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DEVELOPMENT OF WOOD-SUBSTITUTED COMPOSITES FROM HIGHLY FILLED SYSTEMS OF POLYPROPYLENE AND *HEVEA BRASILLIENSIS* WOODFLOUR

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ในปัจจุบัน ได้มีการนำสารเติมที่ได้จากเส้นใยธรรมชาติมาใช้มากขึ้น โดยนำไปใช้ทดแทนสารเติมที่ได้จากการสังเคราะห์ในวัสดุพอลิเมอร์ประกอบแต่ง โดยเฉพาะอย่างยิ่งในวัสดุประกอบแต่งที่มีเทอร์โมพลาสติกเป็นเมตริกซ์ ผลิตภัณฑ์ที่ได้สามารถนำไปใช้แทนไม้ได้ในงานหลายประเภท เนื่องจากสารเติมจากเส้นใยธรรมชาติมีจุดเด่นคือ มีราคาถูก ไม่เป็นอันตรายต่อสิ่งแวดล้อม เกิดใหม่ได้เองในธรรมชาติและช่วยปรับปรุงสมบัติหลายประการของวัสดุพอลิเมอร์ให้ดีขึ้นได้ ในงานวิจัยนี้ได้ทำการเตรียมวัสดุประกอบแต่งระหว่างผงไม้ยางพารา และ พอลิพรอพิลีน ด้วยเครื่องอัดแบบสกรูคู่ แล้วขึ้นรูปเป็นชิ้นตัวอย่างด้วยเครื่องฉีดพลาสติก ในส่วนแรกของงานวิจัยนี้ศึกษาผลของขนาดอนุภาคเฉลี่ยของผงไม้ ปริมาณของผงไม้ และการกระจายตัวของขนาดอนุภาคที่มีผลต่อ สมบัติทางกล สมบัติทางความร้อน และสมบัติทางกายภาพของวัสดุประกอบแต่งที่ได้ โดยพบว่า วัสดุประกอบแต่งที่เตรียมจาก พอลิเมอร์เมตริกซ์ที่มีดัชนีการไหลตัวสูงสุดจะมีคุณสมบัติทางกลดีที่สุด โดยขนาดอนุภาคเฉลี่ย และปริมาณของสารเติมมีผลต่อคุณสมบัติทางกลของวัสดุประกอบแต่ง คือ ค่ามอดูลัสภายใต้แรงดัดโค้งและมอดูลัสภายใต้แรงดึงมีค่าเพิ่มขึ้น ส่วนความแข็งแรงภายใต้แรงดัดโค้งและความแข็งแรงภายใต้แรงดึงจะมีค่าลดลงเมื่อปริมาณผงไม้เพิ่มขึ้น ขนาดของอนุภาคเฉลี่ยของผงไม้ที่ให้สมบัติทางกลที่ดีที่สุดในการพัฒนาวัสดุประกอบแต่งนี้ คือ ขนาดอนุภาคเฉลี่ยที่อยู่ในช่วง 200-300 ไมโครเมตร สำหรับผลของการกระจายตัวของขนาดอนุภาคพบว่า ผงไม้ผสมที่ได้จากการผสมระหว่างอนุภาคขนาด 275 ไมโครเมตร และ 49 ไมโครเมตร ในปริมาณสัดส่วนโดยน้ำหนัก ของอนุภาคขนาดใหญ่ต่อขนาดเล็กเท่ากับ 73 : 27 จะมีค่าความหนาแน่นในการอัดตัวสูงที่สุด นอกจากนี้พบว่าเสถียรภาพทางความร้อนและอุณหภูมิการสลายตัวทางความร้อนของวัสดุประกอบแต่งจะมีค่าลดลงเมื่อปริมาณของผงไม้เพิ่มขึ้น ในส่วนที่สองของงานวิจัยจะศึกษาเกี่ยวกับผลของมาลิอิก แอนไฮไดรด์ กราฟต์ พอลิพรอพิลีน (MAPP) ซึ่งใช้เพื่อช่วยปรับปรุงการยึดเกาะของผงไม้กับพอลิพรอพิลีนเมตริกซ์ ที่มีต่อ คุณสมบัติทางกล ทางความร้อน และทางกายภาพของวัสดุประกอบแต่งที่ได้ พบว่าปริมาณการเติม MAPP ที่เหมาะสมที่สุดของระบบนี้คือการเติม MAPP ที่ 5 % โดยน้ำหนักของผงไม้ซึ่งช่วยให้คอมโพสิทที่ได้มีสมบัติทางกลที่ดีที่สุด โดยค่าความแข็งแรงภายใต้แรงดัดโค้งและแรงดึงมีค่าเพิ่มขึ้น 110% และ 87% เมื่อเทียบกับวัสดุประกอบแต่งที่ไม่ได้เติมMAPP นอกจากนั้นพบว่าเสถียรภาพทางความร้อนและอุณหภูมิการสลายตัวทางความร้อนของวัสดุประกอบแต่งมีค่าเพิ่มขึ้นเล็กน้อยเมื่อมีการเติม MAPP

ภาควิชา...........วิศวกรรมเคมี................ ลายมือชื่อนิสิต......สโรตม์ จิตตารมย์.......

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

ปีการศึกษา........2550..... ลายมือชื่ออาจารย์ที่ปรึกษาร่วม..............

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SAROT JITTAROM: DEVELOPMENT OF WOOD-SUBSTITUTED COMPOSITES FROM HIGHLY FILLED SYSTEMS OF POLYPROPYLENE AND *HEVEA BRASILLIENSIS* WOODFLOUR. THESIS ADVISOR: ASSIST. PROF. SARAWUT RIMDUSIT, Ph.D., THESIS COADVISOR: ASSIST. PROF. WATANACHAI SMITTAKORN, Ph.D., 116 pp.

In recent years, the natural fibers as reinforcement have been increasingly used to replace the conventional inorganic filler in polymer matrix composites. Especially, natural filler reinforced thermoplastics have a good potential in the future as a substitution for wood-based material in many applications. Natural fibers render several advantages, i.e. the filler cost is usually very low. Also, the natural fillers are biodegradable (thus contributing to an improved environmental impact). In addition, this kind of filler is naturally renewable as well. Moreover, many mechanical and thermal properties can be enhanced. In this work, *Hevea Brasiliensis* woodflour filled polypropylene composites were prepared by twin screw extruder followed by injection molding. In the first part of this study, the aims are to determine the effect of polypropylene types (PP-HP644T, PP-HP648N and PP-HP740H), average particle sizes, filler contents and sized distributions on the mechanical, thermal and some related physical properties. The experimental results revealed that the composites based on high melt flow rate polymer matrix (PP-HP644T) had higher mechanical properties than those of wood flour composites with PP-HP648N and PP-HP740H. For the effect of particle sizes, filler contents and sizes distributions, it was found that the particle sizes and woodflour contents played a significant role in the mechanical properties of wood flour composites. Flexural and tensile modulus increased, while flexural and tensile strength decreased with increasing woodflour contents. Furthermore, the average particle size of woodflour that was suitable for improving the mechanical properties of the composite was about 200-300 μm. The appropriate bimodal particle sizes that rendered the greatest packing density of wood flour were 275 μm and 49 μm at a mass ratio of 73:27. Additionally, it was found that the thermal stability and degradation temperature (at 5% weight loss) of wood flour composites decreased with increasing woodflour mass fraction. In the second part, maleic anhydride grafted polypropylene (MAPP) was used as a coupling agent to improve the interfacial bond strength between woodflour filler and polymer matrix. The influence of the amount of MAPP on mechanical and thermal properties of woodflour composites has been investigated. This work recommends MAPP content of 5 wt% (of woodflour) to be introduced into the woodflour composites for optimization of the composite mechanical properties. It was reported that the flexural and tensile strength were 110% and 87% higher than those of the woodflour composite without MAPP, respectively. The thermal stability and degradation temperature of woodflour composites containing the coupling agent were slightly increased with increasing coupling agent content.

Department...Chemical Engineering... Student's signature....Sarot Jittarom.....

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

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

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CHAPTER I

INTRODUCTION

1.1 Overview

Wood is a renewable natural resource which has been used by human being for a long period of time. It possesses many desirable physical properties which make it an ideal material for many different applications such as construction materials, vehicles for transportation, furniture applications, and etc. But nowadays, the forest are depleting because the natural wood is continuously and increasingly utilized. Therefore, searching for new materials to substitute the natural wood has been the focus of renewed interest. Rubber wood (*Hevea brasilliensis*), in particular, is considered a promising alternate raw material because of its rapid growth rate and short rotation rate.

Rubber tree (*Hevea brasilliensis*) is one of the most important plants for both economics of the country and of more than 6 million people (10% of population). Products from rubber trees include latex and sawlogs. For the sawlogs, it is derived from the cutting of rubber wood from plantation in the ages about 25 years. At the old ages, the rubber trees produce only small amount of latex which is not economically worthy. These timbers can be used as raw materials in many types of wood industries. During the year of 1997 – 2001, the amount of cut-down rate of rubber trees was about 150,000 – 230,000 rais per year, equivalent to the volume of wood at 5.1 – 8.7 million cubic meters. Rubber wood will be used for construction materials, furniture, toys and other products. During the year of 2001 – 2005, rubber trees could make a revenue for country about 2,311.77 – 8,017.77 million bahts as shown in table 1.1.

Table 1.1 The Amount of Export Value for Rubber Wood (www.doa.go.th)

Year	2001	2002	2003	2004	2005
Export value (million bahts)	2,311.07	4,183.21	5,983.04	8,317.92	8,017.77

Normally, the rubber plantation of 1 rai (1,600 m^2) can produce an average number of 40 cubic meters of rubber timber to feed wood factories. The amount of wood piece and sawdust, which are waste and valueless, is 7.5 cubic meter (or 18.75 % of 40 cubic meters). This high amount of waste has to be burnt or buried, which caused environmental pollution. The use of *Hevea brasilliensis* sawdust as a filler in polymer composites is a solution to the mentioned problems. The advantage from this solution is the reduction of the environmental pollution that occurs from the disposal of waste.

Over the past two decades, thermoplastic matrix composites have attracted considerable attention in engineering communities. For instance, thermoplastic composites have been widely used in the biomedical, automotive and infrastructure industries. In comparison with thermosetting matrix composites, thermoplastic composites have some advantages, such as fast mass production with a shorter manufacturing cycle time, better resistance to environmental hazards, and higher impact toughness. In particular, thermoplastic composites have the unique advantage of being reprocessable or recyclable through post thermoforming and fusion bonding subject to a reheating/cooling cycle (Friedrich et al., 2005).

In this research, the work will concentrate on the development of a new product derived from industrial processing waste for replacing the natural wood. The mixture of *Hevea brasilliensis* sawdust and polypropylene will be used. Polypropylene is selected to be used because it is a versatile thermoplastic polymer and compatible with many processing techniques. This kind of polymers can be used in many commercial applications. Furthermore, the outstanding benefit of polypropylene is its easiness to recycle. In comparison with PVC, polypropylene does not cause any environmental pollution. Moreover it has higher thermal and mechanical properties than both low density polyethylene (LDPE) and high density polyethylene (HDPE). However, one of the problems found during compositing with woodflour is the agglomeration of filler from insufficient dispersion. Some researchers (Premalal et al., 2006, and Mantia et al., 2005) studied about the rheological behavior of wood composites and reported that the increase in the viscosity of molten composites which resulted in processing difficulties and limited the production of woodflour composites with a high filler content. One way for minimizing these effects is to use polymer matrix with high melt flow rate (MFR), so that the increase in viscosity due to the presence of a significantly high concentration of woodflour could be compensated (Balasuriya et al., 2001).

However, few studies on this aspect have been reported. Qiu et al. (2006) examined the effect of molecular weight of polymer matrix on the properties of fibrous cellulose filled polypropylene composites. They found that the composites with higher molecular weight (low melt flow rate) revealed stronger tensile strength than lower molecular weight (high melt flow rate) at the same cellulose content. The result did not correspond to the work of Balasuriya et al. (2001) who suggested that the composites based on medium melt flow rate HDPE had higher mechanical properties than those of composites with low melt flow rate HDPE

The relationship between melt flow rate of polymer matrix and properties of composites is not clear. Therefore in this work, the effect of melt flow rate of polymer matrix on the properties of woodflour filled polypropylene composites were studied and reported.

Many of the recent works (Kim et al., 2007 and Yang et al., 2007) were focused on the effect of the filler contents and coupling treatment on the properties of wood composites. But, there is a few of the data available on the relationship between particle size and size distribution on the properties of woodflour composites. Thus, the effect of woodflour particle size, content and size distribution on the properties of woodflour composites are investigated.

In general, the main disadvantage of woodflour filler reinforced polymer composites is the inherent incompatibility between the hydrophilic filler and the hydrophobic polymer matrix. As a result, the lack of interfacial adhesion between filler and polymer matrix leads to the unsatisfactory properties of the resultant composites (Sombatsompop et al., 2005 and Danyadi et al., 2007). Hence, in order to improve the adhesion between filler and polymer matrix, coupling agent was considered to be used. The optimum dose of coupling agent applied in woodflur filled polypropylene composites was also determined in this research.

1.2 Objectives of the Research

1. To examine the effect of melt flow rate of polymer matrix on the mechanical properties of wood composites.
2. To study the effects of woodflour particle sizes, content and size distribution on the packing behaviors of polypropylene wood.
3. To investigate mechanical properties and some related physical properties of the obtained wood composites.
4. To examine the effects of coupling agents on the mechanical properties of wood composites.

1.3 Scopes of Research

1. Prepare polypropylene/*Hevea brasiliensis* woodflour at the ratios of 60:40 wt% using different type of polypropylene polymer matrix i.e. PP-HP740H, PP-HP648N and PP-HP644T.
2. Determine the effect of melt flow rate on the mechanical properties i.e. flexural properties and tensile properties of wood composite in (1).
3. Prepare polypropylene/*Hevea brasiliensis* woodflour at the ratios of 90:10, 80:20, 70:30, 60:40, 50:50, 40:60 wt% using filler average particle sizes in the range of 50 - 500 microns.

4. Examine the effect of particle sizes and woodflour content on the mechanical properties, dynamic mechanical properties and some physical properties of wood composite in (3).

5. Determine suitable bimodal particle size distribution of the *Hevea brasiliensis* woodflour and its packing behaviors in PP wood composites.

6. Investigate the effect of woodflour mixing ratios in (5) on flexural properties, tensile properties, dynamic mechanical properties and some essential thermal and physical properties of the wood composite.

7. Evaluate the effect of coupling agent content (0 - 20 wt% of woodflour) on the properties of the obtained wood composite.

CHAPTER II

THEORY

2.1 Composite Materials

Today, with the increasing demand for suitable material with specific properties, it has been clear that naturally occurring materials cannot fulfill all of the requirements. Developments in mankind's technologies have gone a long way towards fulfilling these requirements but even that is not enough (Tewary, 1978).
From the application point of view, an ideal material should be strong, tough and light. Metals and their alloys come close to satisfying these requirements because they are strong and tough but not very light. In addition, some covalent materials are strong but not tough. The plastics invented in this century are light but lack stiffness, strength and toughness. An obvious approach to attain an ideal material, therefore, would be the combination of two or more materials with complementary properties. Such composite materials should have the combined advantage of their constituents.

By definition (Low, 2006), composite materials are formed from two or more materials that have quite different properties. The resultant material has a heterogeneous microstructure with an extraordinary performance that displays a combination of the best characteristics of the component materials. Composites are widely used because their overall properties can be engineered through micro-structural design to become superior to those of the individual monolithic counterparts. There are many reasons for using composite material rather than the simpler homogeneous polymers. Some of these reasons are (Nielsen and Landel, 1994):

-Increased stiffness, strength, and dimensional stability
-Increased toughness or impact strength

-Increased heat distortion temperature
-Increased mechanical damping
-Reduced permeability to gases and liquids
-Modified electrical properties
-Reduced cost

However, all of these desirable features are not found in any composite. The advantages that composite materials have to offer must be balanced against their undesirable properties, which include complex rheological behavior and difficult fabrication techniques as well as a reduction in some physical and mechanical properties.

2.2 Classification of Composite Materials

Composites can be divided into many classes at various manners. One simple classification scheme is to separate them according to reinforcement forms as follows:

2.2.1 Flake or Platelet Reinforced Composites

Fillers and reinforcements primarily in a flake class include mica, glass flakes and aluminum flakes as well as aluminum diboride. Flake composites also have strong resistance to puncturing by sharpy objects. Flake-filled polymers that are brittle with low impact strength have unusually high moduli compared to that of the most particulate-filled composite.

2.2.2 Fiber-reinforced Composites

Fiber-reinforced materials, consisting of fibers in a matrix, contain reinforcements having lengths much greater than their cross-sectional dimensions. Such a composite is considered to be a discontinuous fiber or short fiber composite if its properties vary with fiber length. On the other hand, when the length of the fiber is such that any further increase in length does not, for example, further increase the elastic modulus of the composite, the composite is considered to be continuous fiber reinforced. Most continuous fiber (or continuous filament) composites, in fact, contain fibers that are comparable in length to the overall dimensions of the composite part. Fillers and reinforcements in the fiber class include glass fibers, carbon graphite fibers, metal fibers, asbestos, whiskers and polymeric fibers.

2.2.3 Particle Filled Composites

Particulate composites are composed of particles in a matrix. Reinforcement is considered to be a "Particle" if all of its dimensions are roughly equal. Thus, particle-reinforced composites include those reinforced by spheres, rods, flaked, and many other shapes of roughly equal axes. The aims of the filler addition are not only for the reinforcement purpose but also for the cost reduction.

Fillers and reinforcements primarily in the particle class include calcium carbonate, silica, kaolin, talc, alumina trihydrate, feldspar, baryte, calcium sulfate solid and hollow spheres of glass or other ceramic and carbon black, which are combined within polymer as a matrix. The combination of these materials is called polymer composite.

2.3 Theories of Adhesion

To control the interface which can provide the composite with improve mechanical performance and structural integrity, it is essential to understand the mechanism of adhesion. Adhesion can be attributed to five main mechanisms, which can occur at the interface either in isolation or in combination to produce the bond (Chou, 1993).

2.3.1 Adsorption and Wetting

Wetting of the fiber by the matrix during fabrication processes of composites is very important particularly for polymer matrix composite. Bonding here involves short-range interactions of electron on an atomic scale, which only develop when the atom of the constituents approaches within a few atom diameters of each other. Wetting can be expressed in terms of thermodynamic work of adhesion W_a which represents a physical bonding resulting from highly localized intermolecular dispersion forces between different phases:

$$W_a = \gamma_{SV} + \gamma_{LV} - \gamma_{SL}$$

Where γ_{SV}, γ_{LV} and γ_{SL} are the surface energy of the solid-vapor, liquid-vapor and solid-liquid interfaces, respectively. The surface energy of the fiber (γ_{SV}) should be greater than that of the matrix (γ_{LV}) for proper wetting to occur. The physical situation of a liquid drops on a solid surface as shown in Figure 2.1.

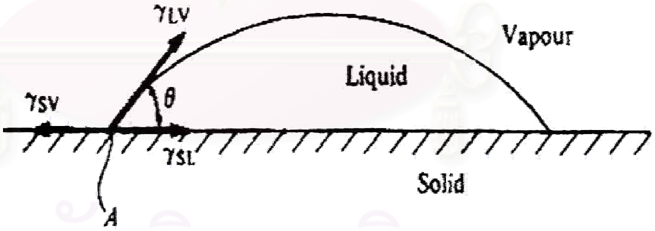


Figure 2.1 Surface Tensions (γ) for a Liquid Drop on a Solid Surface.

2.3.2 Interdiffusion

A bond between two surfaces may be formed by interdiffusion of atom or molecules across the interface. The bond strength in polymer matrix composites will depend on the amount of molecular entanglement, the number of molecules involved and the strength of the bonding between the molecules. Interdiffusion may be promoted by the presence of solvents and the amount of diffusion depends on the molecular conformation, constituents involved and the easiness of molecular motion.

Interdiffusion between two surfaces has been shown in Figure 2.2 (a) and (b), respectively.

2.3.3 Electrostatic Attraction

Forces of attractions occur between two surfaces, when one surface carries a net positive charge and the other surface is a net negative charge as in the case of acid-base interactions, ionic bonding, and coupling agents laid down on the surface of the filler, as shown in Figure 2.2 (c).

2.3.4 Mechanical Bonding

Mechanical bonds involve solely mechanical interlocking or hooking at the surface. The strength of this interface is unlikely to be very high in transverse tension, unless there are large numbers of re-entrant angles on the fiber surface, but the strength in shear possibly significant depends on the degree of roughness. In addition to the simple geometrical aspects of mechanical bonding, there are many internal or residual stresses in composite materials which are developed during fabrication process due to matrix shrinkage and differential thermal expansion between filler and matrix. Some bonding may occur purely by the mechanical interlocking of two surfaces as illustrated in Figure 2.2 (d).

2.3.5 Chemical Bonding

The chemical bonding theory is the oldest and the best known of all bonding theories. A chemical bond is formed between a chemical grouping on the fiber surface and a compatible chemical group in the matrix. The bond strength depends on the number and type of bonds, the formation of which are usually thermally activated chemical reaction. Mechanisms of chemical bonding are shown in Figures.2.2 (e) and (f), respectively.

