4.14 SEM micrographs of tensile fracture surface for the composites with (a) C_4, (b) C_{12} and (c) C_{18}.

4.5 Differential Scanning Calorimeter (DSC)

Thermal transition temperature was characterized by a differential scanning calorimetry (DSC). The melting temperature (T_m) and the glass transition temperature of the composites were taken as the maximum of the endothermic peak. The DSC data for the composite with unesterified sawdust, butyrated sawdust, dodecanoated sawdust and stearoated sawdust were shown in Table 4.8 and Figure 4.15 and Figure 4.16

The melting temperature, T_m of polypropylene was 165.70°C, while that of the composites with unesterified sawdust was 163.05°C. In the presence of esterified sawdust, the observed melting temperature of the composite with butyrated sawdust found at 164.40°C. The increasing of T_m of the composite with butyrated sawdust can be explained that butyryl chloride has a good compatibilizing effect on the composite. The esterification of sawdust with butyryl chloride provides covalent bonds across the interface, thus cohesive coupling between sawdust and polypropylene matrix.

In the case of the composites with dodecanoated sawdust and stearoated sawdust, an increase of side chain length cause a small depression of T_m. Thus the composite with stearoated sawdust has lower T_m than the dodecanoated sawdust, being 160.83°C and 158.48°C, respectively, this is because the longer carbon chain of the acid chloride used in esterification acts as a more efficient internal plasticizer, the increase in the free volume of the polymer, which was caused by the introduction of bulky flexible long chain groups [24, 28].

For the glass transition temperature, T_g of the composites as shown in Table 4.8 and Figure 4.16. These results appear in the same trend as those previously on the melting temperature. Likewise, it can be explained that the increasing in T_g of the composite with butyrated sawdust is owing to the compatibilizing effect on the composite, whereas the reducing in T_g of the composites with dodecanoated sawdust and stearoated sawdust might be due to the plasticizing effect.

Table 4.8 Comparison of Thermal Properties between Polypropylene and the Composites

Type of composite	T_m (°C)	T_g (°C)
Polypropylene	165.70	-
Composite with unesterifed sawdust	163.05	77.45
Composite with butyrated sawdust	164.40	81.40
Composite with dodecanoated sawdust	160.83	60.33
Composite with stearoated sawdust	158.48	52.63

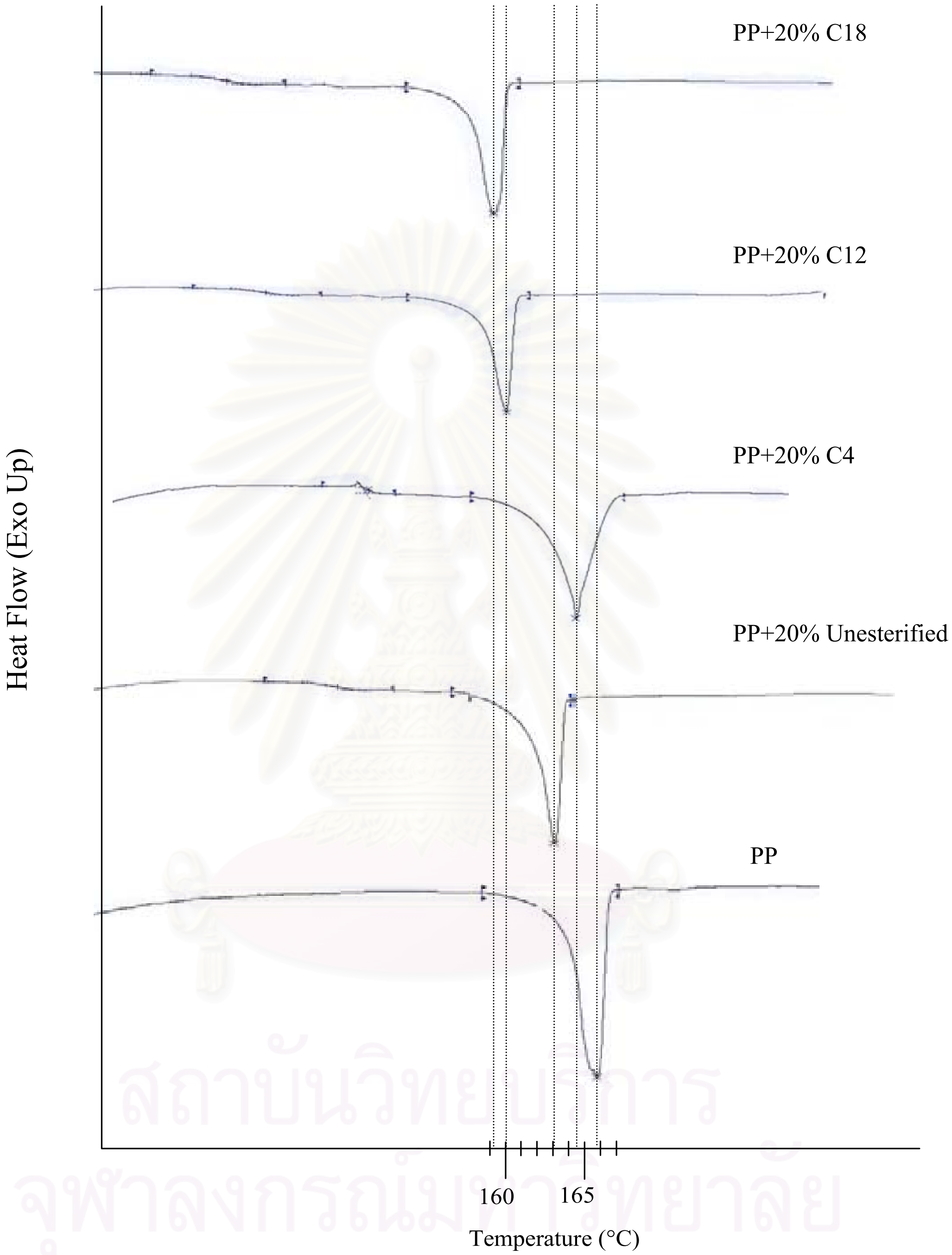


Figure 4.15 Comparison of the melting temperature (T_m) for polypropylene and the composites.