2.4 Matrix Materials

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

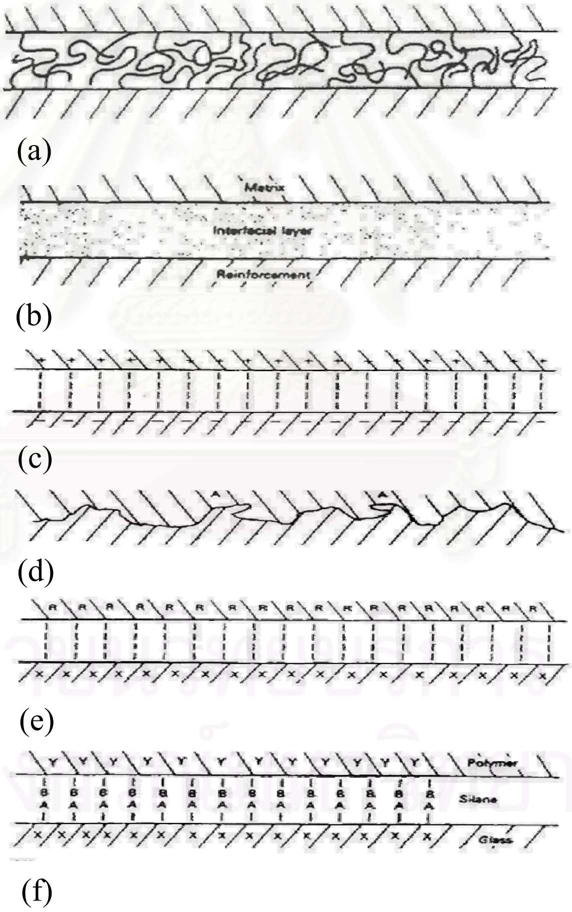


Figure 2.2 Mechanisms of Interfacial Adhesion. Bond Formed by Molecular Entanglement Following Interdiffusion (a), Bond Formed by Interfacial Layer by Interdiffusion (b), Bond Formed by Electrostatic Attraction (c), Mechanical Bond (d), and Chemical Bond (e) and (f), (Matthew, 1994).

2.5 Polypropylene

Polypropylene (PP) is a thermoplastic material produced by the polymerization of propylene molecules, the monomer units, into very long polymer molecule or chains. There are a number of different ways to link the monomers together. Polypropylene differs from polyethylene because there is a methyl group attached to every other carbon atom, which makes the stiff chain. As previously reported, 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. These give rise to a product that is a semicrystalline solid with good physical, mechanical and thermal properties.

Crystallinity is responsible for the stiffness and solvent resistance of the commercial plastic which is the typical thermoplastic materials. For instance polymer, the main properties of polymer in the melt state are derived from the average length of the polymer chains and the breadth of the distribution of the polymer chain lengths in a given product. In the case of solid state, the main properties of the polypropylene material deflect the type and amount of crystalline and amorphous regions formed from the polymer chains.

Semicrystalline polypropylene is a thermoplastic material containing both crystalline and amorphous phases. The relative amount of each phase depends on structural and stereochemical characteristics of the polymer chains and the conditions under which the resin is converted to final products such as fibers, films, and various other geometric shapes during fabrication by extrusion, thermoforming, or molding.

Polypropylene has excellent and desirable physical, mechanical, and thermal properties when used in room-temperature applications. It is relatively stiff and has a high melting point, low density, and relatively good resistance to impact. These properties can be varied in a relatively simple manner by altering the chain regularity (tacticity) content and distribution, the average chain lengths, the incorporation of a comonomer such as ethylene into the polymer chains, and the incorporation of an impact modifier into the resin formulation. Some properties of polypropylene and commodity thermoplastics are compared in Table 2.1.

Table 2.1 Properties of Polypropylene and Commodity Thermoplastics (Fried, 1995)

Property	**ASTM**	**PP**	**HDPE**	**GP-PS**	**ABS**
Specific gravity	D792	0.90-0.91	0.94-0.97	1.04-1.05	1.03-1.58
Crystallinity, (%)	-	82	80-95	-	-
Melt temperature, (^{o}C)	-	165-171	127-135	-	-
Tensile strength, (MPa)	D638	31-41	21-38	37-55	41-52
Tensile modulus, (GPa)	D638	1.10-1.55	0.41-1.24	2.41-3.38	2.07-2.76
Elongation-to-break, (%)	D638	100-600	20-130	1-2	5-25
Impact strength, notched Izod, J/m^{-1}	D256	21-53	27-1068	13.3-21.4	160-320
Heat deflection temperature, ^{o}C ,at 455 kPa	D648	110-125	60-88	75-100	102-107

2.5.1 Classification of Polypropylene Polymer

2.5.1.1 Homopolymer

Polypropylene containing only propylene monomer in the semicrystalline solid form is referred to as homopolymer polypropylene (HPP). Homopolymer polypropylene (HPP) is the most widely used polypropylene material in the polypropylene family of products. Polypropylene is synthesized by placing propylene monomer under controlled conditions of heat and pressure in the presence of organometallic, stereospecific catalyst (Ziegler-Natta type). Depending on the catalyst and polymerization process used, the molecular structure of the resulting polymer consists of three different types of stereochemical configurations in vary amounts. These are referred to an isotactic, syndiotactic, and atactic, for which their structures are shown in Figure 2.3.

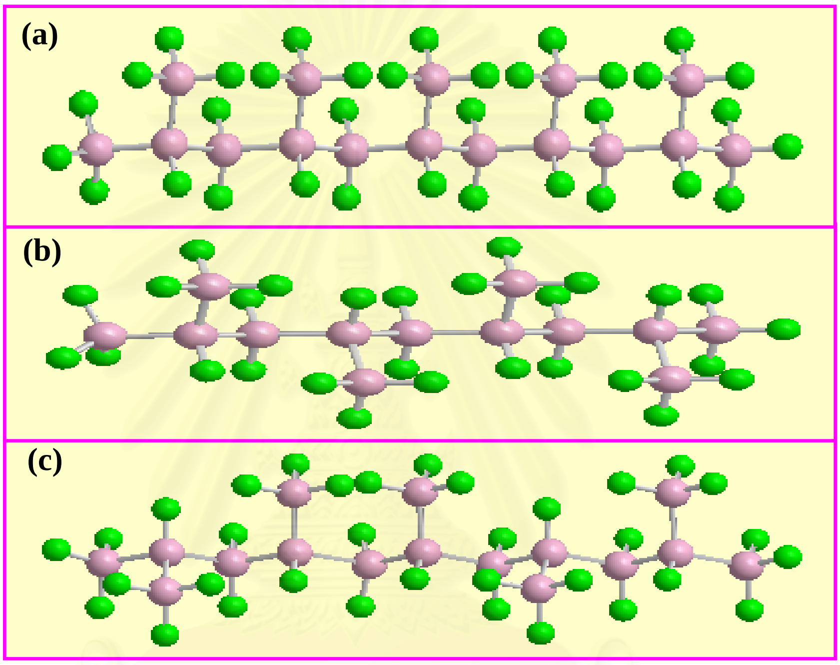


Figure 2.3 Polypropylene Structures. (a) Isotactic (b) Syndiotactic (c) Atactic

In the case of isotactic polypropylene which is the most common commercial form, all of the methyl groups are 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, good mechanical and thermal properties.

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. The primary application of homopolymer is in the extrusion of fibers and filaments for cordage, webs, carpet backing and face yarns, upholstery fabrics, apparel, filters, geotextiles, disposable diapers, medical fabrics, fabric for automobile interiors, bags, and strapping tape. While, injection molded homopolymers are used in automobile parts, appliances, housewares, packaging containers, trigger sprayers, furniture, and toys.

Table2.2 Properties of Isotactic, Syndiotactic, and Atactic Polypropylenes (Kroschwitz, 1990)

Property	**Isotactic**	**Syndiotactic**	**Atactic**
Density , g/cm^3	0.92-0.94	0.89-0.91	0.85-0.90
Melting point, ^{o}C	165	135	-
Solubility in hydrocarbons at 20^{o}C	none	medium	high
Yield strength	high	medium	very low

.

2.5.1.2 Random Copolymers

Polypropylene containing ethylene as a comonomer in the polypropylene chains at level about the 1-8% range is referred to as random copolymer (RCP). The copolymerized ethylene changes the properties of the polymer chains significantly and results in thermoplastic products that are sold into markets in which slightly better impact properties, improved clarity, decreased haze, decreased melting point, or enhanced flexibility. The ethylene monomer in the polypropylene chain manifests itself as a defect in the chain regularity, thus inhibiting the chain's crystallizability. As the ethylene content increases, the crystallite thickness gradually decreases, and this manifests itself in lower melting point. The amount of ethylene incorporated into the chain is usually dictated by the balance between thermal, optical, and mechanical properties.

2.5.1.3 Impact Copolymers

Impact copolymers are formed by the addition of ethylene-propylene rubber (EPR), ethylene propylene diene monomer (EPDM), polyethylene, or plastomers to homopolymers or random copolymers. Copolymer levels in impact copolymers range from 5–25%. Due to the high levels of a copolymer used in impact copolymers, the copolymer is not miscible in homopolymer; it usually forms an amorphous elastomeric or rubber phase that is evenly distributed throughout the polypropylene crystalline matrix. The phase separation results in copolymer nodules distributed throughout the semicrystalline homopolymer matrix. The elastomeric nodules provide impact resistance by acting as small bumpers, absorbing energy that result in local deformation instead of allowing cracks to propagate through the material

Table2.3 Mechanical and Thermal Properties of Commercial Polypropylenes (Harper, 1975).

Properties	**ASTM Test method**	**Polypropylene**		
		Unmodified	**Copolymer**	**Impact (rubber-modified)**
Specific gravity (density)	D 792	0.90-0.91	0.89-0.91	0.89-0.91
Tensile strength, lb/in^2	D 638	4,300-5,500	2,900-4,500	2,800-4,400
Elongation, %	D 638	200-700	200-700 (at break)	350 to more than 500
Flexural yield strength, lb/in^2	D 790	6,000-8,000	5,000-7,000	-
Impact strength, ft-lb/in. of notch ($\frac{1}{2}$-by $\frac{1}{2}$-in. notched bar, Izod test).	D 256	0.5-2.2 at 73^{o}F	1.1-20.0 at 73^{o}F	1.0-15.0 at 73^{o}F
Hardness, Rockwell	D 785	R80-110	R50-96	R50-85
Flexural elastic modulus, lb/in.^{2}x10^5	D 790	1.7-2.5	1.3-2.0	1.2-1.8
Thermal expansion,10^{-5}in./in./^{o}C	D 696	5.8-10.2	8.0-9.5	6.0-8.5

Impact copolymers are primarily used in injection molding parts for appliances, housewares, luggage, outdoor furniture, and automotive applications. Other applications include extruded sheeting and substitutions of super impact grades for engineering thermoplastics such as ABS. Extruded sheets can be thermoformed into large, thick parts such as fender and trunk liners for automotive applications or into small, odd-shaped parts such as food containers for freezer-to-microwave use. Some properties of homopolymer polypropylene, random copolymer and impact copolymer are compared in Table 2.3

2.6 Filler

The term filler is usually applied to solid additive incorporated into the polymer to modify its properties (Brydson, 1999). Moreover, fillers and reinforcements are added to polymer matrix in order to reduce costs or enhance mechanical properties. Extenders are inexpensive fillers that are added primarily to increase bulk, reducing the amount of the more expensive polymer used. They can increase stiffness and heat resistance. As above mentioned, reinforcing fillers provide a substantial improvement in mechanical properties, such as tensile strength, heat distortion temperature, and modulus of elasticity. A number of types of fillers are generally recognized in a polymer technology and these are summarized in Figure2.4.

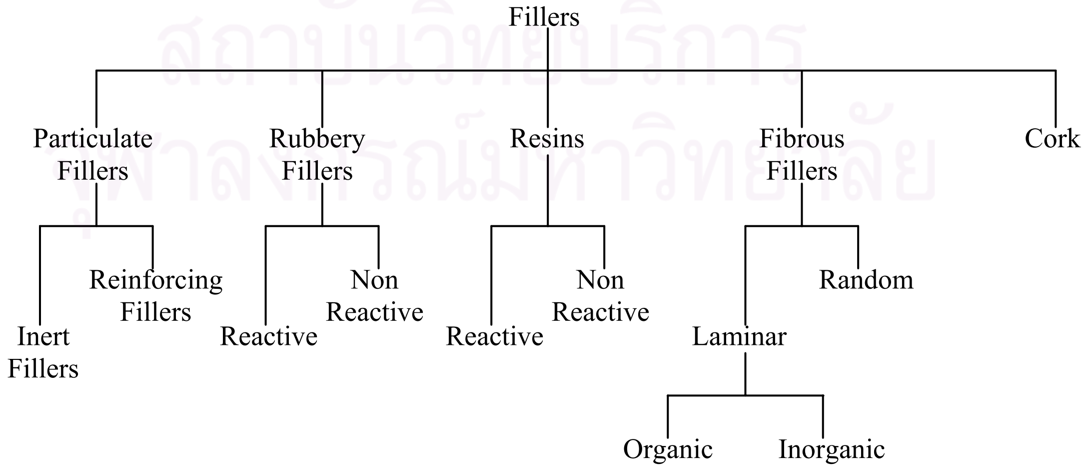


Figure 2.4 Classifications of Fillers in Polymer Compounds (Brydson, 1999)

The effect of a filler on resin properties is dependent on the aspect ratio (ratio of major to minor dimension of a particle or length: diameter) and size of the particle, the particle size distribution of the filler, filler surface treatment, and the filler dispersion in the polymer. The amounts of coarse and fine particles influence to particle packing during compounding and the optical properties of the resin. The size, shape, and type of filler affect to dispersion, in addition to interactions between resin and filler, resin flow properties, filler surface treatment, machine geometry, and processing parameters. Therefore, ultimate filler particle size and spatial uniformity of the filler in the resin is dependent on the degree of dispersion (Maier and Calafut, 1998).

2.7 Woodflour

The term woodflour is somewhat ambiguous. Though its definition is imprecise, the term woodflour is in common use. Practically speaking, woodflour usually refers to wood particles that are small enough to pass through a screen with 850 μm openings (20 US standard meshes) (Xanthos, 2005). Woodflour is derived from various scrap wood from wood processors. High quality woodflour must be of a specific species or species group and must be free from bark, dirt, and other foreign matter. Many different species of tree are offered as woodflour and are often based on the regional availability of clean raw materials from wood processing industries. Though there is no standard method of producing woodflour, some generalities can be discussed. The main steps in woodflour production are size reduction and size classification. If larger raw materials are used, their initial size may be reduced using equipment such as a hammer mill, ball mill of chipper. Once coarsely ground, the wood is pulverized by grinding between disks as in attrition mills, beating with impactors or hammers as in hammer mills or crushing between rollers as in roller mills. Other mills can also be used but are less common. Once pulverized, the wood can be classified using vibrating, rotating, or oscillating screens. Woodflour particle size is often described by the mesh of the wire cloth sieves used to classify the particles. Table2.4 lists the US standard mesh sizes and their equivalent particle diameters.

Table 2.4 Conversion between US Standard Mesh and Particle Diameter.

Mesh US Standard	Particle Diameter(μm)
20	850
30	600
40	425
50	300
60	250
70	212
80	180
100	150
120	125
140	106
170	90
200	75
270	53
325	45

2.7.1 Structure and Property of Wood

2.7.1.1 Wood Anatomy

As with most natural materials, the anatomy of wood is complex. Wood is porous, fibrous, and anisotropic. Wood is often subdivided in to broad classes, namely softwoods and hardwoods, which are classified by botanical and anatomical features rather than actual wood hardness. Figures 2.5 and 2.6 are schematics of softwood and hardwood, respectively, showing the typical anatomies of each wood type. Softwoods include pines, firs, cedars, and rubber wood among other; hardwoods include species such as the oaks and maples. Wood is primarily composed of hollow, elongated, spindle-shaped cells that are arranged parallel to each other along the trunk of the tree. The lumen (hollow center of the fibers) can be completely or partially filled with deposits, such as resins or gums, or growths from neighboring cells called tyloses.

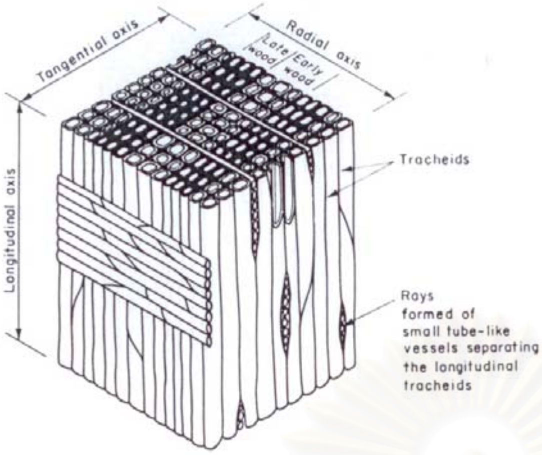


Figure 2.5 Scheme of softwood.

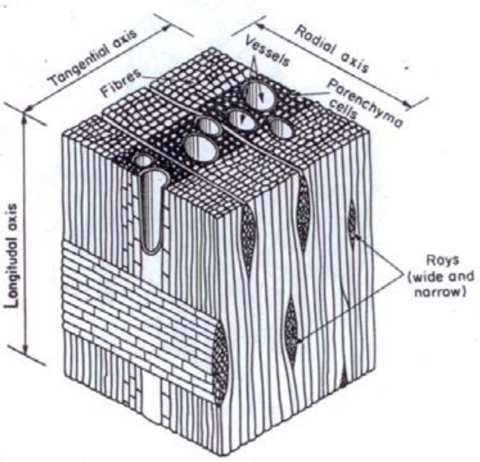


Figure 2.6 Scheme of hardwood.

These fibers are firmly cemented together and form the structure component of wood tissues. When wood is reduced to woodflour, the resulting particles are actually bundles of wood fibers rather than individual fibers and can contain lesser amounts of other features such as ray cells and vessel elements.

2.7.1.2 Chemical Composition

The basic chemical elements of wood are incorporated into a number of organic compounds. Dry wood is primarily composed of cellulose, hemicelluloses, lignin, and minor amounts (5% to 10%) of extraneous materials. Because the chemical composition varies between and among species, it is impossible to define absolute compositions. Nevertheless, the following generalizations can be made. The ranges of composition values can be defined within species, and the average lignin content of softwood is slightly higher than that of hardwood. On average, proportions of three major component i.e. cellulose, hemicelluloses, and lignin differ slightly between hardwood and softwood species as shown in Table 2.5.

Table 2.5 Organic Compounds in Wood (% of Oven-Dry Weight)
(Williamson, 2002)

	Cellulose	Hemicelluloses	Lignin
Hardwoods	40–44	15–35	18–25
Softwoods	40–44	20–32	25–35

Cellulose

Cellulose which is the major component constitutes approximately 40-50% by weight of wood substance (Simpson and Tenwolde, 1999). It is the main component providing the wood’s strength and structural stability. It is a linear polymer of anhydroglucose units linked by β-1, 4 glucosidic bonds. This material has a structure as shown in Figure2.7. Cellulose is typically 60-90% crystalline by weight. The chain length of wood cellulose polymers is between 7,000 and 10,000 glucose units. During growth of the tree, the cellulose molecules are arranged into ordered strands called fibrils, which in turn are organized into the larger structural elements that make up the cell wall of wood fibers. Most of the cell wall cellulose is crystalline.

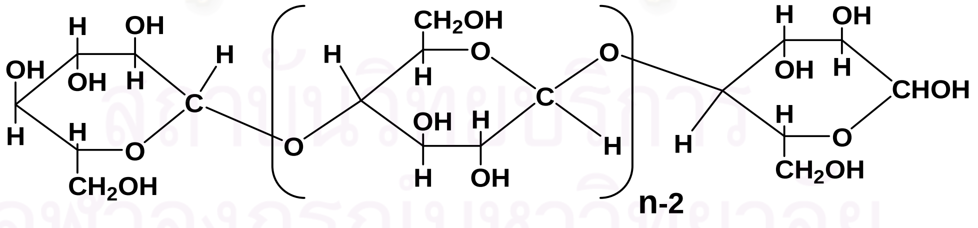


Figure 2.7 Cellulose Structure (Kroschwitz, 1990)

Hemicellulose

The hemicelluloses are associated with cellulose and are branched, low molecular-weight polymers composed of several different kinds of pentose and hexose sugar monomers. The relative amounts of these sugars vary markedly with species. The hemicelluloses have chain lengths of 200 or less sugar units. This material is responsible for the biodegradation, moisture absorption, and thermal degradation of the fiber as it show a least resistance. The formula of hemicelluloses is given by Figure2.8.