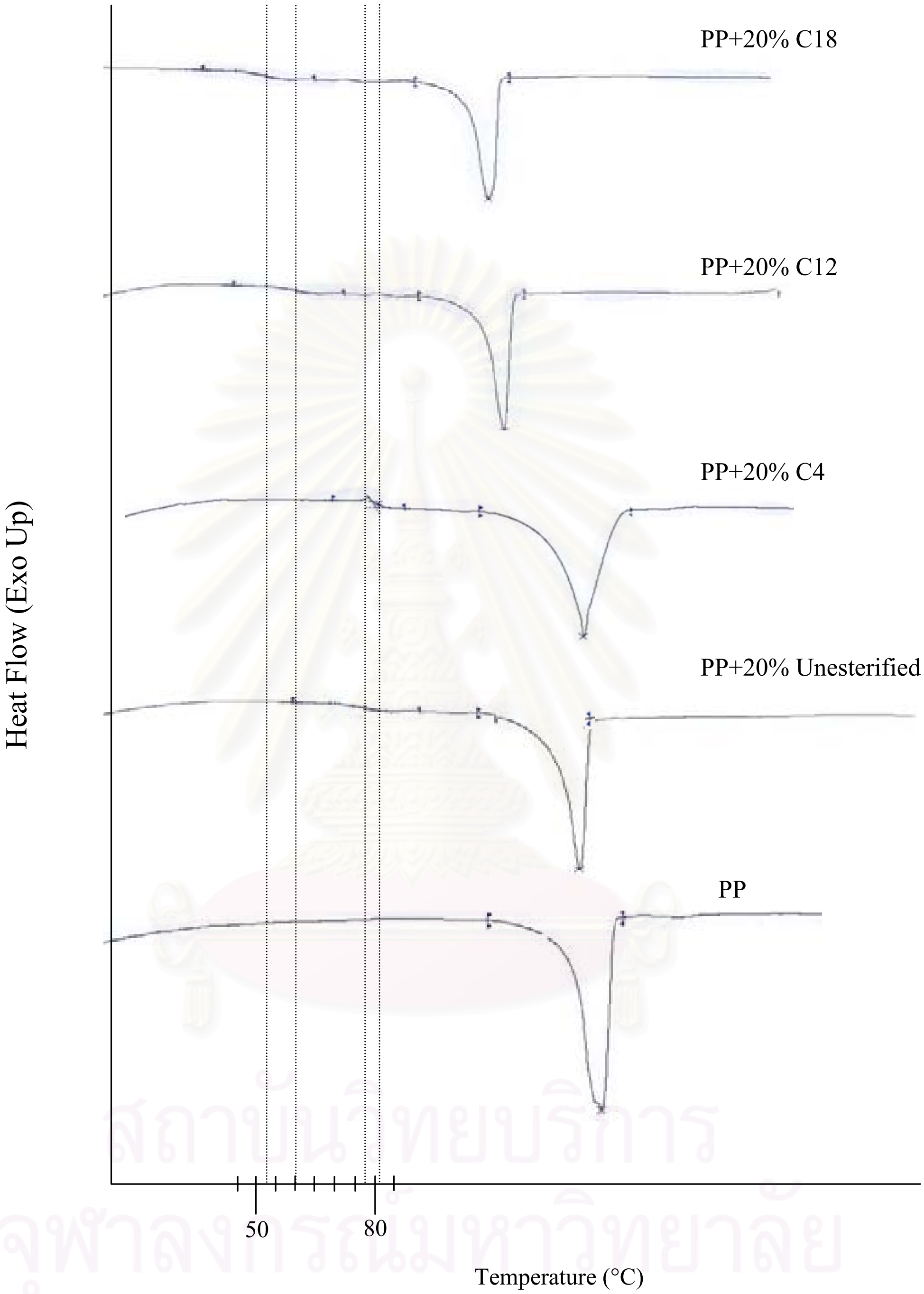


Figure 4.16 Comparison of the glass transition temperature (T_g) for polypropylene and the composites.

CHAPTER V

CONCLUSIONS

As an effort to reuse sawdust, sawdust reinforced polypropylene composite was made. This composite offers a number of benefits including high specific stiffness and strength, low density, and biodegradability. Although, this composite has many advantages, it has a main problem in preparation of this composites. This problem is the incompatility and poor interfacial adhesion between the sawdust and polypropylene, resulting in poor mechanical properties. Thus, the esterification reaction using acid chloride was adopted to modify surface of the sawdust prior to mix with the polypropylene matrix to improve the compatibility and interfacial bond strength between the two phases.

In this work, the mechanical properties of four composites with five levels (10 to 50% by weight) of sawdust in polypropylene matrix were studied. These four composites were PP/unesterified sawdust, PP/butyrated sawdust, PP/dodecanoated sawdust and PP/stearoated sawdust. The properties of all the composite are summarized in Table 5.1, the major findings and conclusion in this work are as follows:

The optimum of the ester content (%) in sawdust-filled PP system was 50% and organic solvent used in the esterification reaction was toluene because they provided good mechanical properties. The higher ester content (%), the darker the color of composites.

Table 5.1 Conclusion of Mechanical Properties of the Polypropylene/Sawdust Composites

Mechanical Properties	Esterified sawdust		
	Butyrated sawdust	Dodecanoated sawdust	Stearoated sawdust
Tensile strength, MPa	***	**	*
Tensile modulus, GPa	***	**	*
Elongation at break, %	*	**	***
Impact strength, J/cm	*	**	***
Hardness, HRR	***	**	*

* = medium ** = good *** = very good

1. For the unesterified sawdust as filler, the deterioration of the tensile strength, elongation at break, impact energy and hardness of composite may be due to the poor adhesion of two phases.

2. The mechanical properties of sawdust-filled PP composite was improved by the chemical modification which gave the better interfacial adhesion. Among the three coupling agents used, butyryl chloride, dodecanoyl chloride and stearoyl chloride.

3. The composite with butyrated sawdust shows the highest tensile strength, decrease with increasing sawdust content. In the case of the composite with stearoated sawdust shows the highest elongation at break and impact strength, decrease with increasing sawdust content. This is due to the plasticizing effect of long chain fatty acid ester.

4. Similar to the case of the tensile strength, the composite with butyrated sawdust shows the highest tensile modulus and hardness properties but, the tensile modulus and hardness properties increase with increasing the sawdust. Whereas the composite with stearoated sawdust has the lowest tensile strength, tensile modulus and hardness properties, decrease with increasing sawdust content.

5. The esterified of sawdust with long chain fatty acid chloride, behave-like typical thermoplastic material, showing poor tensile strength and high elongation at break. The ester group acts like an internal plasticizer, with an increase in the carbon chain length of the fatty–acid, resulting in greater internal plasticization, the stearoic ester acts a better plasticizer than that dodecanoic one.

6. All three coupling agents also acted as dispersing agent, this is confirmed by SEM micrographs of fracture surface of the PP/sawdust composites. The scanning electron micrographs of the PP/esterified sawdust composites showed the good dispersing effect and bonding at the interface evidenced by less sawdust was pulled out from the polypropylene matrix.

7. 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. Among them, the surface modification using butyryl chloride was method for improving the strength, but dodecanoyl chloride and stearoyl chloride for improving the flexibility of the composites.

Recommendations

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

1. Effect of fabrication technique on the distribution of filler in compounding, e.g. in an extruder.

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

3. Sawdust and natural fiber are suitable for using in thermoplastic 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 polymer and further improving the advantage of both the polymer and the fiber.

REFERENCES

1. Tjong, S. C., Xu, Y. and Meng, Y. Z. Composites based on maleated polypropylene and methyl cellulose fiber: mechanical and thermal properties. Journal of Applied Polymer Science 72 (1999): 1647-1653.
2. Nunez, A. J., Sturm, P. C., Kenny, J. M., Aranguren, M. I. and Marcovich, N. E. Mechanical characterization of polypropylene-wood flour composites. Journal of Applied Polymer Science 88 (2003): 1420-1428.
3. Reinhart, T. J., Clement, L. L. Engineered materials handbook. Ohio: ASM internation, 1989: 27-34.
4. Hilling, W. B. Composite material. Encyclopedia of Chemical Technology 6 (1981): 683-699.
5. Chanda, M., and Roy, S. K. Plastic technology handbook. New York: Marcel Dekker, 1987: 7.
6. Richardson, T. Composites: a design guide. New York: Industrial Press, 1987.
7. Gachter, R., and Muller, H. Plastic additive handbook. New York: Houser Pulishers, 1987: 397-440.
8. Walsh, T. S. Polypropylene. Modern plastic. Mid-October (1992): 79-85.
9. Rubin, I. I. Handbook of plastic material and technology. New York: John Wiley & Sons, 1990: 446-44.
10. Brydson, J. A. Plastics material. 4th ed. London: Butterworth Scientific, 1985: 225-243.
11. Demianiw, D. G. Olefin polymer (polypropylene). Encyclopedia of Chemical Technology 16 (1981): 454.
12. Blumberg, J. G., Falcone, J. S., Smiley, L. H., and Netting, D. I. Fillers. Encyclopedia of Chemical Technology 10 (1981): 199-215., 26 (1985): 474.
13. Benjamin, M. W., Organic filler for plastic. In S.K. Harry and V.M. John, (eds.), Handbook of filler for plastics, pp. 420-426. New York: Van Nostrand Reinhold, 1987.
14. Kokta, B. V., Raj, R. G LLDPE filled with silane-coated-wood fibers. High-tech. fibrous materials. 1990: 102-113.