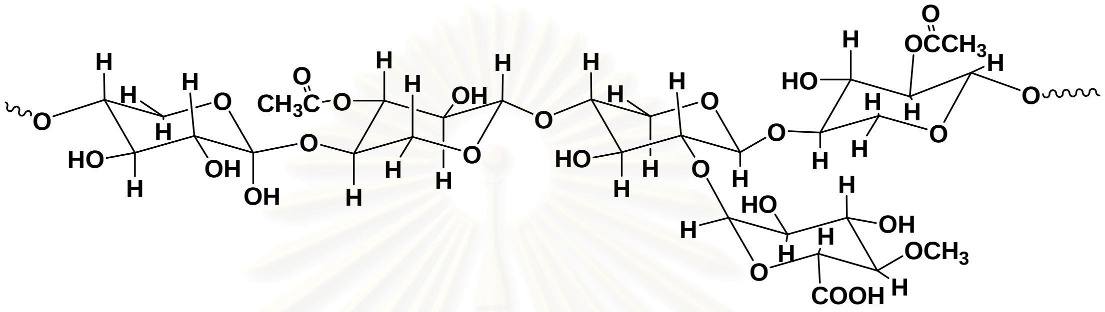


Figure 2.8 Structure of Hemicellulose (A. K. Bledzki and J. Gassan., 1999)

Lignin

Lignin constitutes 23% to 33% by weight of the wood substance in softwoods and 16% to 25% by weight in hardwoods. Although lignin occurs in wood throughout the cell wall, it is concentrated toward the outside of the cells and between cells. Lignin has less polarity than cellulose and often called the cementing agent that binds individual cells together. It is an amorphous, cross-linked polymer network consisting of an irregular array of variously bonded hydroxyl and methoxy substituted phenylpropane units. Its structure and distribution in wood are still not fully understood. Molecular weights of isolate lignin have been measured up to 16,000. The formula of lignin is given by Figure2.9.

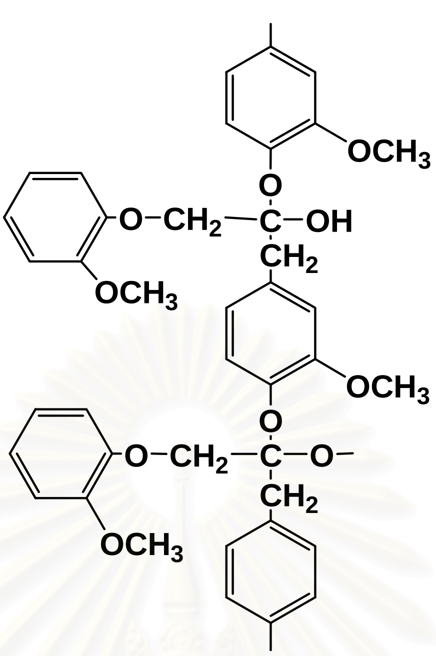


Figure 2.9 Molecular Structure of Lignin (A. K. Bledzki and J. Gassan., 1999)

Extraneous Materials

Unlike the major constituents of wood, extraneous materials are not structural components. Both organic and inorganic extraneous materials are found in wood. The organic component takes the form of extractives, make up about 5-10% by weight of the dry wood grown in temperate climates, but significantly higher quantities are found in wood grown in topical climates (Xanthos, 2005). Extractives include substances such as fats, waxes, resins, proteins, gums, terpenes, and simple sugars, among others. Many of these extractives function in tree metabolism and act as energy reserves or defend against microbial attack. Though often small in quantity, extractives can have large influences on properties such as color, odor, and decay resistance. Small quantities (typically 1% by weight) of inorganic matter, termed ash, are also presented in wood grown in temperate regions.

2.7.1.3 Density and Specific Gravity

Density is the weight or mass of a unit volume of wood, and specific gravity is the ratio of the density of wood to that of water. The density of woodflour depends on factors such as moisture content, particle size, and species. The typical density is about 190-220 kg/m^3. Because of its low bulk density, special equipment, such as a crammer, is sometimes used to aid feeding of woodflour.

As filler, woodflour is unusual in that it is compressible. Though, the density of the wood cell wall is about 1.44 -1.50 g/cm^3, the porous anatomy of solid wood results in overall densities of about 0.32-0.72 g/cm^3 when dry. However, the high pressure encountered during the processing of plastics can cause the hollow fibers of the woodflour to collapse or fill them with low molecular weight additives or polymer. The degree of filling will depend on such variables as particle size, the processing method, and additive viscosity, but wood densities in composites approaching the wood cell wall density can be attained in high pressure processes such as injection molding. As we known that the density of wood is lower than that of the inorganic fillers and reinforcements. Therefore, this density advantage is significant in applications where weight is an important factor, such as in automotive components.

Woodflour is often added to commodity thermoplastics because of a low cost filler to alter mechanical performance, especially the stiffness of low melt temperature with out increasing their density excessively. Furthermore, due to its low thermal stability, woodflour is usually used as a filler only in plastics that are processed at low temperatures, lower than about 200^{o}C. Above these temperatures, the cell wall polymers begin to decompose. The hygroscopic of woodflour can also affect to the performance of the end composite. Because the major chemical constituents of the cell wall bear hydroxyl and oxygen containing groups that attract moisture through hydrogen bonding. Even compounded material often needs to be dried prior to further processing, especially if high weight percentages of woodflour are used.

2.8 Particle Packing Modifications

2.8.1 Packing Structures

Particle packing is important in most forming processes. The packing density dictates the die fill, binder content, and shrinkage in sintering. Random packing structures are typical of powder metallurgy processing. For monosized spheres, the fractional density is between 0.60 and 0.64(German, 1994). In the case of the actual density, the value depends on the powder characteristics, namely the size and shape, and factors including the adsorbed moisture. For common P/M powders, the packing density ranges from 30 to 65% of theoretical value; the lower value is representative of irregular and sponge powders.

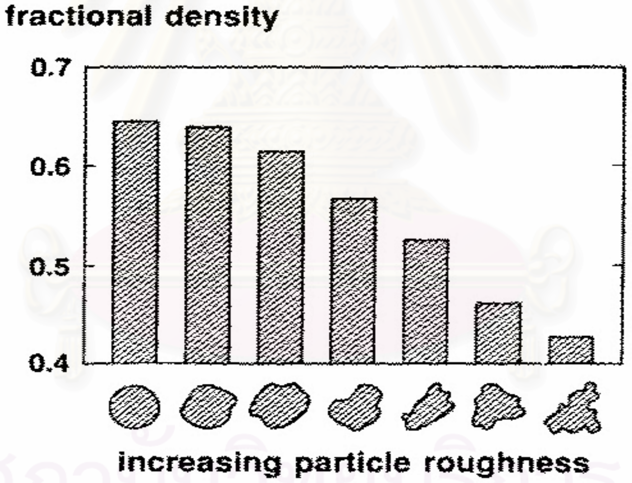


Figure 2.10 Scheme of Fraction Density for Monosized Powders versus Roughness as expressed by a Typical Particle Profile.

The figure shows that interparticle friction depends on particle surface irregularities. The greater the surface roughness or the more irregular the particle shape, the lower the packing density will decrease as the shape departs from equiaxed (spherical). Figure 2.10 gives the fractional packing density for various monosized irregular particle shapes. As the particle shapes become more rounded (spherical) the packing density increases. The packing of fibers provides an illustration of a decreasing packing density as the particles have a larger length to diameter ratio L/D. Figure 2.11 plots the fractional packing density versus the length to diameter ratio for fibers. Obviously, packing improves as the particles approach a smooth, equiaxed shape.

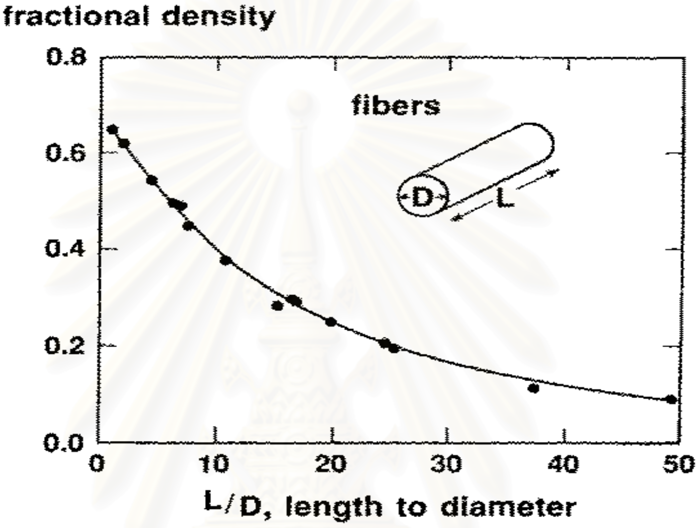


Figure 2.11 Plot of the Change in Packing Density with the Length to Diameter Ratio (L/D) for Fibers. (Best packing occurs with equiaxed particles.)

2.8.2 Improved Packing Techniques

To overcome the inherent packing limits of a powder, it is possible to tailor the particle size distribution for higher packing density. Bimodal particle blends can pack to higher densities than monosized particles. The key to improved packing rests with the particle size ratio. Small particles are selected to fit the interstices between large particles without forcing the large particles apart. In turn, even smaller particles can be select to fit into the remaining pores, giving a corresponding improvement in packing density. The basis behavior is sketched in Figure 2.12. The fraction density is shown as a function of composition for a mixture of large and small spheres. At the maximum packing composition, there is a greater volume of large particles than small particles. The relative improvement in packing density depends on the particle size ratio of the large and small particles. Within a limited range, the greater the size ratio shows the higher the maximum packing density.

Beginning with the large particles, the packing density initially increases as small particles are added to fill the voids between the large particles. That corresponds to the right hand side of Figure 2.12. Eventually, the quantity of small particles fills all of the spaces between the large particles. In contrast, starting with the small particle, clusters of small particles and their associated voids can be removed and replaced with a full density region everywhere a large particle is added. The packing benefit of replacing small particles with the large particle continues until a concentration where the large particles contact one another. Figure 2.12 shows this process as the left-hand plot. The point of maximum packing density corresponds to the intersection of those two curves. At this point, the large particles are in point contact with one another and all of the interstitial voids are filled with the small particles. The optimal composition in terms of the weight fraction of large particle X^* depends on the amount of void spaces between large particles, which equals $1-f_L$, where f_L is the fractional packing density of the large particles,

$$X^* = f_L / f^*$$

with the packing density at the optimal composition f^* given as,

$$f^* = f_L + f_s(1-f_L)$$

and the fraction packing density for the small particle is f_s.

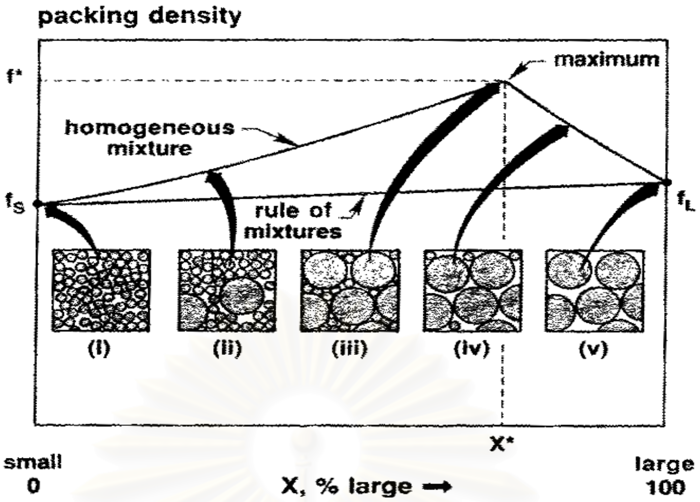


Figure 2.12 Plot of Fractional Packing Density versus Composition for Bimodal Mixtures of Large and Small Spheres.

The ideal fraction density of each of spherical powders, i.e., large and small particle sizes, can pack to obtain the maximum packing density is 0.637. To require the maximum packing density value higher than 0.637, the corresponding weight fraction of large particle for maximum packing is 0.734, while the mass fraction of the small particle sizes is of 0.266. The expected fractional packing density would be 0.86.

Figure 2.13 illustrates how the packing density increases with the particle size ratio (large diameter divided by small diameter). Note the dramatic change in behavior at the particle size ratio corresponding to one particle filling the triangular pores between the large particles at roughly a 7:1 size ratio.

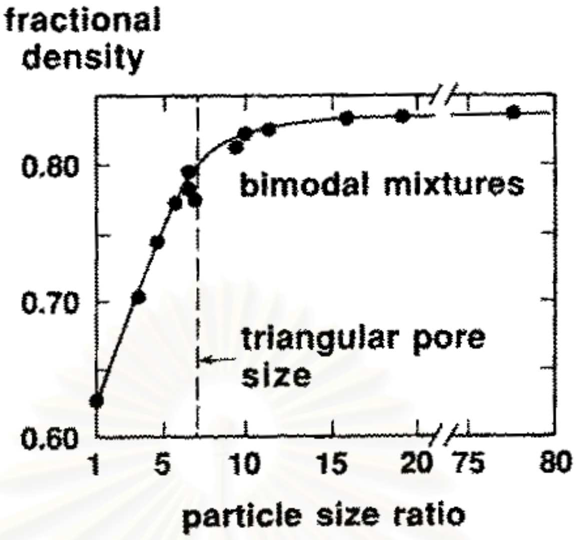


Figure 2.13 Effect of Particle Size Ratio on the Packing Density for Mixtures consisting of 70% Large Particles and 30% Small Particles.

The packing density will increase with the homogeneity of the mixture. Depending in handling practice, randomly mixed systems will range between unmixed and fully mixed, and typically exhibit some inhomogeneities that degrade actual packing from the ideal.

Analogous to the behavior of spheres, a density increase is associated with blending different particle sizes of similar shapes. However, a major difference between spherical and nonspherical particles is that the initial packing is generally higher for spheres. The greater the surface roughness, shape irregularity, or particle aspect ratio, then the lower the inherent packing density. Thus, although the relative density gain is similar for spherical and nonspherical particles, the starting density for nonspherical particles is lower. Accordingly, at all compositions the nonspherical mixture will be lower in density.

The ideas developed for bimodal mixtures can be extended to multimodal systems, as shown in Table 2.6.

Table 2.6 Relation between particle size ratio and maximum packing density

Number of component	Size ratio	Weight percent	Packing fraction
1	-	100	0.64
2	7 : 1	73 : 27	0.86
3	49 : 7 : 1	75 : 14 : 11	0.95
4	343 : 49 : 7 : 1	73 : 14 : 10 : 3	0.98

2.9 Coupling Agent

Various fillers and reinforcements, such as glass fiber, talc, calcium carbonate and woodflour are typical ingredients that are added to polypropylene resin to attain cost effective mechanical properties. These materials tend to increase both mechanical and thermal properties such as tensile modulus, flexural modulus, heat deflection temperature, creep resistance and reducing the final material cost (Karian, 2003).

Most of the fillers and reinforcements used are polar in nature. Polypropylene on the other hand, is nonpolar. Poor adhesion between the filler surface and the polymer matrix prevents necessary wet-out by molten polymer to help break up aggregates of filler particles, resulting in poor dispersion, insufficient reinforcement and poor mechanical properties. When two materials are incompatible, it is often possible to bring about compatibility by introduction a third material that has properties intermediate between those of the other two. There are several mechanisms of coupling in materials:

- Weak boundary layers, coupling agents eliminate weak boundary layers.
- Deformable layers, coupling agent produce a tough, flexible layers.
- Wettability, coupling agents improve the wetting between substrate and polymer.

- Chemical bonding, coupling agent from covalent bonds with both materials.

The important chemical modification method is the chemical coupling method, which improves the interfacial adhesion, consequently, obtains better mechanical properties of composites. One frequently used method is to modify the chemistry of the polypropylene by attaching polar groups such as maleic anhydride, onto the polymer backbone.

Coupling agents are defined primarily as materials that improve the adhesive bond of dissimilar surface. It must involve an increase in true adhesion, but it may also involve better wetting, rheology and other handling properties. To do this effectively, the coupling agent must have a unique structure. On one hand, it must be able to interact with the filler, which is polar in nature, while on the other hand, it must be compatible with the nonpolar molecule chains of polypropylene resin.

In this work, maleic anhydride grafted polypropylene (MAPP) is chosen as a coupling agent for woodflour-filled polypropylene composites. MAPP has been suggested to use as a coupling agent for many fillers or reinforcing materials in polypropylene. For preparation method of maleic anhydride grafted polypropylene (Gauthier et al.,1998), maleic anhydride (MA) is grafted in the presence of peroxide on a polypropylene chain and the resulting sucinic moieties will be further able to react with filler. Maleic anhydride grafted polypropylene (MAPP) may differ not only by the maleic anhydride (MA) content and the molecular weight of the polypropylene backbone, but also by the distribution of the grafted maleic anhydride (MA) moieties, which is of great importance. Experimental conditions during maleic anhydride grafted polypropylene (MAPP) synthesis govern the structure of the final product. If prepared at low temperature or in solution, the grafting of maleic anhydride onto polypropylene occurs along the chain with out modifying the length of the initial polypropylene. A structure results from such grafting (maleic anhydride grafted polypropylene (MAPP (a), Figure 2.14). Further reaction with filler may lead to a coating of the surface with several anchoring points.

At higher temperature, a mechanism which involves a β-scission of the polypropylene chain with formation of maleic anhydride prepolymers at the scission end (maleic anhydride grafted polypropylene (MAPP (b), Figure 2.14). The β-scission is indicated by a decrease in the molecular weight when grafting is performed in the molten polymer

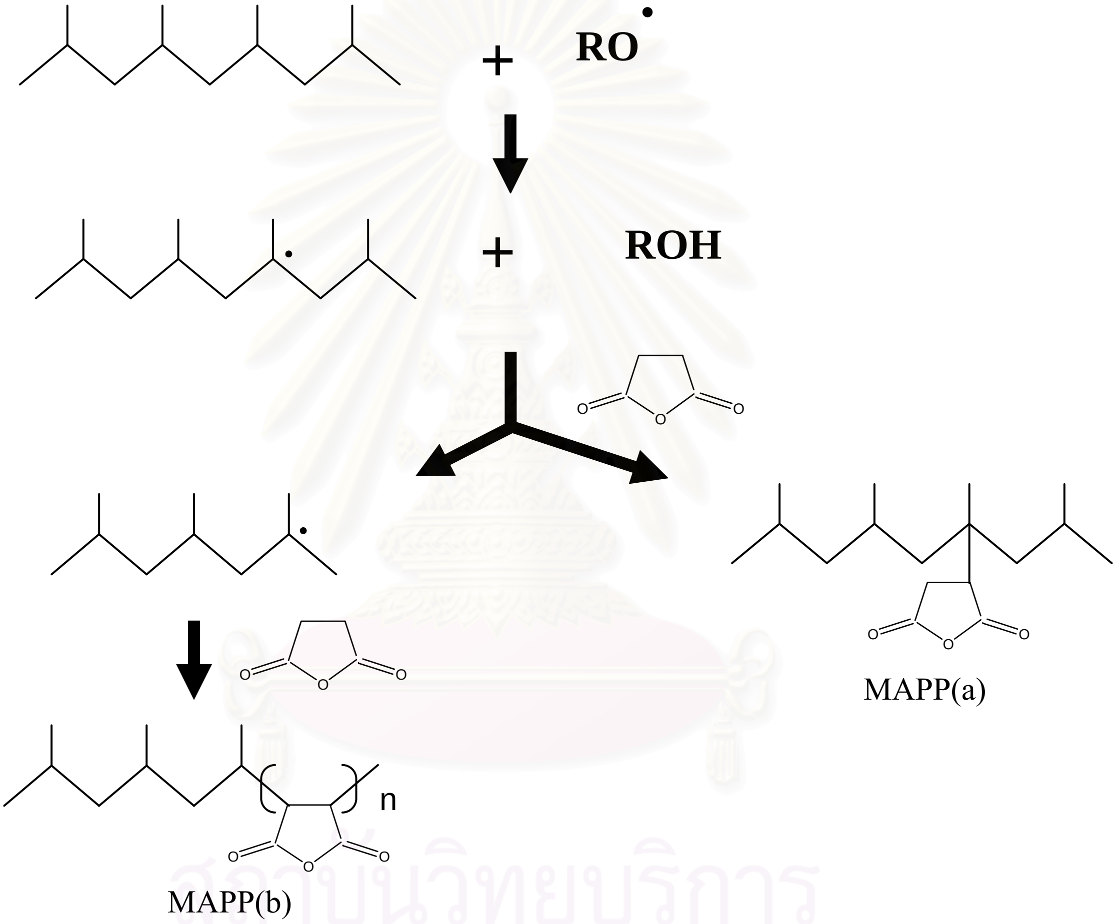


Figure 2.14 Mechanism Proposed for MAPP Synthesis (Gauthier et al., 1998)

Two properties of maleic anhydride grafted polypropylene (MAPP) that could have an influence on their effectiveness as coupling agents for natural fiber/PP composites are molecular weight, which affects entanglement with the matrix chains, and acid number, which determines the functionality present in the coupling agent. To develop sufficient stress transfer properties between the matrix and the fiber, maleic anhydride groups in MAPP should interact or even react with the OH groups on the fiber surface and the polymer chains of the MAPP should be long enough to permit entanglements with the PP in the interphase (Arbelaiz et al., 2005). A schematic of process is given in Figure 2.15.