15. Richardson, T. The influence of coupling agents on mechanical properties of composites containing cellulose fillers. Polymer-plastics technology and engineering. 29 (April 1990): 339-353.

16. Myers, G. E., Chahyadi, I. S., Coberly, C. A., Ermer, D. S., and Gonzalez, C. Wood flour and polypropylene or high density polyethylene composites: Influence of maleated polypropylene concentration and extrusion temperature on properties. International Journal of Polymeric Material 15 (1991): 171-186.

17. Nabi, D. and Jog, J. P. Natural fiber polymer composites: A review. Advances in Polymer Technology 18 (1999): 351-362.

18. Morton-Jones, D. H. Polymer processing. New York: Chapman and Hall, 1987: 491-501.

19. Seymour, R. B. Reinforced plastic:properties applications. New York: Kathleen Mills,1993.

20. R. Gachter and H. Muller, Ed., Plastic additive handbook. New York: Hanser Publisher, 1987.

21. Karian, H. G. Handbook of polypropylene and polypropylene composites. New York: Marcel Dekker, Inc, 1999.

22. www.mse.iastate.edu/microscopy/path.html, SEM, March 2005

23. Mansion, J. A., and Sperling, L. H. Polymer blend and composites. New York: Plenum Press, 1976: 337-410.

24. Sperling, L. H. Introduction to physical polymer science. New York: John Wiley & Sons, 1992.

25. Thiebaud, S., Borrendon, M. E. Solvent-free wood esterification with fatty acid chloride. Bioresource Technology 52 (1995): 169-173.

26. Sagar, A. D. and Merrill, E. W. Properties of fatty-acid ester of starch. Journal of Applied Polymer Science 58 (1995): 1647-1656.

27. Thiebaud, S., Borrendon, M. E., Baziard, G. and Senocq, F. Properties of wood esterified by fatty- acid chlorides. Bioresource Technology 59 (1997): 103-107.

28. Thiebaud, S., Aburto, J., Alric, I., Borredon, E., Bikiaris, D., Prinos, J. and Panayiotou, C. Properties of fatty-acid ester of starch and their blends with LDPE. Journal of Applied Polymer Science 65 (1997): 705-721.

29. Aburto, J., Alric, I., Thiebaud, S., Borredon, E., Bikiaris, D., Prinos, J. and Panayiotou, C. Synthesis, characterization, and biodegradation of fatty-acid ester of amylose and starch. Journal of Applied Polymer Science 74 (1999): 1440-1451.
30. Wu, J., Yu, D., Chan, C. M., Kim, J. and Mai, Y. W. Effect of fiber pretreatment condition on the interfacial strength and mechanical properties of wood fiber/PP composites. Journal of Applied Polymer Science 76 (2000): 1000-1010.
31. Basu, D., Datta, C. and Banerjee, A. Biodegradability, mechanical properties, melt flow index, and morphology of polypropylene/amylose/amylose-ester blends. Journal of Applied Polymer Science 85 (2002): 1434-1442.
32. Hristov, V. N., Krumova, M., Vasileva, St. and Michler, G. H. Modified polypropylene wood flour composites. II. fracture, deformation, and mecanical properties. Journal of Applied Polymer Science 92 (2004): 1286-1292.
33. Suarez, J. C. M., Coutinho, F. M. B. and Sydenstricker, T. H. SEM studied of tensile fracture surface of polypropylene-sawdust composites. Polymer Testing 22 (2003): 819-824.
34. Coutinho, F. M. B., Costa, T.H.S., Suarez, J. C. M. and Melo, D. P. Sawdust reinforced polypropylene: a study of fracture behavior. Polymer Testing 19 (2000): 625-633.
35. Oksman, K. and Clemons, C. Mechanical properties and morphology of impact modified polypropylene-wood flour composites. Journal of Applied Polymer Science 69 (1998): 1503-1513.
36. Coutinho, F. M. B., Costa, T. H. S. and Carvalho, D. L. Polypropylene-wood fiber composites: effect of treatment and mixing conditions on mechanical properties. Journal of Applied Polymer Science 9 (1997): 1227-1235.
37. Li, T. Q., Ng, C. N. and Li, R.Y.K. Impact behavior of sawdust/recycled-PP composites. Journal of Applied Polymer Science 81 (2001): 1420-1428.
38. Geng, Y., Li, K. and Simonsen, J. Effects of a new compatibilizer system on the flexural properties of wood-polypropylene composites. Journal of Applied Polymer Science 91 (2004): 3667-3672.

APPENDICES

APPENDIX A : Mechanical Properties

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/4/47	15:54:00		TRUE	50	25	6	3.16
28/4/47	15:57:15		TRUE	50	25	6	3.33
28/4/47	15:58:54		TRUE	50	25	6	3.23
28/4/47	16:01:10		TRUE	50	25	6	3.33
28/4/47	16:01:10		TRUE	50	25	6	3.23

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP	1	26	60		27.126	24.336	2063.00
PP	2	26	60		26.971	28.132	2359.00
PP	3	26	60		27.633	25.632	2132.00
PP	4	26	60		27.120	25.890	2413.00
PP	5	26	60		26.910	26.010	1933.00
Mean					27.15	26.00	2.18
SD					0.29	1.37	0.20

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/4/47	16:04:49		TRUE	500	25	6	3.10
28/4/47	16:05:48		TRUE	500	25	6	3.10
28/4/47	16:06:45		TRUE	500	25	6	3.15
28/4/47	16:07:20		TRUE	500	25	6	3.20
28/4/47	16:08:50		TRUE	500	25	6	3.20

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+10%	1	26	60		24.336	20.825	2142.00
PP+10%	2	26	60		24.407	22.120	2210.00
PP+10%	3	26	60		24.212	22.659	2356.00
PP+10%	4	26	60		23.257	21.420	1846.00
PP+10%	6	26	60		25.888	23.676	2487.00
Mean					24.42	22.14	2.21
SD					0.94	1.10	0.24

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/4/47	16:32:00		TRUE	500	25	6	3.66
28/4/47	16:32:27		TRUE	500	25	6	3.44
28/4/47	16:32:50		TRUE	500	25	6	3.44
28/4/47	16:33:16		TRUE	500	25	6	3.45
28/4/47	16:33:42		TRUE	500	25	6	3.42

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+20%	1	26	60		19.953	13.27	2684.00
PP+20%	2	26	60		19.56	13.701	2876.00
PP+20%	3	26	60		20.213	12.342	2847.00
PP+20%	4	26	60		19.316	13.673	2371.00
PP+20%	5	26	60		20.408	12.214	2622.00
Mean					19.89	13.04	2.68
SD					0.45	0.72	0.21

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/4/47	16:34:50		TRUE	500	25	6	3.36
28/4/47	16:35:19		TRUE	500	25	6	3.22
28/4/47	16:35:49		TRUE	500	25	6	3.18
28/4/47	16:36:21		TRUE	500	25	6	3.21
28/4/47	16:36:54		TRUE	500	25	6	3.16

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+30%	1	26	60		16.896	8.770	3441.00
PP+30%	2	26	60		16.965	8.760	2885.00
PP+30%	3	26	60		18.270	7.365	3089.00
PP+30%	4	26	60		17.882	9.373	3454.00
PP+30%	5	26	60		18.037	7.782	2831.00
Mean					17.61	8.41	3.14
SD					0.64	0.82	0.30

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/4/47	16:17:44		TRUE	500	25	6	3.31
28/4/47	16:18:17		TRUE	500	25	6	3.17
28/4/47	16:19:09		TRUE	500	25	6	3.18
28/4/47	16:19:47		TRUE	500	25	6	3.19
28/4/47	16:20:19		TRUE	500	25	6	3.21

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+40%	1	26	60		15.06	5.322	3448.00
PP+40%	2	26	60		16.282	4.949	2777.00
PP+40%	3	26	60		15.969	4.858	3908.00
PP+40%	4	26	60		15.385	4.568	4380.00
PP+40%	5	26	60		15.654	9.303	4405.00
Mean					15.67	5.8	3.78
SD					0.48	1.98	0.69