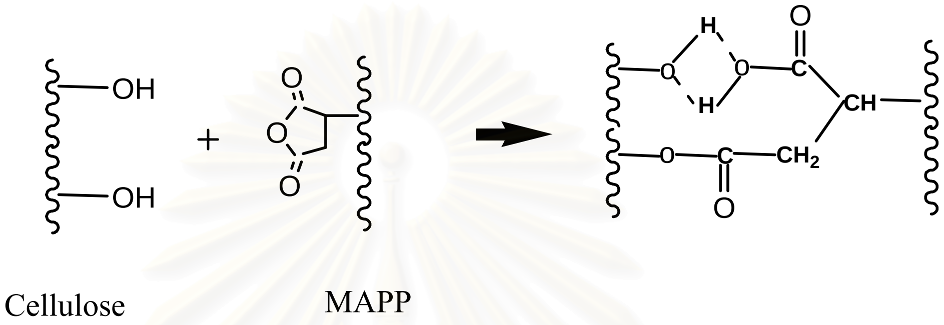


Figure 2.15 Chemical Reaction between Hydroxyl Group of Cellulose and MA of MAPP (Wu et al., 2000)

2.10 Processing

The processing of wood thermoplastic composites is separted into two distinct stages. The first one is a compounding operation in which the polymer and the fiber are combined and processed into granular feedstock for the final injection molding operation.

2.10.1 Extrusion Compounding

The polymer is plasticized in a single or twin screw extruder and blended with the filler. The compound is then extruded through a die to form thin rods which are air or water cooled and then cut into pellets, typically 2 - 3 mm diameter and 3 - 6 mm length. There are several variants to the basic process:

(I) Polymer granules and fillers are dry blended in the appropriate proportions and then charged into the feed hopper of the extruder. The blend is melted and mixed, and then possibly passed through a decompression zone where volatiles are removed by application of a vacuum. The plasticized charge is then recompressed and passed through the extruder die.

(II) The polymer granules and fiber are separately charged into the feed hopper. The polymer granules are plasticized, after that the fiber (acted as a filler) is added at the decompression port. The blends will be moved forward by the screw and passed through a mixing zone, and possibly a further decompression zone, before passing through the die.

From both methods are the causes of a breakage of the filler. The degree of attrition can be reduced by operating the extruder under less severe conditions but this would seriously decrease output, reduce the degree of fiber dispersion and is not commercially acceptable.

2.10.2 Injection Molding

The basic principle of the injection molding process for thermoplastics is that a charge of the material which is plasticized and the material are then injected under high pressure into a cold mold. The charge cools in the mold. After that, the specimens will be removed from the mold, and the cycle repeated. Injection molding machines are highly sophisticated devices, designed for continuous automatic operation at high production rates. The machines and the tools require a high capital investment and their operation is relatively economic in the use of labor. The process is therefore most suited for long runs where many thousands of identical components are to be produced. The major attractions of the process are its high productivity and the fact that very complex shapes may be produced in a single automated operation.

Most modern injection molding machines use a screw pump, similar to that on an extruder, to effect the plasticization. A typical machine layout is shown schematically in Figure 2.16. Compounded granules are charged into the feed hopper from whence they enter the screw. The solid charged is moved forward by the rotation of the screw into the heated barrel, where the charge is melted, by conduction from the hot barrel wall, and mixed by the action of the screw. The plasticized charge is transported forward through the compression and metering stages of the screw towards the nozzle which, at this stage, is closed by a valve. Here the charge sets up a back pressure which forces the screw to retract against a controlled hydraulic pressure in the main cylinder. This continues until a sufficient quantity of the charge built up in the nozzle region. At this stage the screw rotation is stopped. The carriage is moved forward to engage the nozzle in the mold, which is held closed by a hydraulic or mechanical locking device. The nozzle valve is opened and the charge forced into the mold cavity by the action of the main ram pushing the (non-rotating) screw forward. A considerable pressure is built up in the cavity (typically 100 – 200 MPa), and is maintained until the charge has frozen in the feed gate. This is the point at which the charge cannot flow out of the mold when the pressure is relaxed. At this time the carriage can be retracted and the next plasticization cycle initiated. Meanwhile the charge in the mold continues to cool. When it has cooled, the mold is opened. After that the part is removed from the mold then closed again in readiness for the next injection cycle.

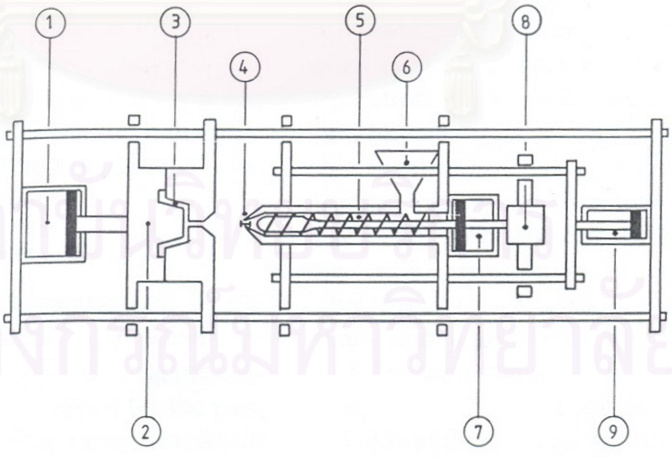


Figure 2.16 Schematic Diagram of an Injection Molding Machine.

The hydraulic ram (1) opens and closes the mold (2), which contains the mold cavity (3). The charge is fed from the hopper (6), and is plasticized as it is moved forward by rotation of the screw (5), where it is trapped by the nozzle valve (4), causing the screw to retract against a “ back pressure ” imposed by the ram (7). When sufficient charge has been plasticized, the carriage is moved forward by the ram (9) to locate the nozzle in the mold. The nozzle valve is opened and the ram (7) drives the stationary screw forward to inject the charge into the mold. After the charge has frozen in the gate the nozzle is disengaged from the mold, the hydraulic motor (8) turns the screw to plasticize the next charge. The mold is opened, the part ejected and the cycle is repeated.

CHAPTER III

LITERATURE REVIEWS

Balasuriya et al. (2001) investigated variation of mixing method (by using of twin screw extruder method and mechanical blending method) and the effect of the melt flow behavior of polymer matrix with relationship between structure of composite and properties of composites. Two types of high density polyethylene (HDPE), i.e. medium melt flow rate HDPE (7 g/10 min) and low melt flow rate HDPE (0.15 g/10 min), were used as polymer matrix. The contents of woodflex added into the HDPE matrix were ranged from 0 to 70% by weight. From the results, they found that the twin screw compounded composites based on medium melt flow rate (MMFR) HDPE had always achieved better flake wetting and distribution, and therefore had higher mechanical properties than those mechanical blended composites or twin screw compounded composites with low melt flow rate (LMFR) HDPE. The results of this experiment indicated the mechanical properties that were shown in Table 3.1.

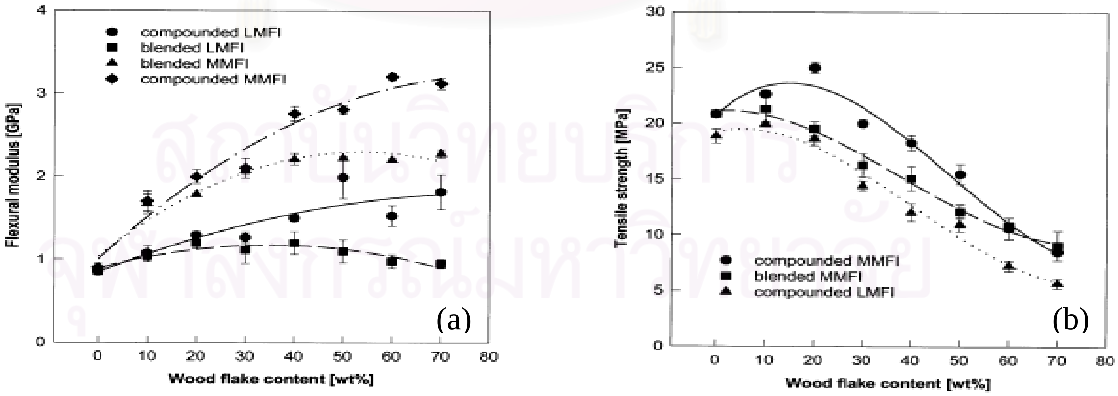


Figure 3.1 Comparison of Flexural Modulus(a) and Tensile Strength(b) of Wood Composites Based on Different HDPE and Processing Techniques.

The effect of molecular weight of polymer matrix on the properties of composites of PP and the fibrous cellulose was also studied by Qiu et al. (2006). In the system, the different molecular weights of polypropylene (i.e. M_w = 250,000, 340,000 and 580,000) were mixed with 30% by weight of fibrous cellulose (50-350 µm in length and 20 µm in diameter and crystallinity 93%). Polypropylene-graft-maleic anhydride,MAPP, (0.6 wt.% MA, melt flow rate 115 g/10 min) was used as a coupling agent. The results demonstrated that at the same composition of the filler, composites derived from higher molecular weight of PP exhibited stronger tensile strength when compared with the lower molecular weight. For MAPP-treated compostes, they observed that tensile strength highly increased with an increase in the MAPP content, and the optimum dose showing around 10wt% of the fibrous cellulose.

Bledzkia et al. (2005) studied the variation of compounding process of composite that had an effect with polypropylene/wood fiber composites properties. The study varied three compounding processes of polypropylene/wood fiber composites, i.e. twin screw extruder, high speed mixer and two roll mill. The woodflour contents was equal to 50% by weight. They found that the composite processed by twin screw extruder had better properties than the ones processed by the other two processes, because of good distribution of woodflour. The results informed that the appropriate mixing process should be selected for the good properties of composite as expectation.

N.M. Stark and J.M. Berger (1997) studied the effects of species and the amount of woodflour on the properties of wood composite. In the study, four spcies of woodflour (Oak, Maple, Ponderosa pine and Loblolly pine) were filled with polypropylene matrix to form the composite The amount of woodflour filled in polymer was varied from about 20 to 60wt%. From the experiment, they found that the composites filled with Oak and Maple had better mechanical properties than the ones filled with Pine species. That meant the species of wood had the effect to adjust the properites to meet the requirement. If the amount of woodflour in composite increased, properties such as flexural modulus, tensile modulus and notch impact strength would be increased., while the flexural strength, tensile strength and tensile elongation would be decreased. The experimental results of the work are indicated as shown in Table 3.2.

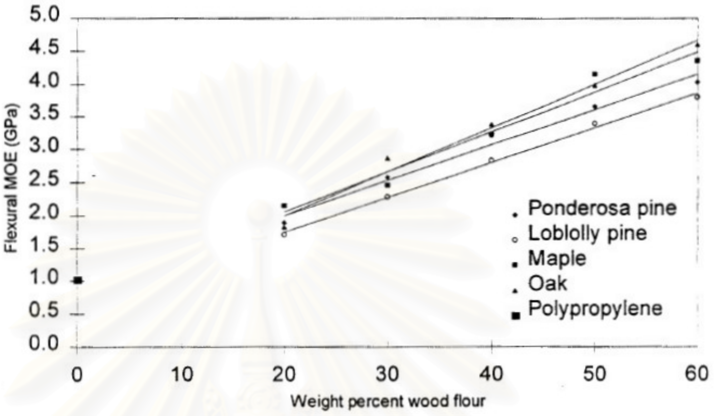


Figure 3.2 Effect of Wood Species and Amount of Sawdust on the Flexural Modulus of Polypropylene-Wood Composite.

Nitz et al. (2000) examined an effect of a coupling agent on the mechanical properties of composites that prepared from polypropylene and woodflour. Maleic anhydride-grafted-polypropylene (MAPP) and maleic anhydride-grafted-poly(styrene)-block-poly-(ethane-co-1-butene)-block-poly(styrene) (SEBS-g-MA) were used as a coupling agent. They found that the composite with 30% by volume of woodflour and 3.5% by volume of SEBS-g-MA increased Young’s modulus for 100%, tensile strength for 20% and impact strength for 24% in comparison with the properties of neat polypropylene. The tensile strength was increased, but the impact strength was not increased with the increase of MAPP. It was also found that the amount of water or humidity decreased tensile strength for 10-15% (for both of coupling agents).

Ichazo et al. (2001) studied the effect of the surface treatment of filler by using of NaOH and vinyl-tris-(2-metoxietoxi)-silane on the properties of polypropylene/wood flour composites and used two types of maleated polypropylene (Polybond 3150 and Polybond 3200) as coupling agents. They found that the treatment of filler surface had the effect to increase tensile modulus and tensile strength. However, it had no effect on melt flow index of the composite. It was found that Polybond 3150 was able to increase tensile modulus and tensile strength (approximate 8% and 5% respectively). However, Polybond 3150 was reported to decrease the elongation at break and impact strength. The use of MAPP together with the surface treatment by silane was able to improve the polymer-filler adhesion and the dispersion of particles in polymer matrix when compared with the composite with the filler treated by NaOH.

Qiu et al. (2005) used maleated anhydride graft polypropylene (MAPP) as a coupling agent in their wood composites that consisted of polypropylene and fibrous cellulose. In the work, the contents of filler added into the PP matrix were ranged from 0 to 60% by weight and coupling agent was added in the range from 0 to 20wt% of filler. From the results, they found that the coupling agent of about 10% by weight of the fibrous cellulose could improve the interfacial adhesion of the wood composites, which resulted in an enhancement of the composite mechanical properties. As aforementioned, an addition of MAPP into wood composite system could generate the esterification reaction between MAPP and hydroxyl groups of cellulose. The mechanical properties were enhanced in this fibrous cellulose composite and evidently attributed to the strong interfacial adhesion between filler and polymer matrix. The wood composite treated with the optimal concentration of MAPP of about 10% by weight of fibrous cellulose was found to increase tensile strength and Young’s modulus of the composite from 24 MPa to 31 MPa and 0.8 GPa to 1.0 GPa, respectively.

Keener et al.(2004) examined the effect of maleated coupling agent in composites of polypropylene matrix and natural fiber such as Flax fiber and Jute fiber. The fiber content was 30% by weight. The types and the amounts of maleated coupling agent were varied, which related to molecular weight and amount of maleic anhydride as shown in Figure 3.3. The result was reported that the use of Epolene G-3015 had the appropriate balance of molecular weight and acid number of 3wt%. That provided better properties of composite filled with Flax fiber, i.e. increasing the flexural strength for 63%, tensile strength for 61% and charpy impact for 55% in comparison with the composites without coupling agent. For the composites filled with Jute fiber, the use of Epolene G-3015 was able to increase flexural strength for 57%, tensile strength for 64% and charpy impact for 81% compared with the composites without coupling agent.

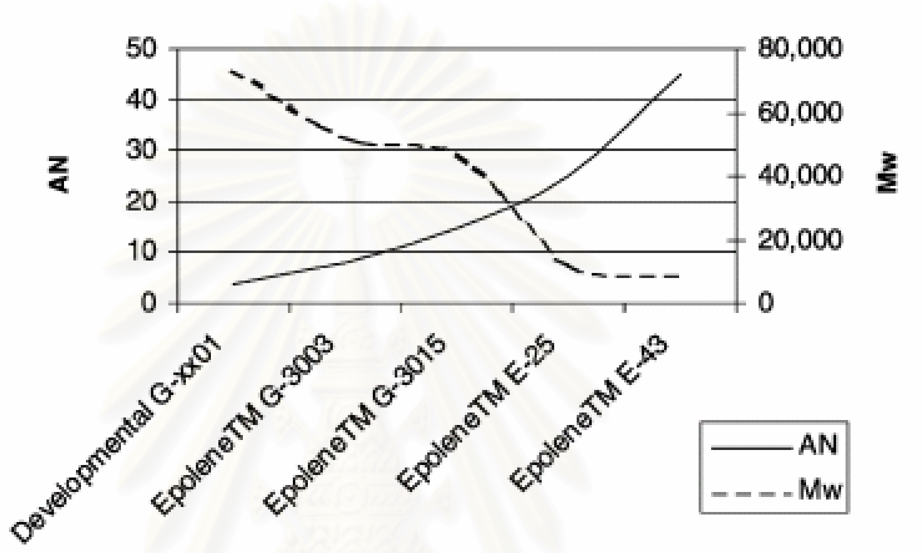


Figure 3.3 Illustration of the Relation between Acid Number and Molecular Weight of Maleated Polypropylene

Rozman et al. (2003) studied the effect of chemical modification of oil palm empty fruit bunch (EFB) filler on the flexural and impact properties of EFB-filled polypropylene (PP) composites. In this work, the filler was chemically modified with maleic anhydride (MAH). The modification involved the reaction of EFB and MAH (dissolved in dimethylformamide) at 90°C. From the experiment, they found that the strength of the composites decreases with increasing the filler loading of EFB. The composites with MAH-treated EFB showed higher flexural and impact strength (approximate 225% and 200% respectively) than those with untreated EFB. The modification had significantly improved the flexural modulus and toughness of the composites.

The effect of the contents and types of MAPP on the mechanical properties of wood composites was also studied by Sombatsompop et al. (2005). The particles sizes of wood sawdust used were in the ranges of 100-300 microns. The contents of wood sawdust particles added into the PP matrix were ranged from 0 to 30% by weight. The results demonstrated that the addition of 30% by weight of woodflour into polypropylene matrix was found to enhance the tensile modulus from 830 MPa to 1200 MPa and was found to decrease the elongation at break from 21% to 5.5% compared with those of polypropylene (tensile modulus = 830 MPa, % elongation = 21%). At the same composition of woodflour, the tensile strength decreased from 35 MPa (of the polypropylene matrix) to 27 MPa. The decrease of tensile strength was probably caused by poor dispersion of the fibers in the matrix, moisture pick-up, and an increase of interfacial defects between the polypropylene matrix and the untreated fibers. In addition, the interfacial adhesion improvement of the wood composite was studied using three types of MAPP coupling agent, namely; MZ203D, MD353D, and MD411D. They found that the excess concentrations of MAPP of approximately 4.2% to 11.1% by weight of woodflour showed marginal improvement of the mechanical properties. Furthermore, the optimal concentration of MAPP was found to be 2% by weight of woodflour resulted in the maximum tensile modulus and tensile strength of the composites.

Danyani et al.(2007) studied the influence of MAPP characteristic and contents on the properties of PP/wood composite. They used two different coupling agents (MAPP) and mass fraction of MAPP/wood ratio varied from 0 to 0.25 in 0.05 steps. The coupling agent of Licomont AR 504 was a low molecular weight polymer (Mn = 3500 g/mol) with high maleic anhydride content (3.5 wt%). The other coupling agent was Orevac CA 100 polymer that has a much lower functionality(1.0 wt%), but larger molecular weight (Mn = 25,000 g/mol).They reported that MAPP with larger molecular weight and smaller functionality proved to be more advantageous in the improvement of composite strength than the small molecular weight compound. Additionally, the amount of MAPP had a maximum efficiency at around 0.05–0.10 MAPP/wood ratio in the PP/wood composite composites.

CHAPTER IV

EXPERIMENT

4.1 Raw Materials

4.1.1 Polypropylene

The commercial polypropylene (Moplen HP740H, HP648N and HP644T) used in this experiment was supplied by HMC POLYMERS Co., Ltd., Thailand. Typical characteristic and physical properties of Moplen HP740H, HP648N and HP644T was shown in Table 4.1

Table 4.1 Typical Data of Commercial Polypropylene (Moplen HP740H, HP648N and HP644T)

Polymer Properties	Moplen HP740H	Moplen HP648N	Moplen HP644T	ASTM Method
Melt flow rate, g/10min	2.1	12	60	D 1238
Density, g/cm^3	0.9	0.90	0.90	D 792B
Tensile strength at yield, MPa	36	38	38	D 638
Elongation at yield, %	9	8	8	D 638
Flexural modulus, MPa	1750	1870	1,840	D 790A
Notched izod impact strength at 23^{o}C, J/m	40	32	22	D 256A
Deflection temperature, at 455 kPa, ^{o}C	115	122	122	D 648

4.1.2 Woodflour

Woodflour from *Hevea brasiliensis* tree was used as reinforcing filler in this work because of its availability and this wood is widely grown in Thailand. Woodflour used was a waste in the wood manufacturing which is in Suratthani Province, Thailand. The woodflour density determined by using a gas pycnometer is 1.49 g/cm^3 as previously reported (Rimdusit et al., 2006). Moreover, the light brown color of the woodflour was observed.

4.1.3 Coupling Agent

Maleic anhydride grafted polypropylene (MAPP) was used as a coupling agent to improve the interfacial adhesion between a filler and a matrix in the composite system. It was supplied by Creative Polymer Co., Ltd., Thailand. The trade name of MAPP is Fusabond MZ109D. MAPP has melt flow rate (MFR) of 120 g/10min, according to ASTM D-1238 and maleic anhydride grafted to polypropylene is 0.55% by weight.

4.2 Apparatuses and Instruments

4.2.1 Ball Mill
4.2.2 Sieve Shaker
4.2.3 Vacuum Oven
4.2.4 Grinder Machine
4.2.5 Twin Screw Extruder
4.2.6 Injection Molding
4.2.7 Universal Testing Machine
4.2.8 Dynamic Mechanical Analyzer (DMA)
4.2.9 Differential Scanning Calorimeter (DSC)
4.2.10 Thermogravimetric Analyzer (TGA)
4.2.11 Scanning Electron Microscopy (SEM)

4.3 Methodology

4.3.1 Preparation of Woodflour

Wood sawdust of *Hevea brasiliensis* tree, which is a natural material composing of cellulose, was used in this work. The sawdust was ground into small particles by using ball mill apparatus. After grinding, the particle size of woodflour was determined by test sieve. The woodflour was sieved to seven sizes i.e. 325-270, 200-140, 100-80, 80-60, 60-50, 50-40 and 40-30 mesh. The average particle sizes and corresponding screen sizes are shown in Table 4.2. For example, a designated 215 µm woodflour corresponds to particles that can pass through a 60 mesh screen, but can not pass an 80 mesh screen. All woodflour was dried at 105°C for 24 hr in vacuum oven before use.

Table 4.2 Standard Mesh Sizes Used to Classify Woodflours.

Mesh size range(mesh)		Screen hole size(µm)		Average particle sizes(µm)
Minimum	Maximum	Minimum	Maximum	
40	30	425	600	512
50	40	300	425	362
60	50	250	300	275
80	60	180	250	215
100	80	150	180	165
200	140	75	106	90
325	270	45	53	49

4.3.2 Preparation of the Polypropylene Woodflour Composites.

4.3.2.1 Effect of polymer matrix melt flow rate (MFR) on the mechanical properties of polypropylene woodflour composites.

To investigate the effect of melt flow rate (MFR) of polymer matrix on the mechanical properties of woodflour composites. The woodflour filler (average particle size = 215 μm) was mixed with polypropylene matrix at the ratio of 40:60wt% using different types of polypropylene polymers, i.e. PP-HP740H (MFR=2.1 g/10min), PP-HP648N (MFR=12 g/10min), and PP-HP644T (MFR=60 g/10min). Polypropylene pellet and woodflour filler were mixed thoroughly before the compounding by co-rotating twin screw extruder at a screw speed of 20 rpm. The blending temperature profiles on the extruder were 170, 175,180 and 185^{o}C, respectively, from hopper to die zones. The extrudate strands were cooled in air before to produce composite granules. The compound was dried at 105^{o}C for 24 hr and then injection molded using a processing temperature of 190^{o}C and injection pelletizing pressure of 0.65 MPa to obtain the test specimens designed by ASTM standard. Mechanical, thermal, and some related physical properties of the wood composites were investigated.

4.3.2.2 Effect of particle sizes and woodflour content on the mechanical properties of polypropylene woodflour composites.

To examine the effect of particle sizes and woodflour contents on the mechanical properties of wood composites. The woodflour filler at different particle sizes as above mentioned was mixed with polypropylene matrix at different loadings i.e.10, 20, 30, 40, 50, and 60% by weight. Polypropylene pellet and woodflour filler were mixed thoroughly before the compounding by co-rotating twin screw.

4.3.2.3 Effect of bimodal particle size distribution on the maximum packing and the corresponding mechanical characteristics of composite.

In this part, the mixture of two particle sizes of woodflour filler i.e. size ratio of 7:1 with a mass ratio of 73:27, was mixed with polypropylene pellet to investigate the effect of filler particle size distribution on the maximum packing and the corresponding mechanical characteristics.

4.3.2.4 Effects of coupling agents on the mechanical properties of wood composites.

To evaluate the effect of coupling agent content on the properties of wood composites. Maleic anhydride grafted polypropylene (5 - 20 wt % of woodflour) was mixed with the optimal composition in the previous part. Polypropylene pellet, woodflour filler and MAPP were mixed thoroughly before compounding by co-rotating twin screw extruder.

4.3.3 Characterization of Polypropylene Woodflour Composites.

4.3.3.1 Density measurement

The density of neat polypropylene and wood composites were measured by water displacement method according to the ASTM D792-91 (Method A). The specimens were rectangular in shape with dimensions of 60 mm in length, 19 mm in width, and 3 mm in thickness. All specimens were weighed both in air and in water. The density was calculated by following equation:

$$\rho = (\frac{A}{A-B})\rho_o$$

Where ρ = Density of the specimen, g/cm^3

A = Weight of the specimen in air, g

B = Weight of the specimen in liquid, g

ρ_0 = Density of the liquid at the given temperature, g/cm^3

The average value from five specimens was calculated.

4.3.3.2 Flexural property measurement

Flexural properties of wood composites were determined using a universal testing machine (model 5567) from Instron Co., Ltd. Flexural tests were conducted according to ASTM D790M-93 standard. The testing was performed with the support span to specimen depth ratio of 16:1. The test method used was a three-point loading by the support span of 48 mm. The crosshead speed during the flexural testing was 1.2 mm/min. Five specimens with dimensions of 60 mm × 19 mm × 3 mm were tested. The flexural modulus (E_B) or modulus of elasticity (MOE) and flexural strength (σ) or maximum flexural stress were calculated from the following equations.

$$E_B = \frac{L^3 m}{4bd^3}$$

$$\sigma = \frac{3PL}{2bd^2}$$

Where E_B = Flexural modulus, MPa

σ = Flexural strength, MPa

L = Support span, mm

b = Width of beam tested, mm

d = Depth of beam tested, mm

m = Slope of the tangent to the initial straight-line portion of the load-defection curve, N/mm

P = Load at break on the load-defection curve of specimen, N

4.3.3.3 Tension property measurement

Tensile properties of wood composites were determined using a universal testing machine (model 5567) from Instron Co., Ltd.. Tensile tests were investigated according to ASTM D638-03 using the dumbbell shaped specimens (Type IV). Five specimens for each specimen were tested. The test specimens have a uniform thickness and the tabs are pinched in grips attached to the testing machine with a crosshead speed 5 mm/min. The tensile modulus is defined as the ratio of stress to strain, and determined from the initial slope of the stress-strain curve. The tensile strength was determined as the maximum load divided by the initial section of the specimen.

4.3.3.4 Dynamic mechanical measurement

Dynamic mechanical thermograms of wood composite specimens were investigated using dynamic mechanical analyzer (DMA) model DMA242 from NETZSCH. The test specimens were rectangular in shape, having 50 mm in length, 10 mm in width, and 2 mm in thickness and tested under the bending mode. The specimens were tested in temperature sweep mode under nitrogen atmosphere. The measurements were carried out at temperatures ranging from -100^{o}C to 180^{o}C at a heating rate of 2^{o}C /min. The strain was applied sinusoidally with a frequency of 1 Hz. The storage modulus (E'), loss modulus (E''), and loss tangent or damping curve (tan δ) were then obtained. The glass transition temperature (T_g) was taken as the maximum point on the loss modulus curve in the temperature sweep test.

4.3.3.5 Differential scanning calorimeter (DSC) measurement

Differential scanning calorimeter (DSC) model 2910 from TA instruments was used to evaluate the thermal behaviors of neat polypropylene and wood composites. The specimen sizes with a weight in the range of 5-10 mg were sealed in an aluminum pan. The heating rate used was 10^{o}C/min from room temperature to 200 ^{o}C under nitrogen atmosphere. The purge nitrogen gas flow rate was 50 ml/min.

From the thermograms, the melting temperature (T_m) and melting enthalpy (ΔH_f) of each specimen were obtained from the maxima and area of the melting peaks.

4.3.3.6 Thermogravimetric analysis

Thermal stability and decomposition temperature of polypropylene and wood composites were studied using a Perkin Elmer’s TG/DTA thermogravimetric analyzer model SII Diamond at heating rate of 20°C/min from room temperature to 900°C under nitrogen atmosphere. The specimen was measured to be approximately 8-10 mg. Weight loss of the specimens was measured as a function of time and temperature. The degradation temperature (T_d) of the specimens was reported at 5 % weight loss. Char yield of polypropylene and wood composites were reported at 800°C.

4.3.3.7 Morphological study

The fracture surface of composites was observed by using ISM-5400 Scanning Electron Microscope at an acceleration voltage of 10 kV. The specimen was coated with gold before being scanned. The morphology such as phase structure, dispersion, and adhesion of the components were investigated.

CHAPTER V

RESULTS AND DISCUSSION

5.1 Effects of Polypropylene Types on the Mechanical Properties of *Hevea brasiliensis* Woodflour filled Polypropylene Composites.

5.1.1 Characteristics of the Polymer Matrices

5.1.1.1 Differential Scanning Calorimetry (DSC)

The purpose of using polymer as a matrix is to hold the filler together so that mechanical loads transferred from the weak matrices to the higher strength filler. Service temperature as well as processing temperature during fabrication is often the main consideration in the selection of a matrix material. Melting temperature (T_m) of the polymer matrices can be determined by Differential Scanning Calorimetry (DSC). Figure 5.1 presents DSC thermograms of the second heating of various polypropylene types used in this study. It can be observed that all types of polypropylene showed only one endothermic peak, which is characteristic of semi-crystalline polymer. The temperature at the peak maxima corresponds to the melting temperature (T_m) of each polypropylene. The values are listed in the Table 5.1. It can be seen that all types of polypropylene revealed a melting temperature (T_m) at about 165^{o}C. This value is similar to the DSC results observed by Doh et al. (2005) and Qiu et al. (2006).

5.1.1.2 Average Mixing Torque

The average mixing torque during processing is a useful parameter for evaluating the processability of the molten polymer system. It is well-known that the torque is proportional to the melt viscosity of the polymer in the processing conditions. The average torque value was recorded at the steady state condition during the extrusion of the polypropylene. Figure 5.2 and Table 5.2 present the average torque values of different types of polypropylene. It can be seen that the PP-HP740H (MFR = 2.1 g/10min, torque = 50.47 Nm) has the highest average torque value comparing with PP-HP648N (MFR = 12 g/10min, torque = 34.71 Nm) and PP-HP644T (MFR = 60 g/10min, torque = 17.79 Nm) respectively. As expected, the higher torque value for the PP-HP740H was due to the higher melt viscosity of the molten polymer. This is possibly because PP-HP740H has the highest molecular weight, which can be indicated by the lowest value of melt flow rate. In practice, this great value of average mixing torque means the high energy consumption for processing of a certain material at a given condition.

5.1.1.3 Flexural Properties

Flexural properties of the neat polypropylene were studied by using a universal testing machine. Figures 5.3 and 5.4 show the effect of polypropylene types on flexural modulus and flexural strength, respectively. The result was also summarized in Table 5.3. From the table, it indicates that the flexural modulus and flexural strength of PP-HPP740H (MFR=2.1g/10min) was higher than those of PP-HPP648N (MFR=12g/10min) and PP-HP644T (MFR=60 g/10min) respectively. The reason for the observed behavior is because PP-HP740H possesses the highest molecular weigh, which can be indicated by the lowest value of melt flow rate. It is generally known that the higher melt flow polymer possesses the lower modulus and strength due to its low molecular weight. Hence, the results obtained from this experiment followed this common trend. This statement is supported by Balasuriya et al. (2001), who reported that the flexural modulus and flexural strength of low melt flow index HDPE (0.15 g/10 min) were higher than those of medium melt flow index HDPE (7 g/10 min).

5.1.1.4 Thermogravimetric Analysis (TGA)

Thermal stability of woodflour-filled polypropylene composites is one of important parameters for processing and service condition of materials. The manufacture of such composites sometimes requires high temperature for mixing the fiber and the matrix which can cause thermal degradation of the material, thus can generate undesirable effects on the final properties.

Figure 5.5 shows the thermogravimetric curves of neat polypropylene and woodflour in nitrogen atmosphere. The thermograms of polypropylene occurred in a single stage degradation process between 400-470^{o}C and the degradation temperature at 5 % weight loss of the polypropylene is approximately 409^{o}C. Kim et al. (2006), explained thermal degradation and thermal depolymerization of PP as random scission occurring at the weak sites of the polypropylene main-chain. On the other hand, the thermal degradation of woodflour shows more than one decomposition step. The first part of this process occurs in the temperature range of 260-320^{o}C, and the second one occurs in the range of 360-430^{o}C. The lower temperature degradation process was assigned to the thermal degradation of hemicellulose and the cleavage of the glycosidic linkages of cellulose, whereas the high temperature process corresponds to the decomposition of lignin. From this figure, it could be calculated that the woodflour has the degradation temperature about 270^{o}C at 5 % weight loss. In addition, at below 120^{o}C, there is a sign of dehydration of moisture that was trapped inside the woodflour particles as all the hydroxyl and carboxylic groups in the woodflour were capable of absorbing moisture. Similar results were also reported by Nunez et al. (2002) and Rimdusit et al. (2006).

5.1.2 Effect of Polypropylene Types on the Mechanical Properties of the Wood Composites.

The effect of matrix flow behavior is important to achieve good dispersion of woodflour and to optimize the final properties of woodflour filled polypropylene composites. To establish a relationship between mechanical properties and matrix melt flow behavior, several matrix polymers with varied MFRs were used, i.e. PP-HP740H (MFR=2.1 g/10min), PP-HP648N (MFR=12 g/10min) and PP-HP644T (MFR=60 g/10min). Figures 5.6 and 5.8 show the effect of polypropylene types and number of passing extruder on the tensile modulus and flexural modulus of woodflour filled polypropylene composites, respectively. The woodflour composites containing

40% by weight of woodflour (average particle size = 215 μm) was selected for the investigation. From the result, it can be observed that the woodflour composites produced from polypropylene with high melt flow rate (PP-HP644T) seemed to render the highest tensile modulus and flexural modulus in comparison with the ones produced from PP-HP648N and PP-HP740H. This result can be explained by considering the woodflour distribution, particle wetting and polymer matrix penetration as follows. As the viscosity of polymer matrix is lower (i.e. high MFR), the polymer matrix flows well around the woodflour particle and has better wetting on the woodflour particles. Due to these mechanisms, higher mechanical properties can be expected for the composites. This result is also in good agreement to the study of Balasuriya et al. (2001).

Figures 5.7 and 5.9 show the tensile strength and flexural strength of woodflour-filled composites (40wt% woodflour) with various polypropylene types and numbers of times of passing through an extruder, respectively. It was found that the trends of the tensile strength and flexural strength (affected by the polypropylene types) are similar to those observed in tensile modulus and flexural modulus. The tensile strength and flexural strength of woodflour composite which was processed from high melt flow rate polypropylene (PP-HP644T, MFR = 60 g/10min) was superior to those of composite produced from PP-HP648N (MFR = 12 g/10min) and PP-HP740H (MFR = 2.1 g/10min). It is possibly due to the better stress propagation of the former which is caused by the improved wetting of polymer matrix to the woodflour filler resulting in better tensile strength and flexural strength.

Furthermore, it is well known that the aggregation of particle is another factor that has an influence on the final properties of woodflour composites. Hence, re-compounding process was applied to the PP wood molding compound to eliminate the aggregation of woodflour filler. However, it can be seen that the number of times of passing through an extruder showed no significant effect on the ultimate tensile properties and flexural properties (regardless of melt flow behavior of polymer matrix). This indicates the relatively well distribution of woodflour in the polymer matrix and there was no significant filler agglomeration in the compounding process using only one time of passing through an extruder. In addition, the tensile and flexural properties showed no significant change in values even though the molding compound was passed through a twin screw extruder up to 4 times. This results was similar to the work studied by Arbelaiz et al. (2005), who reported that the tensile properties of short flex fiber/polypropylene composites had no significant change after passing through an extruder for 3 times. Therefore, in this work, one time of passing through an extruder was enough for achieving the ultimate mechanical properties.

As mentioned before, the tensile properties and flexural properties of the composite after several times of passing through an extruder are similar to those using one time of passing. This result also implies one major advantage of wood thermoplastic composite, which was feasible to be recycled and reused to reduce the environmental wastes. In the other words, the woodflour polypropylene composites had high potential to be recycled at least up to four times as suggested in this study.

5.2 Effects of Particle Sizes, Woodflour Contents and Size Distributions on the *Hevea brasiliensis* Woodflour filled Polypropylene Composites.

The flexural properties and tensile properties results of PP wood composites are shown in Figure 5.6 to Figure 5.9. The figures clearly indicate that woodflour composites from PP-HP644T possessed the highest mechanical properties. Therefore, this experiment aims to study the effect of woodflour particle sizes, filler contents and size distribution on the mechanical properties and some related physical properties of woodflour filled polypropylene composites based on PP-HP644T.

5.2.1 Effects of Woodflour Contents and Particle Sizes on the Density of the Wood Composites

The presence of voids in the woodflour filled polypropylene composites was verified by measuring the density of the composites. The actual density and theoretical density of woodflour composites at various woodflour contents were shown in Figure 5.10 and Table 5.4. The theoretical density of the composites was calculated from the mixing rule based on the woodflour density of 1.49 g/cm^3 (Rimdusit et al., 2006) and the polypropylene density of 0.90 g/cm^3.

From the results, the actual density of woodflour composite was increased with increasing woodflour contents. The actual density of the composite at 60wt% filler content was about 29 % higher than that of neat polypropylene, because the density of woodflour is higher than that of polypropylene. Furthermore, the addition of woodflour filler having higher surface area slightly affected the density of woodflour composite as shown in Table 5.4. From the results, the actual density of composites trended to be lower than the theoretical density with increasing the mass fraction of filler. The increase in woodflour content led to the increase of the filler surface area; therefore, there is insufficient polymer matrix to encapsulate the woodflour. This led to the presence of voids in the specimens. Hence, the actual density was slightly lower than the theoretical value.

5.2.2 Effects of Woodflour Contents on the Composite Thermal Properties

The DSC thermograms of pure polypropylene and woodflour-filled polypropylene at different filler contents (average particle size of woodflour is 275 μm) are shown in Figure 5.11 and Table 5.5. Generally, the melting temperature (T_m) of the material is obtained from the endothermic peak temperature. From this figure, all specimens of woodflour-PP composites showed only one endothermic peak with the same peak maxima at about 165°C. Moreover, the T_m of all specimens was not significantly changed by the addition of woodflour filler. This implies that woodflour content has no effect on the melting process of the polypropylene-woodflour composites. However, the filler content affected the melting thermograms in such a way to decrease the area under endothermic peaks or heat of fusion (ΔH_f). This can be due to the fact that heat of fusion (ΔH_f) was proportional to the amount of the PP matrix in the sample. Thus the heat of fusion was decreased with increasing the filler contents in the PP wood composites.

Table 5.5 summarizes the melting temperature and heat of fusion of our PP wood. It reveals that percent crystallinity is relatively unchanged when the filler is incorporated in PP matrix. This result is also in agreement with those of Doh et al., (2005). Consequently, we can conclude that woodflour content has no effect on the melting process of the polypropylene woodflour composites.

5.2.3 Effects of Particle Sizes and Filler Contents on Mechanical Properties of PP Wood Composites

Figures 5.12 and 5.14 show flexural modulus and tensile modulus of woodflour-filed polypropylene composite as a function of particle sizes (i.e. 50-500 µm) and woodflour contents (i.e. 10-60 wt %). From the result, it can be seen that the flexural modulus and tensile modulus of woodflour composites for all woodflour content increase to a maximum value at an average particle size of about 275 µm. At this average size, the flexural modulus and the tensile modulus of woodflour composite (60wt %) increase about 300% and 250% from the values of the neat polypropylene i.e. flexural modulus = 1.63 GPa, tensile modulus = 1.57 GPa, respectively. Nevertheless, the flexural modulus and tensile modulus tend to decrease with average particle size of greater than 275 µm. The effects of average particle size of woodflour on the flexural modulus and tensile modulus of the woodflour filled polypropylene composites can be explained as follows.

In case of small average particle size, the lower modulus and tensile modulus are probably caused by the following reasons.

(I) Woodflour filler and polypropylene matrix are rather incompatible due to the hydrophilicity of woodflour and hydrophobicity of the polypropylene matrix (Bledzki et al., 2005). As a result, interfacial adhesion between woodflour and polypropylene is relatively weak. The lack of interfacial adhesion between woodflour and polypropylene possibly results in some unsatisfactory properties of the composites. In addition, the small average particle size possesses relatively high surface area. Therefore, the wetting of the polypropylene matrix may not be sufficient to encapsulate the woodflour. This leads to the presence of void in the specimens. Hence, the obtained flexural modulus and tensile modulus are slightly low when the average particle size was lower than 275 μm (Nunez et al., 2002). This explanation can be substantiated by considering the density of woodflour filled polypropylene composites shown in Table 5.4. From this table, it can be seen that the woodflour composites filled with the woodflour of the average particle size of 275 μm render the actual density close to theoretical density than the ones with the smaller average particle size. It signifies that the composite had the less void content using relatively larger particle size i.e. > 275 μm in our case.

(II) Smaller woodflour filler tends to cling or agglomerate together, due to hydrogen bonding, or other secondary forces, and resists dispersion of the individual filler particle as the filler content is increased (Sombatsompop et al., 2005). This phenomenon can be proven by using a re-compounding through a twin screw extruder to enhance the dispersion of woodflour filler in the composites. Figures 5.16 and 5.17 show flexural properties and tensile properties of our PP wood composites at 60wt % of woodflour having an average particle size of 49 μm as a function of number of times of passing through an extruder. It can be observed that the flexural properties and tensile properties of the woodflour composites slightly increase with the number of times of passing. After four times of passing through an extruder, the flexural modulus and the tensile modulus slightly increase about 10% and 22% respectively, whereas both the flexural strength and the tensile strength are increased about 7% from the values of the composites processed by single passing through the extruder. It can be interpreted that the improved flexural properties and tensile properties are due to the better dispersion of woodflour in the composites. However, the tensile properties and flexural properties show only a marginal change with the number of times of passing through an extruder. It means that the woodflour is relatively well distributed in the polymer matrix using only one passing in the twin screw extruder and there is no significant filler agglomeration in the first-passing compounding.

This experiment also implies the recycling ability of our PP wood composites that they can be reprocessed more than one time without the property deterioration from the processing technique.