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/4/47	16:22:58		TRUE	500	25	6	3.2
28/4/47	16:24:17		TRUE	500	25	6	3.21
28/4/47	16:24:57		TRUE	500	25	6	3.21
28/4/47	16:25:29		TRUE	500	25	6	3.21
28/4/47	16:26:06		TRUE	500	25	6	3.26

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+50%	1	26	60		13.187	4.958	4120.00
PP+50%	2	26	60		13.204	3.315	4320.00
PP+50%	3	26	60		12.362	4.164	3260.00
PP+50%	4	26	60		14.838	4.548	4380.00
PP+50%	5	26	60		12.808	4.165	4520.00
Mean					13.28	4.23	4.12
SD					0.94	0.61	0.50

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/4/47	16:28:13		TRUE	500	25	6	3.3
28/4/47	16:29:03		TRUE	500	25	6	3.32
28/4/47	16:29:37		TRUE	500	25	6	3.39
28/4/47	16:30:06		TRUE	500	25	6	3.35
28/4/47	16:30:31		TRUE	500	25	6	3.56

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+10%, C4	1	26	60		27.457	19.433	2390.00
PP+10%, C4	2	26	60		25.904	20.760	2745.00
PP+10%, C4	3	26	60		26.956	19.416	2285.00
PP+10%, C4	4	26	60		26.810	19.754	2001.00
PP+10%, C4	5	26	60		27.323	19.637	2279.00
Mean					26.89	19.8	2.34
SD					0.61	0.56	0.27

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/4/47	16:10:19		TRUE	500	25	6	3.24
28/4/47	16:10:58		TRUE	500	25	6	3.28
28/4/47	16:11:34		TRUE	500	25	6	3.32
28/4/47	16:12:30		TRUE	500	25	6	3.17
28/4/47	16:13:16		TRUE	500	25	6	3.29

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+20%, C4	1	26	60		24.100	11.870	3101.00
PP+20%, C4	2	26	60		24.555	11.531	3340.00
PP+20%, C4	3	26	60		23.579	12.896	2940.00
PP+20%, C4	4	26	60		24.475	11.540	3046.00
PP+20%, C4	5	26	60		23.791	11.653	3323.00
Mean					24.10	11.87	3.15
SD					0.42	0.70	0.18

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/4/47	16:14:23		TRUE	500	25	6	3.19
28/4/47	16:15:00		TRUE	500	25	6	3.2
28/4/47	16:15:35		TRUE	500	25	6	3.24
28/4/47	16:16:06		TRUE	500	25	6	3.16
28/4/47	16:16:40		TRUE	500	25	6	3.17

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+30%, C4	1	26	60		21.261	7.360	3253.00
PP+30%, C4	2	26	60		21.538	6.966	3720.00
PP+30%, C4	3	26	60		20.687	8.123	4166.00
PP+30%, C4	4	26	60		22.023	6.637	2755.00
PP+30%, C4	5	26	60		21.241	8.114	3706.00
Mean					21.35	7.44	3.52
SD					0.52	0.67	0.54

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
29/6/47	14:28:03		TRUE	500	25	6	3.13
29/6/47	14:29:21		TRUE	500	25	6	3.19
29/6/47	14:30:19		TRUE	500	25	6	3.16
29/6/47	14:30:56		TRUE	500	25	6	3.17
29/6/47	14:31:40		TRUE	500	25	6	3.22

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+40%, C4	1	25	60	19/7/47	17.300	4.565	3786.00
PP+40%, C4	2	25	60	19/7/47	17.225	4.971	4345.00
PP+40%, C4	3	25	60	19/7/47	17.338	4.763	4060.00
PP+40%, C4	4	25	60	19/7/47	17.659	4.475	4189.00
PP+40%, C4	5	25	60	19/7/47	16.512	5.776	3920.00
Mean					17.21	4.91	4.06
SD					0.42	0.52	0.22

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
29/6/47	14:35:02		TRUE	500	25	6	2.99
29/6/47	14:35:49		TRUE	500	25	6	2.95
29/6/47	14:36:27		TRUE	500	25	6	2.94
29/6/47	14:37:10		TRUE	500	25	6	2.95
29/6/47	14:37:41		TRUE	500	25	6	2.92

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+50%, C4	1	25	60	19/7/47	14.207	3.199	4365.00
PP+50%, C4	2	25	60	19/7/47	13.78	3.359	4761.00
PP+50%, C4	3	25	60	19/7/47	14.531	2.941	3962.00
PP+50%, C4	4	25	60	19/7/47	13.612	4.195	4441.00
PP+50%, C4	5	25	60	19/7/47	14.924	2.906	4371.00
Mean					14.21	3.32	4.38
SD					0.54	0.52	0.53

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
10/8/47	15:27:41		TRUE	500	25	6	3.19
10/8/47	15:28:27		TRUE	500	25	6	3.19
10/8/47	15:28:58		TRUE	500	25	6	3.21
10/8/47	15:29:41		TRUE	500	25	6	3.32
10/8/47	15:30:45		TRUE	500	25	6	3.32

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+10% C12	1	25	70	19/7/47	21.711	26.698	2498.00
PP+10% C12	2	25	70	19/7/47	21.682	26.680	1263.00
PP+10% C12	3	25	70	19/7/47	22.111	26.536	2385.00
PP+10% C12	4	25	70	19/7/47	22.064	26.206	2131.00
PP+10% C12	5	25	70	19/7/47	22.382	25.830	2323.00
Mean					21.99	26.39	2.12
SD					0.29	0.37	0.50

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
10/8/47	15:30:59		TRUE	500	25	6	3.06
10/8/47	15:32:27		TRUE	500	25	6	3.14
10/8/47	15:33:09		TRUE	500	25	6	3.12
10/8/47	15:33:33		TRUE	500	25	6	3.11
10/8/47	15:34:01		TRUE	500	25	6	3.14

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+20%, C12	1	25	70	19/7/47	17.947	14.586	1443.00
PP+20%, C12	2	25	70	19/7/47	17.713	14.133	1493.00
PP+20%, C12	3	25	70	19/7/47	18.193	13.927	2245.00
PP+20%, C12	4	25	70	19/7/47	18.053	14.433	2258.00
PP+20%, C12	5	25	70	19/7/47	18.094	13.921	1511.00
Mean					18.00	14.20	1.79
SD					0.18	0.30	0.42

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
10/8/47	15:35:25		TRUE	500	25	6	3.17
10/8/47	15:35:58		TRUE	500	25	6	3.11
10/8/47	15:36:32		TRUE	500	25	6	3.04
10/8/47	15:37:03		TRUE	500	25	6	3.04
10/8/47	15:37:30		TRUE	500	25	6	3.05

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+30%, C12	1	25	70	19/7/47	15.599	8.745	1878.00
PP+30%, C12	2	25	70	19/7/47	15.47	8.954	1756.00
PP+30%, C12	3	25	70	19/7/47	16.046	8.56	1336.00
PP+30%, C12	4	25	70	19/7/47	16.597	8.521	1454.00
PP+30%, C12	5	25	70	19/7/47	16.188	8.369	1628.00
Mean					15.98	8.63	1.61
SD					0.46	0.23	0.48

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
10/8/47	15:38:38		TRUE	500	25	6	3.27
10/8/47	15:39:13		TRUE	500	25	6	3.37
10/8/47	15:39:43		TRUE	500	25	6	3.34
10/8/47	15:40:14		TRUE	500	25	6	3.32
10/8/47	15:40:40		TRUE	500	25	6	3.28