Additionally, it was found that the flexural properties and the tensile properties of the PP wood composites with the average woodflour particle size of 49 μm, after passing four times through an extruder, remained lower than those of the composites filled with 275 μm woodflour after passing only one time through an extruder. This behavior can be explained using the same reason in previous section, i.e. the woodflour particle size of 49 μm was too small with relatively large surface area, and the wetting of polypropylene matrix may not be sufficient to cover all surface area of the woodflour particles. In case of large average particle size, the decrease in flexural modulus and tensile modulus of woodflour filled polypropylene composite was expected. It is likely to be due to the fact that the large particle renders less interface between the woodflour filler and the polypropylene matrix than the small particle. Hence, the lower degree of reinforcement by the woodflour leads to the reduction of the flexural modulus and tensile modulus of woodflour composites. Moreover, based on the same average particle size in the composites, flexural modulus and tensile modulus tend to increased with increasing in the woodflour contents. The increase in the modulus is primarily influenced by the fact that the woodflour possesses greater stiffness than the polypropylene matrix.

The flexural strength and tensile strength of woodflour filled polypropylene composites as a function of average woodflour particle sizes (50-500 μm) and woodflour contents (10-60wt%) are illustrated in Figures 5.13 and 5.15. These figures reveal that the flexural strength and tensile strength of our woodflour-filled polypropylene composites increase with increasing the average particle size in the range of 49 µm to 275 µm. However, for the average particle sizes larger than 275 µm, the flexural strength and tensile strength tend to decrease with increasing the particle size. This phenomenon confirms the similar trend observed in the flexural modulus and tensile modulus. The reasons for these behaviors can be explained using the same reasons as those behaviors in the flexural modulus and tensile modulus.

In addition, the flexural strength and tensile strength of woodflour filled polypropylene composites (at the same average particle size) decrease with increasing the woodflour contents. This result suggests that the interfacial adhesion between woodflour filler and polymer matrix was rather poor. The weak bonding between the woodflour filler and the polymer matrix obstructs the stress propagation in the wood composites (Yang et al., 2007), and causes the flexural strength and tensile strength to decrease as the filler contents increase. In other words, polypropylene matrix and woodflour filler are incompatible because of the discrepancy in polarity of the hydrophilic filler and the hydrophobic polypropylene matrix (Qiu et al., 2002).

5.2.4 Effects of Bimodal Particle Size Distribution on Flexural Properties of PP Wood Composites

Figure 5.18 exhibits the effect of bimodal particle size distributions on flexural properties of wood composites that were filled with the mixed size of woodflour at 60wt %. The particle size mixture is consisted of two particle sizes at the mass ratio of large particle: small particle = 73:27. The plots reveal that the composites, filled with the mixed woodflour of particle size 275 and 49 µm, provide the highest flexural modulus and flexural strength. In theory, this ratio of mixed woodflour possesses the greatest packing density of the woodflour-filled polypropylene system that was confirmed by the density measurement of the composites as summarized in Table 5.6. From the table, we can see that the measured density values of the composite, filled with the woodflour of the mixed particle size of 275 µm and 49 µm, are relatively close to the theoretical density values. This implies that the composites have negligible amount of void content inside and the woodflour has the greatest packing density at this packing condition. Furthermore, the composite filled with the mixed particle size of 275 µm and 49 µm possesses the lower surface area than that of the composite filled with the mixed woodflour of 215 and 49µm. The wetting of the PP matrix, therefore, might not be sufficient to encapsulate the larger surface area of the mixed woodflour, while the large average particle size incorporated into the polymer matrix has less interfacial area than that of the small average particle size.

5.2.5 Effects of Woodflour Contents on Thermal Stability of PP Wood Composites

Weight loss of woodflour filled polypropylene composites as a function of temperature is commonly determined by thermogravimetric analysis (TGA) and is an irreversible process due to thermal degradation. TGA curves of woodflour filled polypropylene composite at different woodflour contents are shown in Figure 5.19. From the thermograms, the thermal degradation of PP wood composites occurs in a three-stage degradation process. Those in the range of 260-320°C and 360-430°C are corresponded to the degradation of hemi-cellulose and lignin. The other process in the range of 400-470°C is assigned to the degradation of the polypropylene matrix. This three-step degradation process suggests the thermal degradation temperature of the major constituents in woodflour occurs at relatively temperature lower than that of polypropylene. The polypropylene woodflour composites have the decomposition thermogram with combined characteristics of the woodflour and the polypropylene and were typically observed in heterogeneous materials. The corresponding degradation temperatures at 5 % weight loss and char yield values are also listed in Table 5.7. The table reveals that thermal stability and degradation temperature of woodflour-filled polypropylene decrease with increasing woodflour mass fraction in the composites. The phenomenon implies that the degradation temperature of woodflour is lower than that of neat polypropylene. The degradation temperature at 5 % weight loss of the woodflour-filled polypropylene composites in the range of 10 to 60 % by weight of woodflour is ranging from 353 to 288°C under nitrogen atmosphere comparing with the value of 409°C of the neat polypropylene. Another important feature observed in these thermograms is the percent residue at 800°C or the char yield, one of the parameters related to the material flame resistance. The presence of the woodflour in the PP wood composites was found to enhance the char yield of the composites. For example, the char yield of composites at 10 to 60 % by weight of filler is ranging from 2 to 12 %. The ring structures of cellulose and the phenolic structures in lignin, thus, clearly render greater char formation than the linear structure of the polypropylene used.

5.3 Effects of Coupling Agents on the *Hevea brasiliensis* Woodflour Filled Polypropylene Composites

5.3.1 Effects of Coupling Agents on the Average Mixing Torque

The change of mixing torque during mixing of woodflour-filled polypropylene is related to the change of melt viscosity of the molten composites. In this work, MAPP was selected as the coupling agent of our PP wood due to its high coupling efficiency as reported in the work of Qiu et al.(2002); Arbelaiz et al.(2005); Kim et al.(2007) etc. Figure 5.20 and Table 5.8 show the effect of concentrations of MAPP coupling agent on the average mixing torque of the woodflour-filled polypropylene composites at 60 wt%, of woodflour and the average particle size of 275 μm. The mixing torque values were recorded at steady state during the compounding. It can be observed that the average mixing torque increases with the presence of the filler, for example, average mixing torque of non-treated woodflour filled polypropylene composites increases about 98% from the value of 17.8 Nm of the neat polypropylene to the value of 35.3 Nm of the 60 wt% wood composite. The observed behavior is typical phenomenon of the filled system as the filler particles tend to hinder the normal flow pattern of pure molten polymer by preventing polymer chain mobility. This result has greater effects on the filled systems with high melt viscosity which requires higher torque for compounding (Mantia et al., 2004). From Figure 5.20, the average torque for the MAPP-treated composites slightly decreases with an addition of the MAPP coupling agent. The average mixing torque of MAPP-treated woodflour composites at various MAPP contents in the range of 5 to 20 wt% of woodflour ranges from 31.6 to 27.1 Nm or about 10.2 to 23.2% from the value of 35.26 Nm of the non-treated MAPP composites.

When adding MAPP into woodflour composites, it leads to the reduction of melt viscosity of the woodflour composites as described above. That is because MAPP (MFR= 120 g/10min) has the lower molecular weight or higher melt flow rate than that of the polypropylene matrix. The same phenomenon has also been reported in the study of Li et al. (1998) and Pracella et al. (2006).

5.3.2 Effects of Coupling Agents on Thermal Properties of PP Wood Composites

Figure 5.21 presents the DSC thermograms of pure polypropylene and woodflour-filled polypropylene composites at 60 wt% of woodflour with different maleic anhydride-grafted polypropylene (MAPP) contents. It can be observed that all thermograms show single endothermic melting peak at the same peak maxima at approximately 165°C. The presence of MAPP in the composites seems to have no a major influence on the melting temperature of the composites as evidently shown in the thermograms due to its small quantity in the wood composites.

Table 5.9 summarizes the melting temperature (T_m) and melting enthalpy (ΔH_f) of the pure polypropylene and the woodflour-filled polypropylene composites at different coupling agent contents. The melting enthalpy (ΔH_f) of composites is almost unchanged with increasing MAPP content due to the small quantity of the MAPP in the composites.

5.3.3 Effects of Coupling Agents on Mechanical properties of PP Wood Composites

Flexural and tensile properties of woodflour filled polypropylene composites at various coupling agent contents (0 to 20 % by weight of woodflour) were obtained using a universal testing machine. The woodflour-filled polypropylene composites containing 60 % by weight of woodflour with average particle size of 275 μm was selected to study the effect of the coupling agent concentrations on the properties. Figures 5.22 and 5.23 show the effect of MAPP coupling agent on flexural and tensile properties as a function of the amount of coupling agent used. From the results, flexural strength and tensile strength was found to increase with increasing MAPP content until plateau region was reached. It is worth noting that, the 5wt% of MAPP renders the optimum flexural strength which is about 110 % enhancement. The maximum improvement of about 87 % from the value of the non-treated MAPP composite was obtained in the case of tensile strength. Beyond 5wt% of MAPP, the flexural and tensile strengths tend to be relatively stable. This improvement is due to the enhanced interfacial interaction between the woodflour and the polypropylene polymer matrix. In the report by Sombatsompop et al. (2005) suggested this phenomenon to be associated with the ester linkages formed by chemical reaction of coupling agent and woodflour filler. Furthermore, the long PP segments of MAPP are also compatible with the PP matrix and long enough to get entangled with the PP chains. The explanation can be substantiated by analyzing scanning electron micrographs. Figure 5.24 shows the SEM micrographs of the fracture surfaces of MAPP-treated and the non-treated composites. The fracture surface of the non-treated composites indicates the presence of interfacial debondings and gaps between the PP matrix and the woodflour filler revealing the smooth surface of the woodflour. This observation confirms the relatively poor interfacial adhesion between the woodflour and the polypropylene matrix thus resulting in the obtained poor flexural and tensile strengths. The appearance of the fracture surface of the MAPP-treated composites exhibits a sign of strong interfacial adhesion between the filler and the matrix i.e. the coverage of the matrix on the woodflour particles and the tight interface. These results are in good accordance with the enhancement in the composite mechanical properties mentioned above.

Moreover, the flexural modulus and tensile modulus of the composites were also found to slightly increase with increasing in MAPP content up to the MAPP content of 5 % by weight of woodflour. At this optimum MAPP content, flexural modulus and tensile modulus slightly increase about 8 % and 3 % from the value of the non-treated composites. This phenomenon may be due to the better reinforcement by MAPP at this composition. However, the flexural modulus and tensile modulus of woodflour-filled polypropylene composites decrease with the MAPP content beyond 5 % by weight of woodflour. It is possibly because the excess concentration of MAPP i.e. at 10 to 20 % by weight of woodflour does not provide any further enhancement on the interfacial adhesion (on the basis of constant woodflour fraction). In addition, the flexural and tensile moduli of MAPP are lower than those of the polypropylene and the woodflour. Therefore, the excess amount of MAPP is likely to cause the reduction of the flexural and tensile moduli of the composites base on the rule of mixture. The results are also in good agreement with the reports by Fernanda et al., (1998) and Nitz et al. (2000).

5.3.4 Effects of Coupling Agent on Dynamic Mechanical Properties of PP Wood Composites

Dynamic mechanical characteristic i.e. storage modulus as a function of temperature, of the neat polypropylene and woodflour-filled polypropylene composites (60wt%) at various MAPP contents are depicted in Figure 5.25. The dynamic mechanical data are also summarized in Table 5.10. In the range of temperature analyzed, woodflour-filled polypropylene composites show higher storage modulus than neat polypropylene matrix in all temperature domains. For example, at -50^{o}C, storage modulus of non-treated woodflour composites is 11.32 GPa, and that of the neat polypropylene is 4.87 GPa. The improvement of stiffness with the woodflour content is, in principle, caused by the addition of rigid filler into the polymer matrix. The result was also in agreement with those of flexural modulus and tensile modulus of the untreated systems in Figure 5.12 and 5.14.

The storage modulus of the composites (at the MAPP content in the range of 0-5wt %) slightly increases with increasing the MAPP content. At the MAPP content > 5 wt% of woodflour, the storage modulus of MAPP-treated woodflour composites, again, tends to decrease with increasing the MAPP content. This result is consistent with the trends in the flexural modulus and tensile modulus shown in Figure 5.22 and Figure 5.23, respectively. This observed phenomenon was also attributed to the optimal reinforcing composition of MAPP as those of the flexural modulus and tensile modulus obtained under static load.

Figure 5.26 shows the temperature dependence of the loss modulus of the neat polypropylene and the woodflour-filled polypropylene composites (60wt %) at various MAPP contents. The measured temperature range is from -50°C to 140°C. In this figure, two relaxation peaks are evidently observed, i.e. the β-relaxation peak between -5°C to 5°C, and the α-relaxation peak between 70°C to 90°C. The α-relaxation peak was attributed to a lamellar slip mechanism and rotation in the crystalline phase (Nunez et al., 2002). Whereas the β-relaxation was related to the glass transition of amorphous phase (Qiu et al., 2005). These results suggest that the MAPP coupling agent shows negligible effect on the relaxation process of the woodflour composites.

5.3.5 Effects of Coupling Agents on Thermal Stability of PP Wood Composites

Figure 5.27 depicts TGA thermograms of the woodflour-filled polypropylene composites with the MAPP contents varied from 0 to 20 % by weight of woodflour. All the woodflour-filled polypropylene composites show more than one decomposition step as a result of various species presented in the composites, i.e. PP matrix, cellulose, hemi-cellulose and lignin, and the MAPP coupling agent. The corresponding degradation temperature at 5 % weight loss is also summarized in Table 5.11. These results reveal that the thermal stability and degradation temperature of our PP wood composites containing the coupling agent slightly increases with increasing the coupling agent content. The degradation temperature (at 5 % weight loss) of the woodflour-filled polypropylene composites at various MAPP contents (in the range of 5 to 20wt% of woodflour) is ranges from 291 to 297°C under nitrogen atmosphere i.e. about 3°C to 9°C from the value of 288°C of the non-treated MAPP composites. The results suggest that the use of MAPP coupling agent can slightly improve the thermal stability of the composites. This implies that the compatibility and the interfacial bonding increased by the presence of the coupling agent in the PP wood can help improving the thermal stability of the composites though at a marginal improvement level. The work by Kim et al.(2006) reported the 7 ^{o}C improvement in degradation temp of PP-rice huskflour composite whereas about 10 ^{o}C enhancement was reported in the system of polypropylene wood composite (Nachtigall et al., 2007).

Table 5.1: Melting Temperature of Polypropylene at Various Types of Polypropylene.

Type of Polypropylene	**Melting Temperature(^{o}C)**
HP740H	166.3
HP648N	165.6
HP644T	165.4

Table 5.2: Average Mixing Torque of Neat Polypropylene with Different Types of Polypropylene.

Type of Polypropylene	**Melt Flow Index (g/10 min)**	**Average Mixing Torque (Nm)**
HP740H	2.1	50.47 ± 3.11
HP648N	12	34.71 ± 3.41
HP644T	60	17.79 ± 2.31

Table 5.3: Flexural Properties of Polypropylene at Various Types of Polypropylene.

Type of Polypropylene	**Flexural Modulus (GPa)**	**Flexural Strength (GPa)**
HP740H	1.75 ± 0.03	60.49 ± 0.38
HP648N	1.69 ± 0.02	59.58 ± 0.10
HP644T	1.63 ± 0.03	59.18 ± 0.36

Table 5.4: Density of Woodflour Filled Polypropylene Composites at Various Woodflour Contents.

Woodflour Content (wt%)	**Theoretical Density (g/cm^3)**	**Measured Density(g/cm^3)**						
		49μm	**90μm**	**165μm**	**215μm**	**275μm**	**362μm**	**512μm**
10	0.937	0.935	0.936	0.9368	0.936	0.936	0.936	0.936
20	0.977	0.975	0.975	0.9767	0.977	0.977	0.976	0.976
30	1.021	1.018	1.019	1.019	1.020	1.020	1.020	1.020
40	1.069	1.054	1.057	1.058	1.063	1.065	1.065	1.065
50	1.122	1.097	1.101	1.103	1.104	1.104	1.105	1.109
60	1.180	1.147	1.151	1.153	1.155	1.159	1.160	1.159

Table 5.5: DSC Results of Woodflour Filled Polypropylene Composites at Various Woodflour Contents.

Woodflour Content (wt %)	Melting temperature(^oC)	Heat of fusion,ΔH_f (J/g)	Crystallinity, Xc (%)
0	164.5	109.3	79.2
10	163.9	98.1	78.9
20	163.7	87.0	78.8
30	164.1	76.1	78.7
40	164.4	65.2	78.7
50	165.5	54.5	78.9
60	164.2	43.2	78.2

Table 5.6: Density of Woodflour Filled Polypropylene Composites (Bimodal Particle Size).

Average Particle Size	Theoretical density (g/cm^3)	Measured density (g/cm^3)
215+49	1.180	1.152
275+49	1.180	1.157
362+49	1.180	1.154
512+49	1.180	1.151

Table 5.7: Degradation Temperature and Char Yield of Woodflour Filled Polypropylene Composites at Various Woodflour Contents.

Woodflour Content (wt %)	**Degradation Temperature (^oC)**	**% Char Yield at 800 ^oC**
0	409.0	0
10	353.0	2
20	319.0	3
30	306.0	4
40	296.0	6
50	294.0	8
60	288.0	12
100	270.0	17

Table 5.8: Average Mixing Toque of Woodflour Filled Polypropylene Composites at Various Coupling Agent Contents.

Materials	**Average Mixing Toque (Nm)**
Pure PP	17.78 ± 2.30
MAPP 0 %	35.26 ± 2.02
MAPP 5 %	31.64 ± 1.64
MAPP 10 %	29.82 ± 1.72
MAPP 15 %	28.61 ± 1.58
MAPP 20 %	27.08 ± 1.30

Table 5.9: DSC Results of Woodflour Filled Polypropylene Composites at Various Coupling Agent Contents.

Coupling Agent Content (wt% of woodflour)	**Melting temperature (^{o}C)**	**Heat of fusion,ΔH_f (J/g)**
0	164.5	42.7
5	164.9	43.3
10	164.7	44.4
15	164.5	45.4
20	164.1	45.9

Table 5.10: DMA Results of Woodflour Filled Polypropylene Composites at Various Coupling Agent Contents.

Materials	**Storage Modulus at $-50^{o}C$ (GPa)**	**Glass transition temperature (^{o}C)**
Pure PP	4.87	3.1
MAPP 0 %	11.32	-1.5
MAPP 5 %	11.94	-2.5
MAPP 10 %	10.52	-2.2
MAPP 15 %	10.35	-2.4
MAPP 20 %	9.45	2.3

Table 5.11: Degradation Temperature of Woodflour Filled Polypropylene Composites at Various Coupling Agent Contents.