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+40%, C12	1	25	70	19/7/47	13.893	6.367	1592.00
PP+40%, C12	2	25	70	19/7/47	13.489	6.359	1686.00
PP+40%, C12	3	25	70	19/7/47	14.024	6.173	1242.00
PP+40%, C12	4	25	70	19/7/47	14.206	6.159	1440.00
PP+40%, C12	5	25	70	19/7/47	14.438	6.046	1236.00
Mean					14.01	6.22	1.44
SD					0.36	0.14	0.20

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
10/8/47	15:50:39		TRUE	500	25	6	2.89
10/8/47	15:51:09		TRUE	500	25	6	2.83
10/8/47	15:51:36		TRUE	500	25	6	2.97
10/8/47	15:52:14		TRUE	500	25	6	2.9
10/8/47	15:52:41		TRUE	500	25	6	2.86

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+50%, C12	1	25	70	19/7/47	12.139	5.009	1188.00
PP+50%, C12	2	25	70	19/7/47	11.872	6.634	1097.00
PP+50%, C12	3	25	70	19/7/47	12.393	3.789	1221.00
PP+50%, C12	4	25	70	19/7/47	12.435	4.181	1620.00
PP+50%, C12	5	25	70	19/7/47	12.006	4.737	1174.00
Mean					12.17	4.87	1.26
SD					0.24	1.10	0.21

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/9/47	14:15:45		TRUE	500	25	6	3.12
28/9/47	14:16:29		TRUE	500	25	6	3.08
28/9/47	14:17:07		TRUE	500	25	6	3.09
28/9/47	14:18:20		TRUE	500	25	6	3.09
28/9/47	14:19:45		TRUE	500	25	6	3.10

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+10%, C18	1	25	70		20.662	28.144	1595.00
PP+10%, C18	2	25	70		21.510	27.997	1797.00
PP+10%, C18	3	25	70		20.281	28.196	2168.00
PP+10%, C18	4	25	70		21.563	26.962	1728.00
PP+10%, C18	5	25	70		19.250	28.701	2345.00
Mean					20.65	28.00	1.93
SD					0.96	0.64	0.32

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/9/47	14:19:24		TRUE	500	25	6	2.93
28/9/47	14:20:00		TRUE	500	25	6	2.88
28/9/47	14:20:39		TRUE	500	25	6	2.9
28/9/47	14:21:39		TRUE	500	25	6	2.92
28/9/47	14:23:09		TRUE	500	25	6	2.93

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+20%, C18	1	25	70		16.549	15.981	1607.00
PP+20%, C18	2	25	70		16.566	14.850	1923.00
PP+20%, C18	3	25	70		16.573	14.484	1676.00
PP+20%, C18	4	25	70		15.891	15.191	2125.00
PP+20%, C18	5	25	70		17.071	15.350	1853.00
Mean					16.53	15.17	1.84
SD					0.42	0.56	0.21

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/9/47	14:22:01		TRUE	500	25	6	3.12
28/9/47	14:22:37		TRUE	500	25	6	3.11
28/9/47	14:23:10		TRUE	500	25	6	3.15
28/9/47	14:24:19		TRUE	500	25	6	3.15
28/9/47	14:25:10		TRUE	500	25	6	3.05

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+30%, C18	1	25	70		13.513	8.500	1127.00
PP+30%, C18	2	25	70		14.668	10.871	1371.00
PP+30%, C18	3	25	70		13.576	9.344	1501.00
PP+30%, C18	4	25	70		14.021	9.362	1390.00
PP+30%, C18	5	25	70		14.222	8.530	1811.00
Mean					14.00	9.32	1.44
SD					0.47	0.96	0.25

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/9/47	14:27:01		TRUE	500	25	6	3.11
28/9/47	14:28:37		TRUE	500	25	6	3.43
28/9/47	14:29:10		TRUE	500	25	6	3.00
28/9/47	14:31:15		TRUE	500	25	6	3.06
28/9/47	14:32:23		TRUE	500	25	6	3.20

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+40%, C18	1	25	70		13.010	8.100	1326.00
PP+40%, C18	2	25	70		12.200	7.113	1157.00
PP+40%, C18	3	25	70		11.489	6.951	1049.00
PP+40%, C18	4	25	70		11.916	6.644	1637.00
PP+40%, C18	5	25	70		11.385	6.251	1031.00
Mean					12	7.01	1.24
SD					0.65	0.69	0.25

Tensile Test ASTM D638

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/9/47	14:35:00		TRUE	500	25	6	3.32
28/9/47	14:36:23		TRUE	500	25	6	3.01
28/9/47	14:37:25		TRUE	500	25	6	3.05
28/9/47	14:38:30		TRUE	500	25	6	3.10
28/9/47	14:39:35		TRUE	500	25	6	3.01

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+50%, C18	1	25	70		10.056	4.860	864.00
PP+50%, C18	2	25	70		9.874	5.416	1188.00
PP+50%, C18	3	25	70		9.742	5.513	931.00
PP+50%, C18	4	25	70		9.833	5.762	1025.00
PP+50%, C18	5	25	70		10.395	6.110	947.00
Mean					9.98	5.53	0.99
SD					0.26	0.46	0.12

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/4/47	16:38:51		TRUE	500	25	6	3.40
28/4/47	16:39:19		TRUE	500	25	6	3.48
28/4/47	16:39:44		TRUE	500	25	6	3.40
28/4/47	16:40:13		TRUE	500	25	6	3.33
28/4/47	16:41:25		TRUE	500	25	6	3.41

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+20%, 20%ester	1	26	60		22.021	12.383	2868.00
PP+20%, 20%ester	2	26	60		19.418	13.121	2653.00
PP+20%, 20%ester	3	26	60		18.820	13.348	2493.00
PP+20%, 20%ester	4	26	60		19.260	13.122	2847.00
PP+20%, 20%ester	5	26	60		20.481	12.526	2639.00
Mean					20.00	12.90	2.70
SD					1.28	0.42	0.16

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/4/47	16:10:19		TRUE	500	25	6	3.24
28/4/47	16:10:58		TRUE	500	25	6	3.28
28/4/47	16:11:34		TRUE	500	25	6	3.32
28/4/47	16:12:30		TRUE	500	25	6	3.17
28/4/47	16:13:16		TRUE	500	25	6	3.29

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+20%, 50%ester	1	26	60		24.100	11.870	3101.00
PP+20%, 50%ester	2	26	60		24.555	11.531	3340.00
PP+20%, 50%ester	3	26	60		23.579	12.896	2940.00
PP+20%, 50%ester	4	26	60		24.475	11.540	3046.00
PP+20%, 50%ester	5	26	60		23.791	11.653	3323.00
Mean					24.10	11.87	3.15
SD					0.42	0.70	0.18

Tensile Test ASTM D638-02

Date	Time	User	Sample Passed	Test Speed (mm/min)	Gauge Length (mm)	Width (mm)	Thickness (mm)
28/4/47	16:41:26		TRUE	500	25	6	3.38
28/4/47	16:41:48		TRUE	500	25	6	3.40
28/4/47	16:42:30		TRUE	500	25	6	3.32
28/4/47	16:42:54		TRUE	500	25	6	3.33
28/4/47	16:43:15		TRUE	500	25	6	3.30

Batch Reference	Sample Reference	Temperature	Humidity	Date of Vulcanisation	Tensile Strength (MPa)	Ultimate Elongation (%)	Tensile Modulus (MPa)
PP+20%, 80%ester	1	26	60		24.252	11.045	3101.00
PP+20%, 80%ester	2	26	60		24.149	11.568	3440.00
PP+20%, 80%ester	3	26	60		24.159	11.049	2971.00
PP+20%, 80%ester	4	26	60		23.637	11.655	3015.00
PP+20%, 80%ester	5	26	60		24.703	10.883	3073.00
Mean					24.18	11.24	3.12
SD					0.38	0.35	0.19