Coupling Agent Content **(wt% of woodflour)**	**Degradation Temperature (^{o}C)**
0	288.0
5	291.0
10	293.0
15	295.0
20	297.0

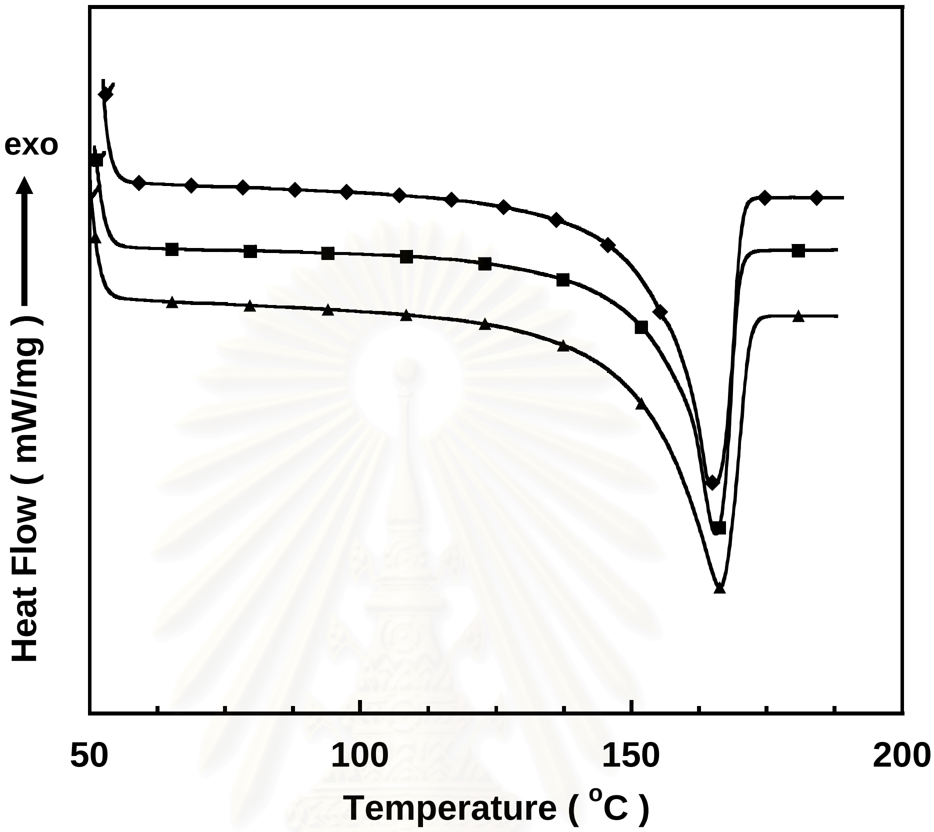


Figure 5.1: DSC thermograms of neat polypropylene with different types of polypropylene: (▲) HP740H (■) HP648N, (♦) HP644T

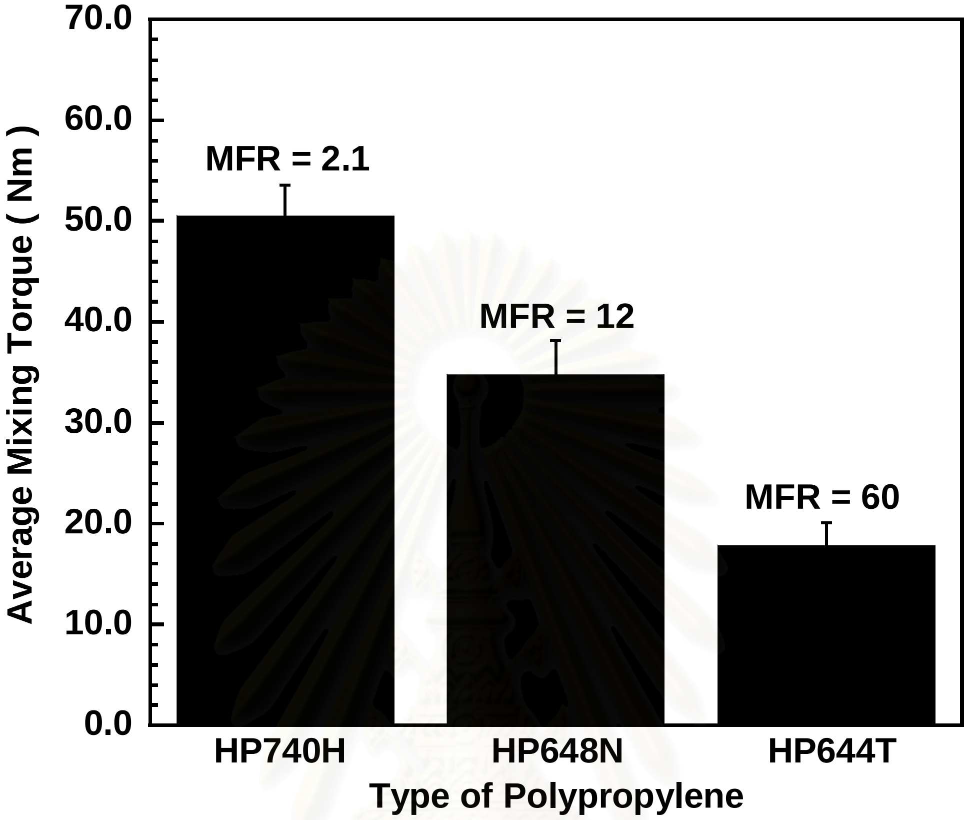


Figure 5.2: Average mixing torque of neat polypropylene with different types of polypropylene: (■) average mixing torque

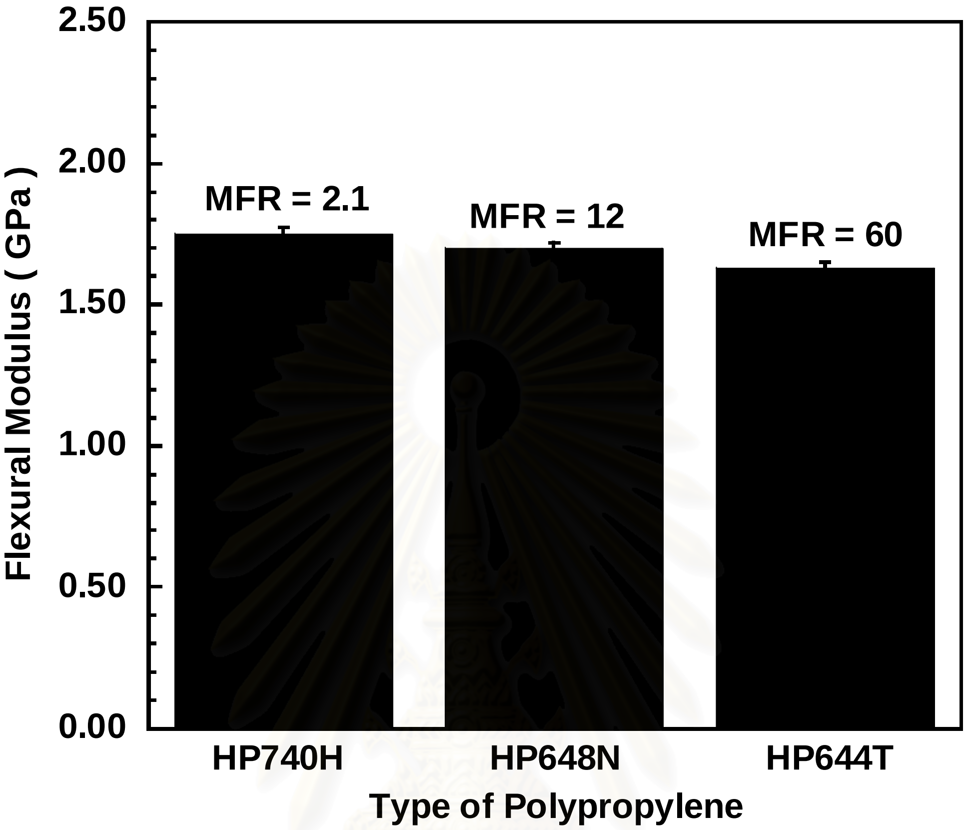


Figure 5.3: Flexural modulus of neat polypropylene with different types of polypropylene

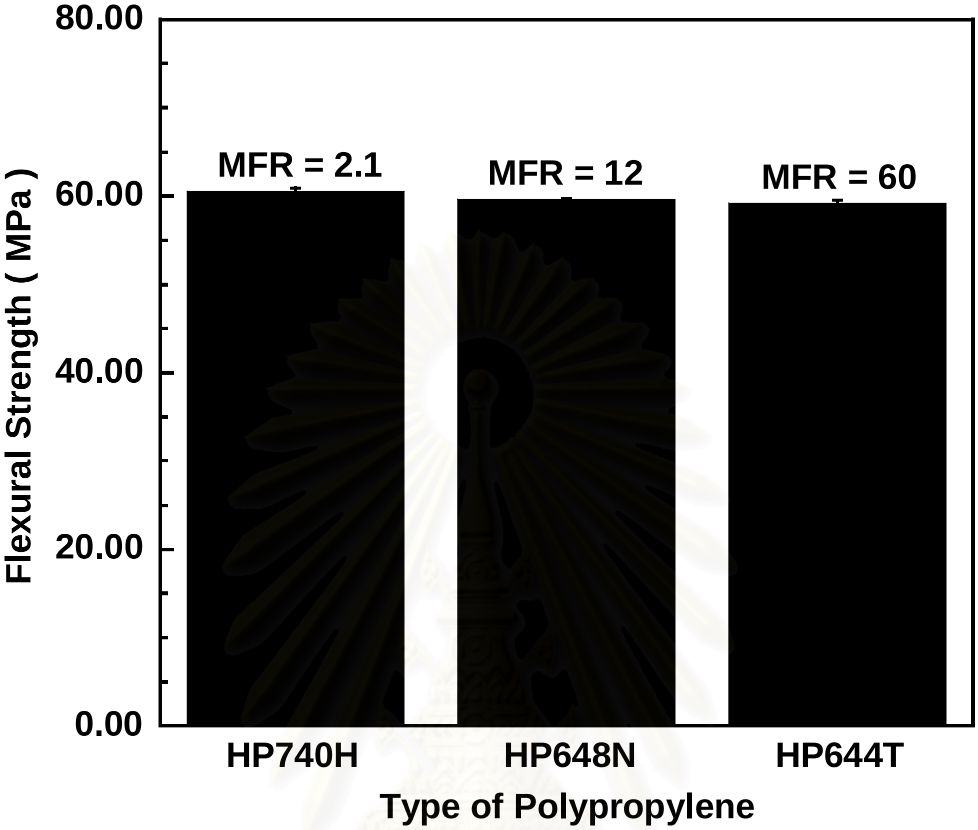


Figure 5.4: Flexural strength of neat polypropylene with different types of polypropylene

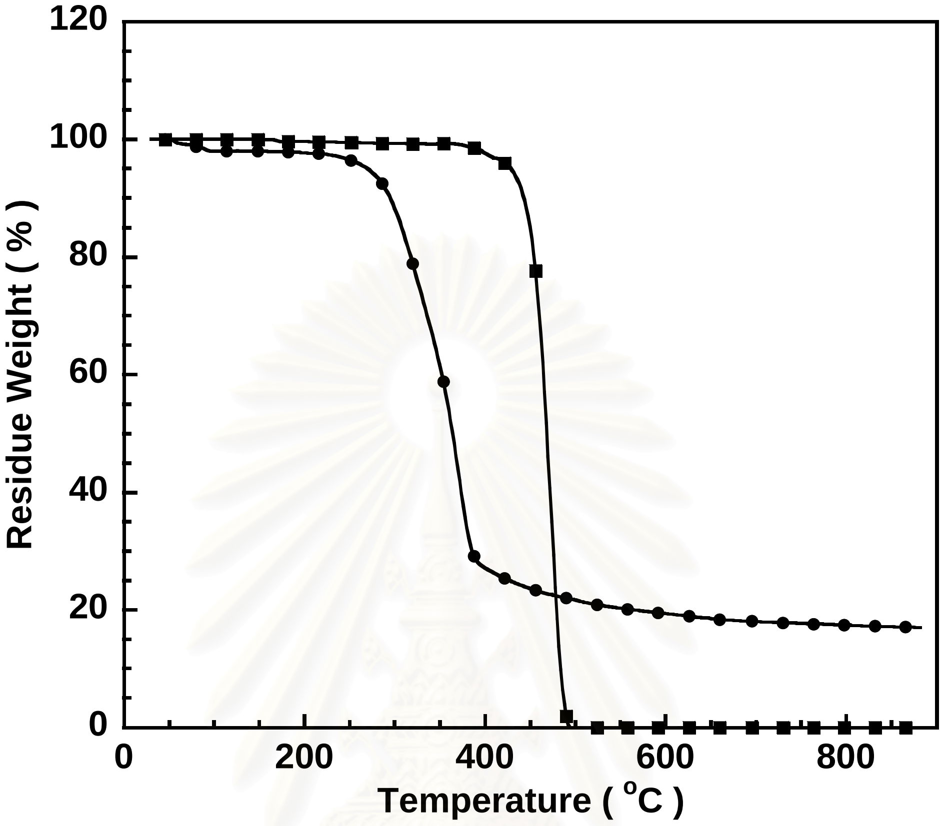


Figure 5.5: TGA thermograms of woodflour and polypropylene: (●) Woodflour, (■) neat Polypropylene

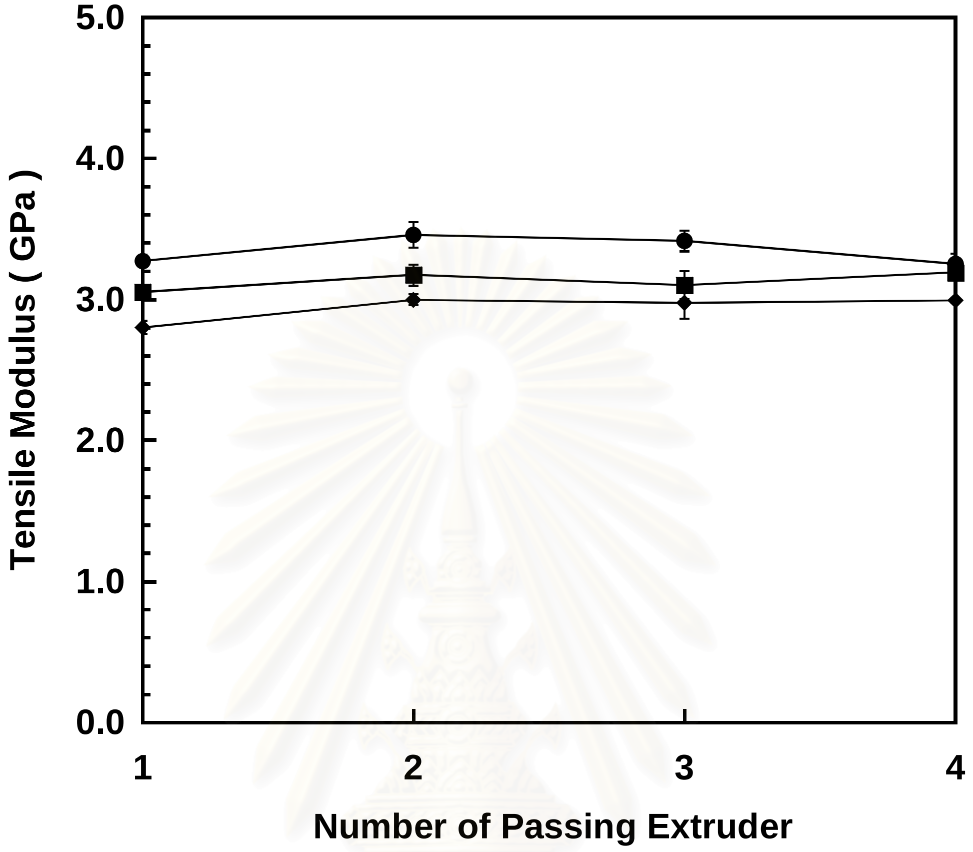


Figure 5.6: Tensile modulus of polypropylene woodflour composites (40 wt%, 215μm) as a function of type of polypropylene and number of passing extruder: (●) HP644T , (■) HP648N, (♦) HP740H

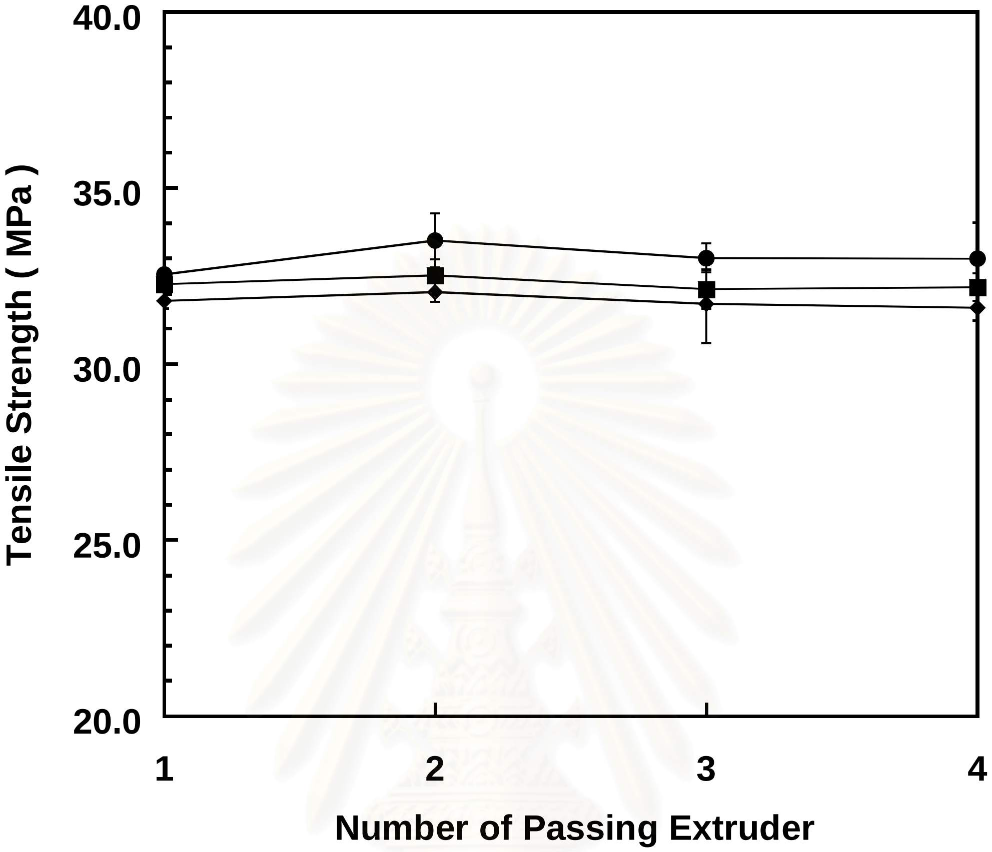


Figure 5.7: Tensile strength of polypropylene woodflour composites (40 wt%, 215μm) as a function of type of polypropylene and number of passing extruder: (●) HP644T, (■)HP648N, (♦) HP740H

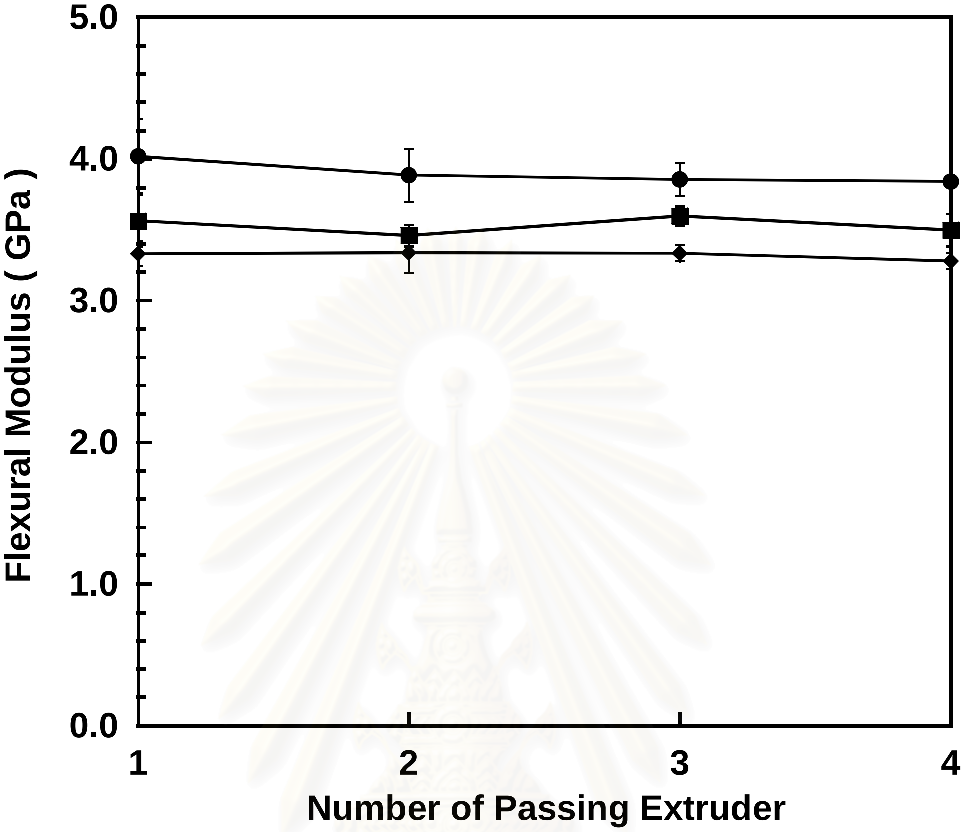


Figure 5.8: Flexural modulus of polypropylene woodflour composites (40 wt%, 215μm) as a function of type of polypropylene and number of passing extruder: (●) HP644T, (■) HP648N, (♦) HP740H

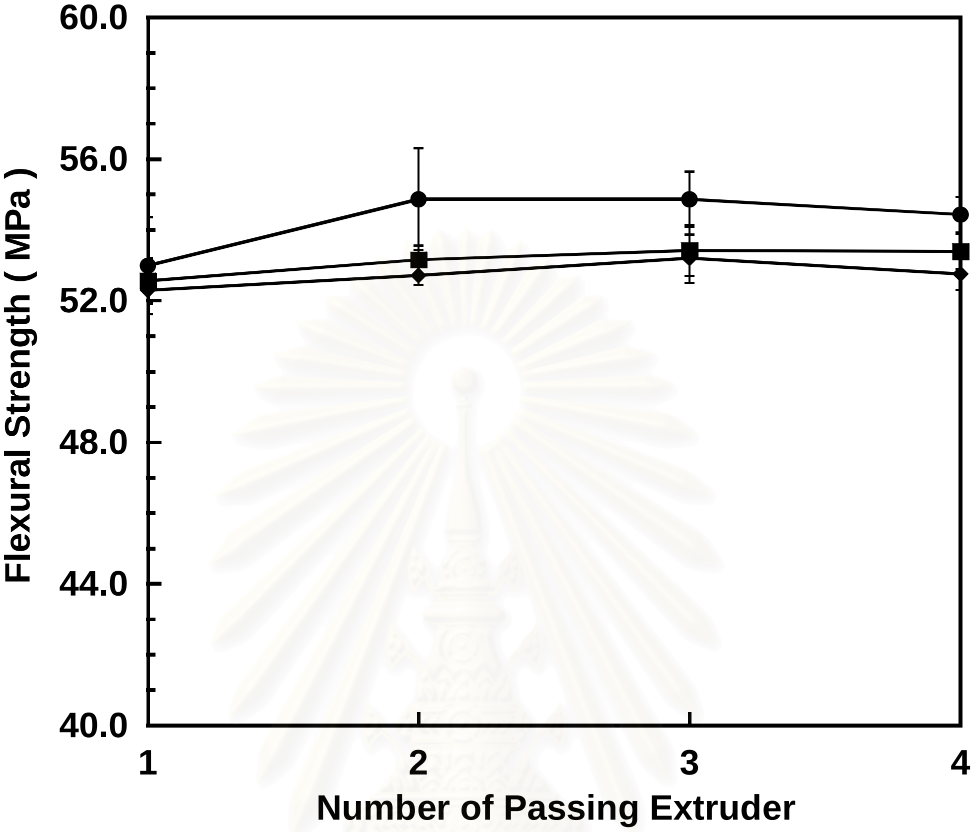


Figure 5.9: Flexural strength of polypropylene woodflour composites (40 wt%, 215μm) as a function of type of polypropylene and number of passing extruder: (●) HP644T , (■) HP648N, (♦) HP740H