Impact strength ASTM D256-02

Specimen	Width (mm)	Impact strength (J/cm)	Specimen	Width (mm)	Impact strength (J/cm)
Detail: 10%, unesterified			Detail: 10%, C4		
1	3.15	6.780	1	3.02	6.075
2	3.15	5.845	2	3.02	6.000
3	3.10	5.951	3	3.05	6.015
4	3.10	4.942	4	3.05	5.902
5	3.10	5.932	5	3.00	6.108
mean		5.89	mean		6.02
SD		0.65	SD		0.08
Detail: 20%, unesterified			Detail: 20%, C4		
1	3.10	5.079	1	2.95	5.845
2	3.10	6.105	2	2.95	5.655
3	3.10	4.272	3	2.95	5.486
4	3.10	4.508	4	3.00	5.758
5	3.10	5.386	5	2.95	5.690
mean		5.07	mean		5.69
SD		0.73	SD		0.13
Detail: 30%, unesterified			Detail: 30%, C4		
1	2.85	4.299	1	3.05	4.00
2	2.85	4.223	2	3.05	4.255
3	2.80	5.536	3	3.05	5.213
4	2.80	3.995	4	3.00	4.413
5	2.85	3.147	5	3.00	4.469
mean		4.24	mean		4.7
SD		0.86	SD		0.45
Detail: 40%, unesterified			Detail: 40%, C4		
1	2.90	3.944	1	3.12	4.395
2	2.85	3.625	2	3.12	4.095
3	2.9	3.307	3	3.12	3.823
4	2.90	3.307	4	3.10	3.924
5	2.90	4.166	5	3.10	4.163
mean		3.67	mean		4.08
SD		0.38	SD		0.22
Detail: 50%, unesterified			Detail: 50%, C4		
1	3.00	3.304	1	3.00	3.271
2	3.00	2.998	2	3.05	3.195
3	3.00	2.105	3	3.05	2.842
4	3.12	2.693	4	3.05	3.280
5	3.12	3.900	5	3.00	3.362
mean		3.00	mean		3.19
SD		0.67	SD		0.20

Impact strength ASTM D256-02

Specimen	Width (mm)	Impact strength (J/cm)	Specimen	Width (mm)	Impact strength (J/cm)
Detail: 10%, C12			Detail: 10%, C18		
1	3.05	6.419	1	3.10	6.419
2	3.10	6.81	2	3.10	6.54
3	3.10	6.537	3	3.10	6.176
4	3.05	5.758	4	3.05	6.625
5	3.10	6.525	5	3.00	6.844
mean		6.41	mean		6.52
SD		0.39	SD		0.24
Detail: 20%, C12			Detail: 20%, C18		
1	3.00	6.419	1	3.00	6.015
2	3.00	5.932	2	3.00	5.845
3	3.05	6.015	3	3.15	5.960
4	3.05	5.986	4	2.95	6.105
5	3.10	5.967	5	3.00	6.275
mean		6.01	mean		6.04
SD		0.26	SD		0.16
Detail: 30%, C12			Detail: 30%, C18		
1	3.00	5.176	1	2.90	5.536
2	3.00	5.223	2	2.90	5.254
3	3.00	5.068	3	2.95	5.176
4	3.06	4.942	4	3.00	4.817
5	3.06	5.542	5	3.05	5.917
mean		5.19	mean		5.34
SD		0.22	SD		0.41
Detail: 40%, C12			Detail: 40%, C18		
1	2.90	3.842	1	3.00	4.331
2	2.90	4.272	2	3.00	4.304
3	2.90	4.299	3	3.00	4.299
4	3.00	4.372	4	3.00	5.254
5	3.00	4.464	5	3.05	3.862
mean		4.25	mean		4.41
SD		0.24	SD		0.51
Detail: 50%, C12			Detail: 50%, C18		
1	2.90	3.944	1	3.0	4.105
2	2.85	3.624	2	2.95	4.056
3	2.85	3.842	3	2.95	3.944
4	2.90	3.728	4	3.00	3.842
5	2.90	3.661	5	3.00	4.153
mean		3.76	mean		4.02
SD		0.13	SD		0.13

Impact strength D256-02

Specimen	Width (mm)	Impact strength (J/cm)
Detail: PP		
1	2.85	3.944
2	2.85	4.272
3	2.90	3.625
4	2.85	3.693
5	2.90	4.316
mean		3.97
SD		0.32
Detail: 20%, 0% ester		
1	3.10	5.079
2	3.10	6.105
3	3.10	4.272
4	3.10	4.508
5	3.10	5.386
mean		5.07
SD		0.73
Detail: 20%, 20% ester		
1	3.00	5.223
2	2.95	5.095
3	2.95	4.942
4	3.00	4.845
5	3.00	5.395
mean		5.10
SD		0.22
Detail: 20%, 50% ester		
1	2.95	5.845
2	2.95	5.655
3	2.95	5.486
4	3.00	5.758
5	2.95	5.690
mean		5.69
SD		0.13
Detail: 20%, 80% ester		
1	2.85	4.944
2	2.85	4.657
3	2.80	5.176
4	2.80	5.216
5	2.85	5.007
mean		5.00
SD		0.22

Rockwell Hardness D785-03

Specimen	Width (mm)	Hardness	Specimen	Width (mm)	Hardness
Detail: 10%, unesterified			Detail: 10%, C4		
1	5.85	91.8	1	5.60	95.6
2	5.85	92.3	2	5.60	92.5
3	5.80	90.5	3	5.60	96.2
4	5.80	90.6	4	5.60	96.0
5	5.85	87.0	5	5.60	92.4
mean		90.1	mean		94.5
SD		2.07	SD		1.92
Detail: 20%, unesterified			Detail: 20%, C4		
1	5.80	93.8	1	5.80	97.3
2	5.80	92.2	2	5.80	97.5
3	5.75	92.5	3	5.75	96.8
4	5.75	92.1	4	5.75	95.7
5	5.80	93.5	5	5.80	96.7
mean		92.8	mean		96.8
SD		0.80	SD		0.70
Detail: 30%, unesterified			Detail: 30%, C4		
1	5.95	95.6	1	5.95	96.6
2	5.90	94.5	2	5.85	96.8
3	5.95	94.4	3	5.95	97.0
4	5.90	94.4	4	5.95	97.4
5	5.90	96.0	5	5.90	98.2
mean		95.0			97.2
SD		0.76			0.63
Detail: 40%, unesterified			Detail: 40%, C4		
1	6.00	95.5	1	6.10	100.1
2	6.00	97.2	2	6.00	98.0
3	5.95	97.0	3	6.00	100.3
4	5.90	96.6	4	5.95	99.5
5	5.90	96.9	5	6.00	99.6
mean		96.6	mean		99.5
SD		0.67	SD		0.90
Detail: 50%, unesterified			Detail: 50%, C4		
1	5.80	97.8	1	5.75	102.5
2	5.85	98.9	2	5.70	100.7
3	5.75	98.7	3	5.80	103.1
4	5.80	96.7	4	5.80	103.7
5	5.85	100.4	5	5.80	105.5
mean		98.5	mean		103.1
SD		1.37	SD		1.50

Rockwell Hardness D785-03

Specimen	**Width (mm)**	**Hardness**	**Specimen**	**Width (mm)**	**Hardness**
Detail: 10%, C12			Detail: 10%, C18		
1	5.70	83.3	1	5.70	78.1
2	5.80	85.8	2	5.75	71.9
3	5.85	89.1	3	5.75	74.2
4	5.80	83.7	4	5.80	76.7
5	5.80	86.1	5	5.70	89.6
mean		85.6	mean		77.6
SD		2.31	SD		6.85
Detail: 20%, C12			Detail: 20%, C18		
1	5.95	82	1	6.00	70.4
2	5.95	75.1	2	6.00	73.2
3	5.90	85.6	3	5.95	69.9
4	6.00	83.7	4	5.80	72.4
5	6.00	75.8	5	5.85	80.1
mean		80.4	mean		73.2
SD		4.73	SD		4.09
Detail: 30%, C12			Detail: 30%, C18		
1	5.80	78.1	1	5.80	68.2
2	5.85	76.7	2	5.80	64.3
3	5.75	79.9	3	5.80	70.4
4	5.80	81.4	4	5.90	67.0
5	5.80	79.9	5	5.85	67.1
mean		79.2			67.4
SD		1.82			2.20
Detail: 40%, C12			Detail: 40%, C18		
1	5.90	79.2	1	5.70	64.4
2	5.95	74.4	2	5.65	68.2
3	6.00	77.1	3	5.70	60.9
4	6.00	75.1	4	5.75	67.4
5	6.00	69.4	5	5.75	60.6
mean		75.0	mean		64.3
SD		3.66	SD		3.53
Detail: 50%, C12			Detail: 50%, C18		
1	5.75	75.2	1	5.80	64.3
2	5.75	75	2	5.80	59.6
3	5.80	73.9	3	5.85	61.4
4	5.80	73.2	4	5.90	60.3
5	5.85	76.3	5	5.95	58.9
mean		74.7	mean		60.9
SD		1.20	SD		2.11

Rockwell Hardness D785-03

Specimen	Width (mm)	Hardness
Detail: PP		
1	5.60	85.6
2	5.60	84.8
3	5.65	87.8
4	5.70	85.2
5	5.65	90.5
mean		86.8
SD		2.38
Detail: 20%, 0% ester		
1	5.80	93.8
2	5.80	92.2
3	5.75	92.5
4	5.75	92.1
5	5.80	93.5
mean		92.8
SD		0.80
Detail: 20%, 20% ester		
1	5.90	95.9
2	5.90	94.1
3	5.80	95.9
4	5.85	92
5	5.85	95.8
mean		94.9
SD		1.68
Detail: 20%, 50% ester		
1	5.80	97.3
2	5.80	97.5
3	5.75	96.8
4	5.75	95.7
5	5.80	96.7
mean		96.8
SD		0.70
Detail: 20%, 80% ester		
1	6.00	97.4
2	5.90	96.9
3	5.90	96.7
4	5.95	96.3
5	5.90	97.2
mean		96.9
SD		0.43

APPENDIX B : Thermal properties

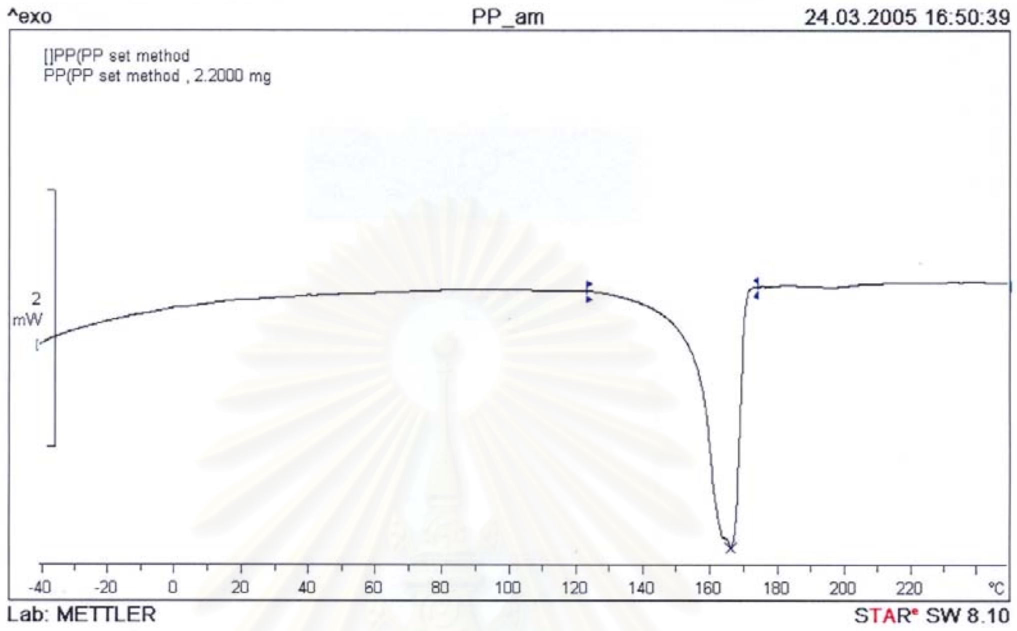


Figure B1 DSC thermogram of polypropylene.

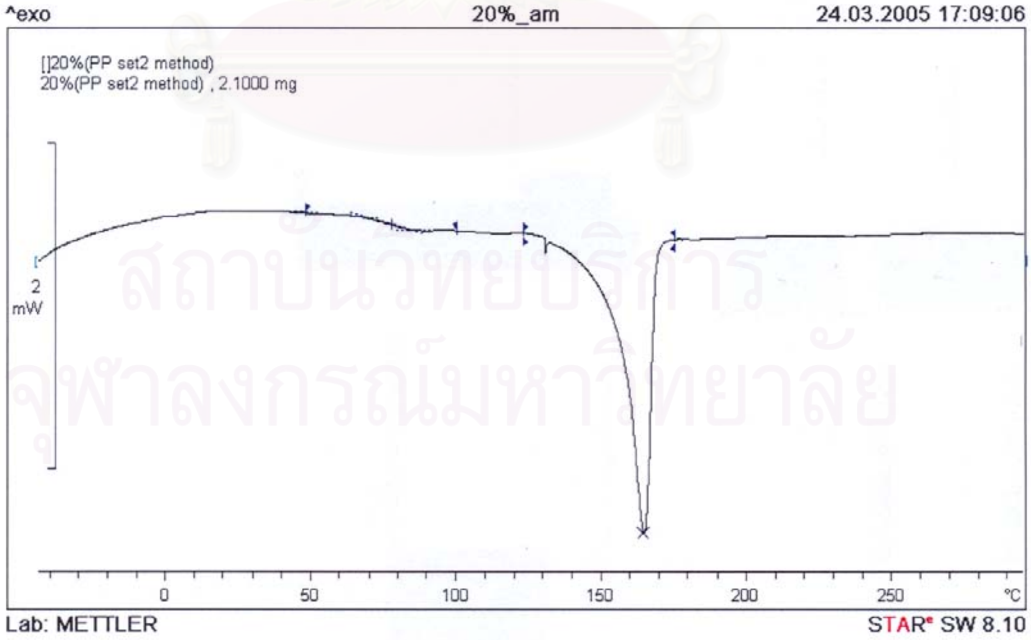


Figure B2 DSC thermogram of the composites with unesterified sawdust.

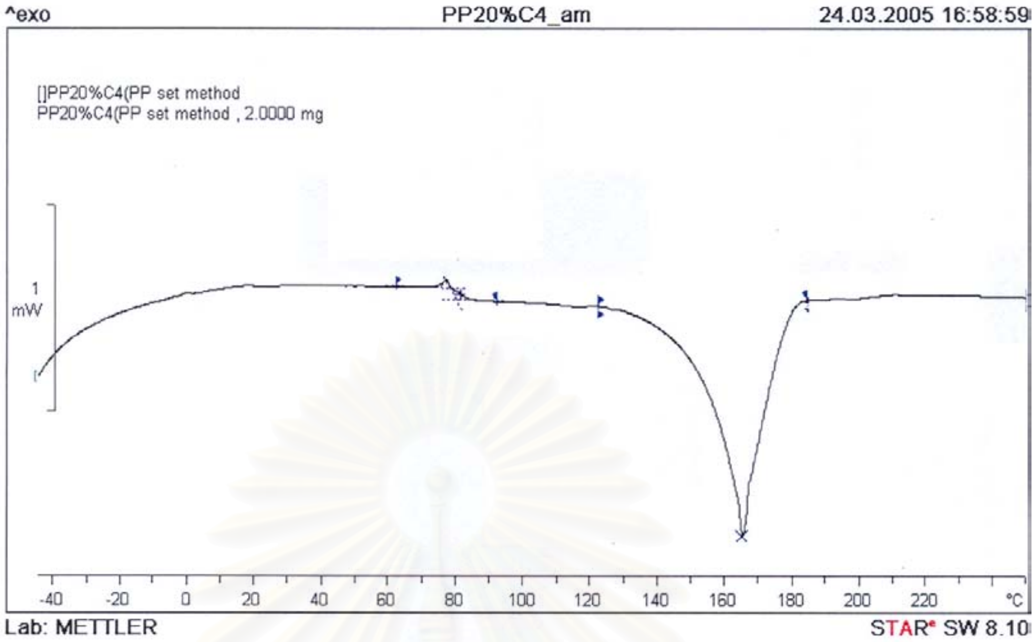


Figure B3 DSC thermogram of the composites with butyrated sawdust.

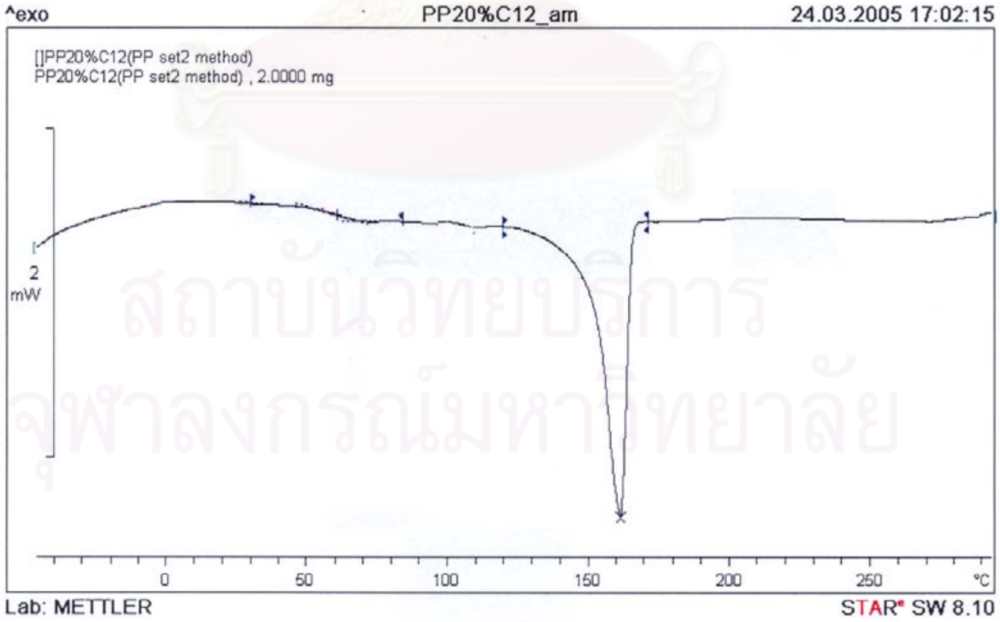


Figure B4 DSC thermogram of the composites with dodecanoated sawdust.

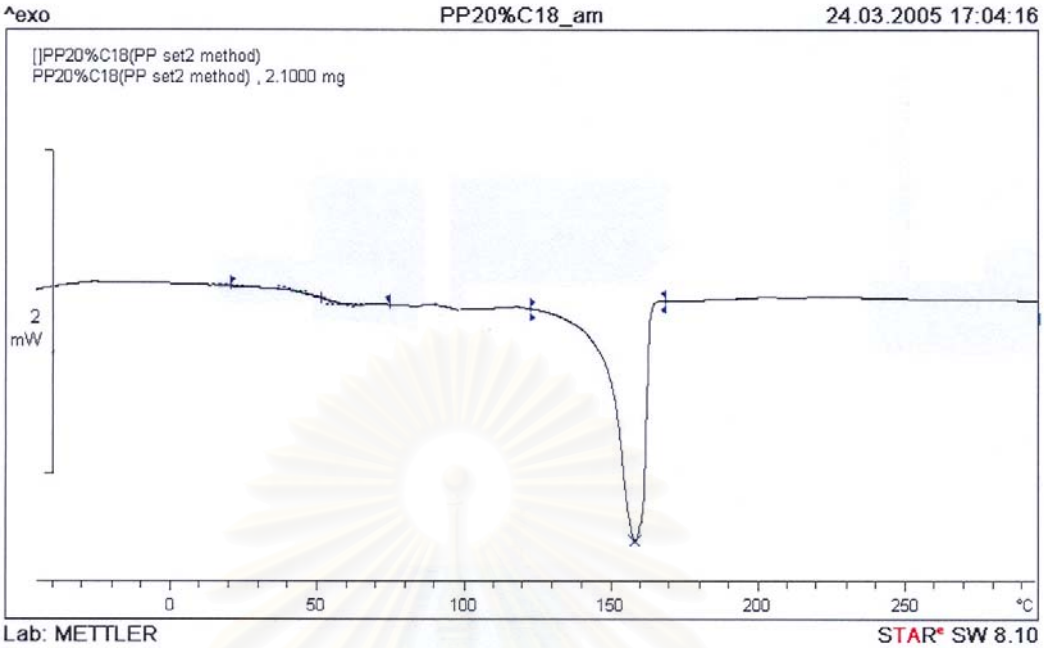


Figure B5 DSC thermogram of the composites with stearoated sawdust.

APPENDIX C

PHYSICAL PROPERTIES OF POLYPROPYLENE BLOCK-COPOLYMER

POLENE 2300 NC

Typical data	Unit	Value	Test method
Property			
MFI 2.16 kg/230°C	g/10min	10	ASTM D 1238
Tensile strength at yield	N/mm^2	27	ASTM D 638
Charpy notched impact strength			
at -20°C	mJ/mm^2	3.3	DIN 53453
Shear modulus	N/mm^2	590	DIN 53457
Ball indentation hardness	N/mm^2	74	DIN 53456
Heat distortion temperature			
at 0.45 N/mm^2	°C	98	ASTM D 648
Application			
Injection molding			
high impact, high flow			
for automotive industry			
Processing temperature 190-280°C			

Remark : the values presented on the above are typical laboratory average.

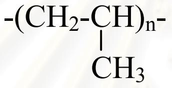
ISSUE NO. 01 13 03 REV.01

MATERIAL SAFETY DATA SHEET

POLYPROPYLENE

Type general

Section I

Chemical name	Polypropylene resin
Trade name	Polene
Synnonyms	PP
Chemical family	Thermoplastic resin
Formula	 $-(CH_2-\underset{CH_3}{\underset{\vert}{CH}})_n-$
CAS registry no.	9003-07-0

Section II – Physical data

Boiling point (°C)	-	Vapor density	-
Melting point (°C)	165	Volatile material (%)	< 0.5
Decomposition temp. (°C)	-	Water absorption	0.01-0.03 %of
Specific gravity	0.900-0.907		volume
Solubility in water	Insoluble	Gas transmission-rate	187 cc of O2
Appearance	Pellet		through 1 mill
pH	N/A		film / 24 /100 in^2
Abrasion resistance	Good		/ 1 atm
Vapor Pressure (mm Hg)	-	ODOR	N/A
At 20 (°C)			

Section III – Fire and explosion hazard data

Burning rate	slow
Flammability	will burn with blue flame

Section IV – Chemical stability data

Resistance to	Result
Acids	Good
Bases	Excellent
Solvents	Good, excellent againt fuels and gasoline
Oils and fats	Excellent
Sunlight	Poor, craze
Bacteria and fungi attack	will not support growth

Section V – Toxicity data

Some food – containing grade are available

ISSUE NO 23 05 07 REV.01

VITA

Miss Nattiya Panyanuch was born in Bangkok, Thailand, on October 10, 1979. She received the Bachelor's Degree in Chemistry from the Faculty of science, Burapha University in 2001. She has been a graduate student in the Program of Petrochemistry and Polymer Science, Faculty of Science, Chulalongkorn University since 2002 and finished her study in 2005.