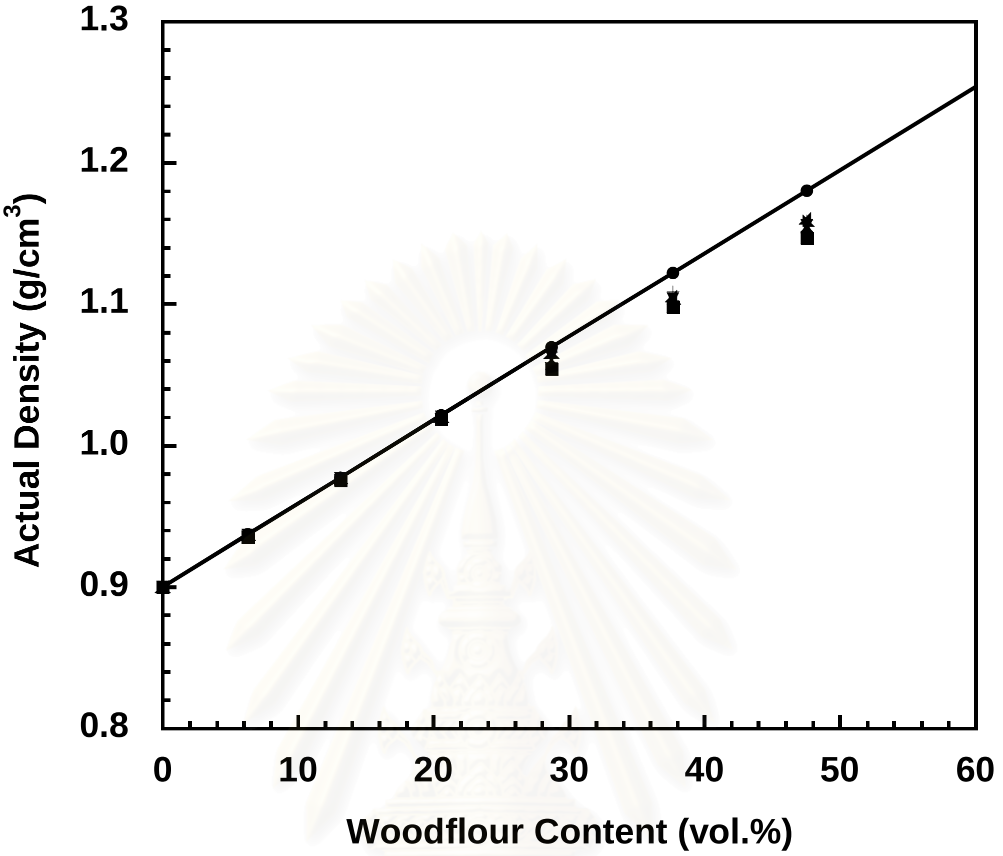


Figure 5.10: Density of polypropylene and woodflour filled polypropylene composites at various woodflour contents: (●) Theoretical density, (■) 49 µm, (♦) 90µm, (▲) 165µm, (▼) 215µm, (◣) 275µm, (◢) 362µm, (+) 512µm

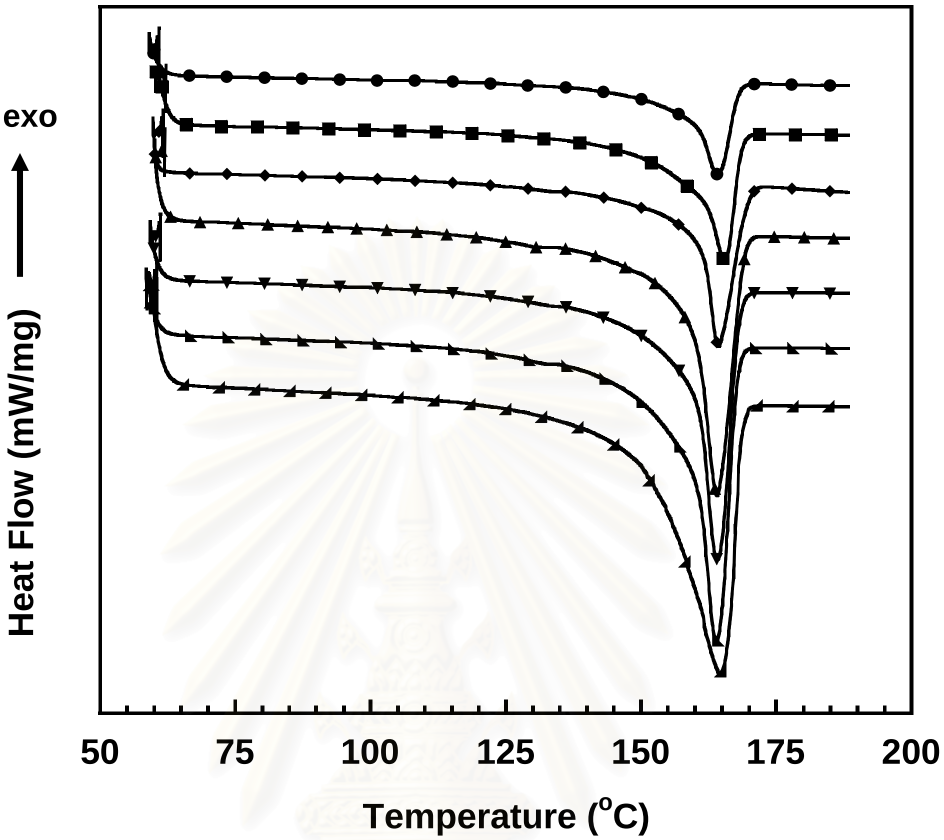


Figure 5.11: DSC thermograms of polypropylene and woodflour filled polypropylene composites at various woodflour contents: (◢) neat polypropylene, (◣) 10 wt% WF, (▼) 20 wt% WF, (▲) 30 wt% WF, (♦) 40 wt% WF, (■) 50 wt% WF, (●) 60 wt% WF

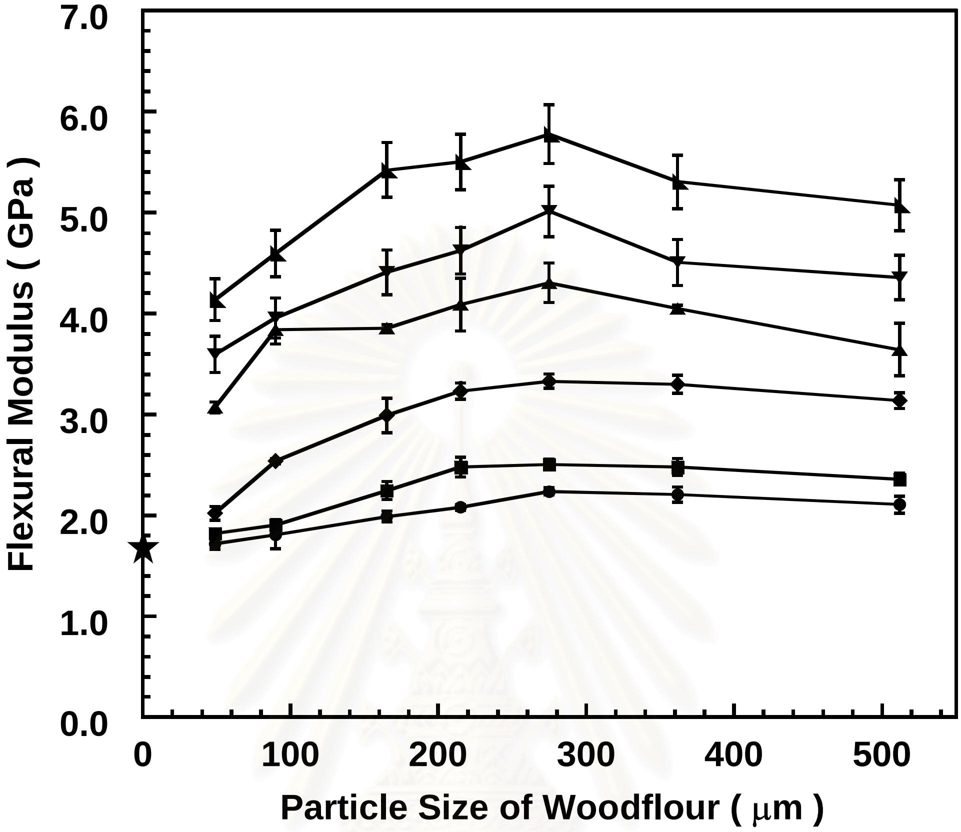


Figure 5.12: Effect of woodflour particle size on flexural modulus for polypropylene/woodflour composites: ★ Pure PP, (●) PP/Wood 10%, (■) PP/Wood 20%, (♦) PP/Wood 30%, (▲) PP/Wood 40%, (▼) PP/Wood 50%, (◣) PP/Wood 60%

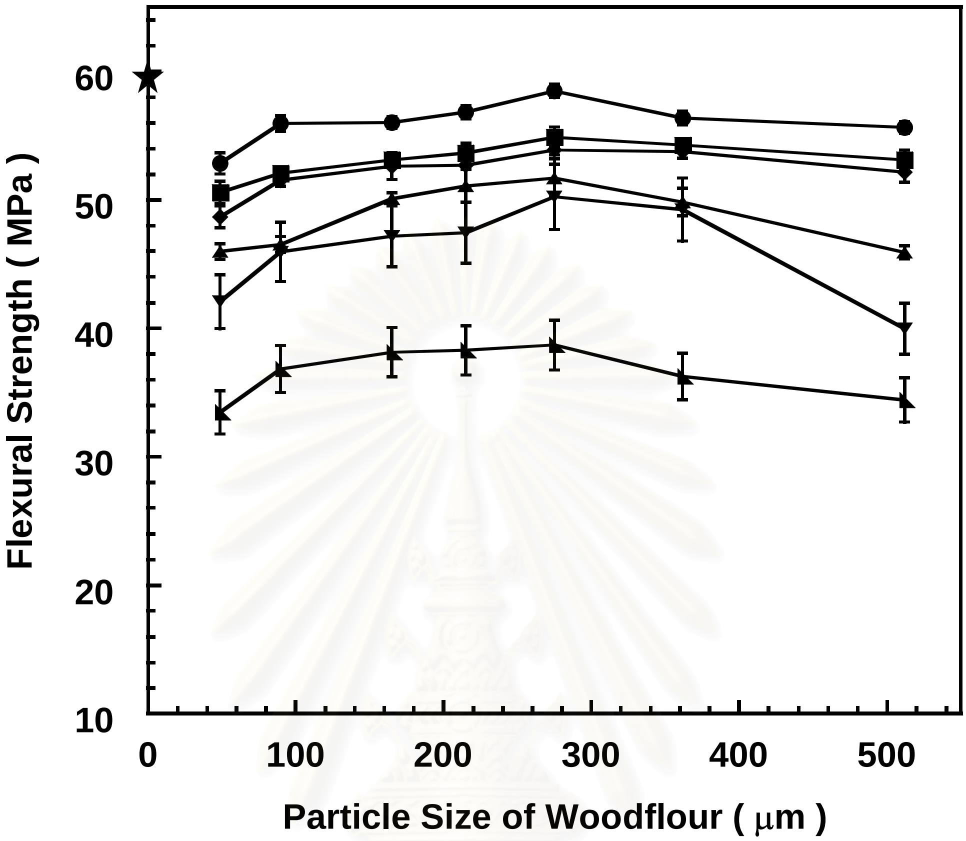


Figure 5.13: Effect of woodflour particle size on flexural strength for polypropylene /woodflour composites : ★ Pure PP, (●) PP/Wood 10%, (■) PP/Wood 20%, (♦) PP/Wood 30%, (▲) PP/Wood 40%, (▼) PP/Wood 50%, (◣) PP/Wood 60%

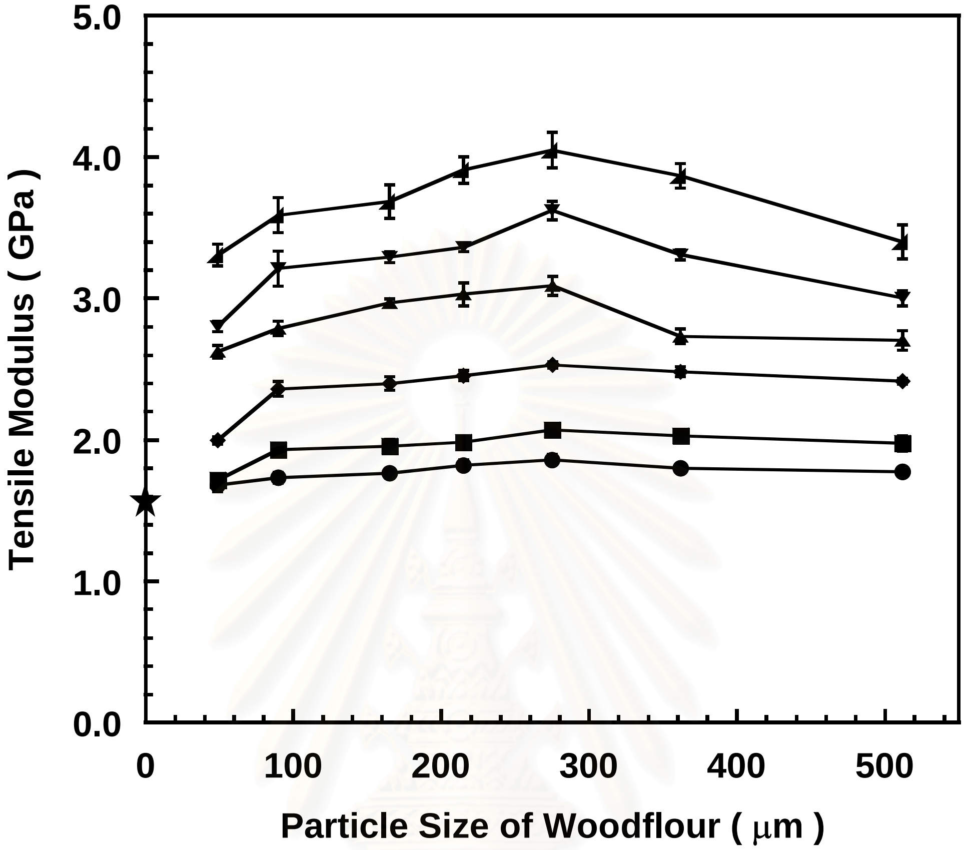


Figure 5.14: Effect of woodflour particle size on tensile modulus for polypropylene /woodflour composites: ★ Pure PP, (●) PP/Wood 10%, (■) PP/Wood 20%, (♦) PP/Wood 30%, (▲) PP/Wood 40%, (▼) PP/Wood 50%, (◢) PP/Wood 60%

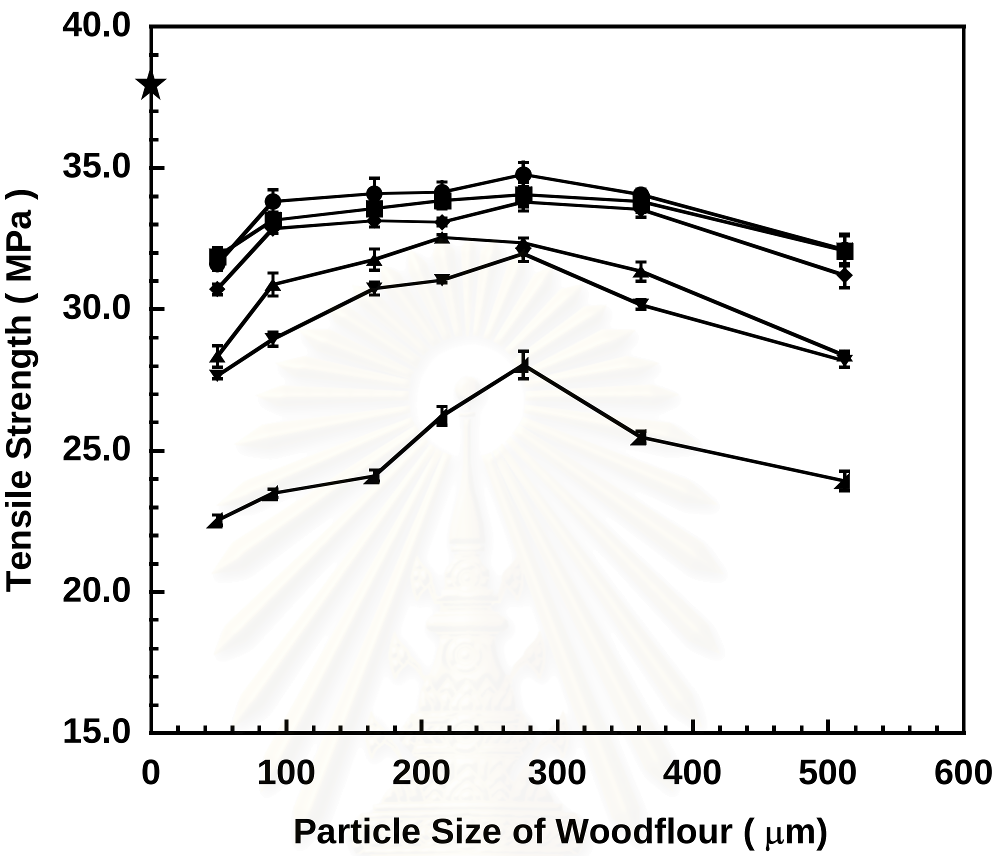


Figure 5.15: Effect of woodflour particle size on tensile strength for polypropylene/woodflour composites: ★ Pure PP, (●) PP/Wood 10%, (■) PP/Wood 20%, (♦) PP/Wood 30%, (▲) PP/Wood 40%, (▼) PP/Wood 50%, (◢) PP/Wood 60%

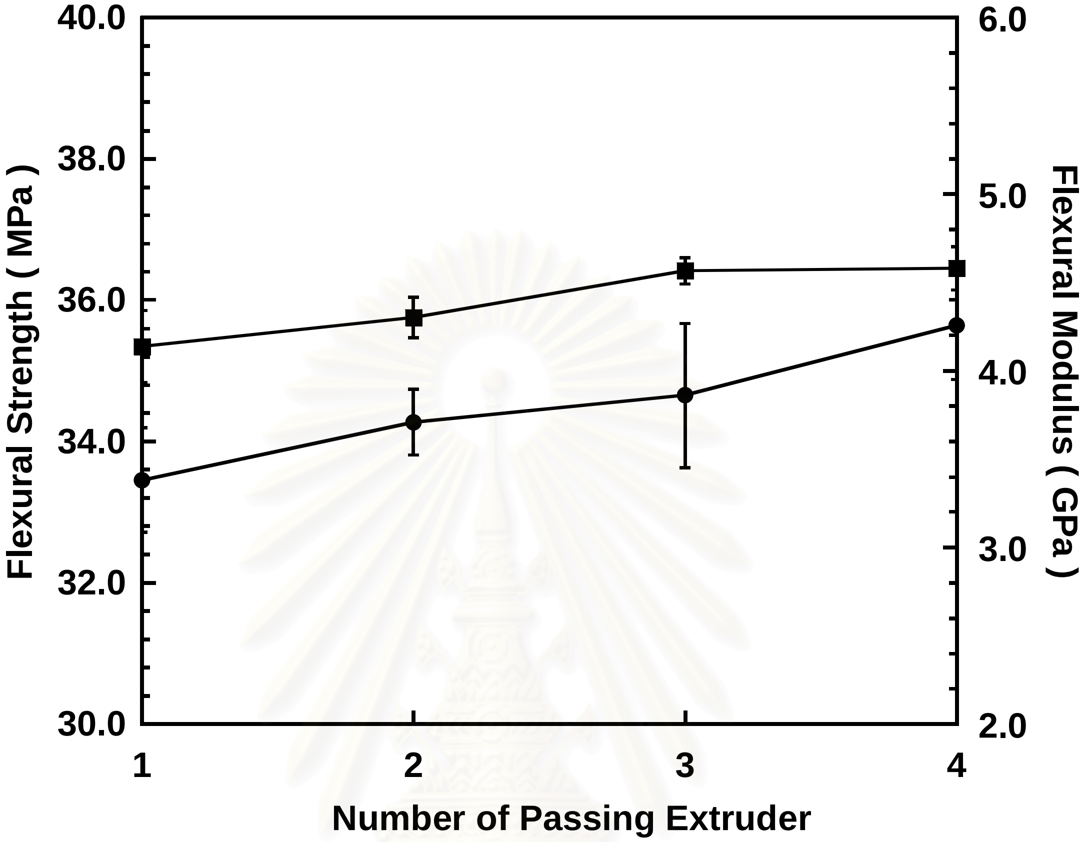


Figure 5.16: Flexural properties of polypropylene woodflour composites (60 wt%, 49 μm) at various numbers of passings extruder: (■) flexural modulus, (●) flexural strength

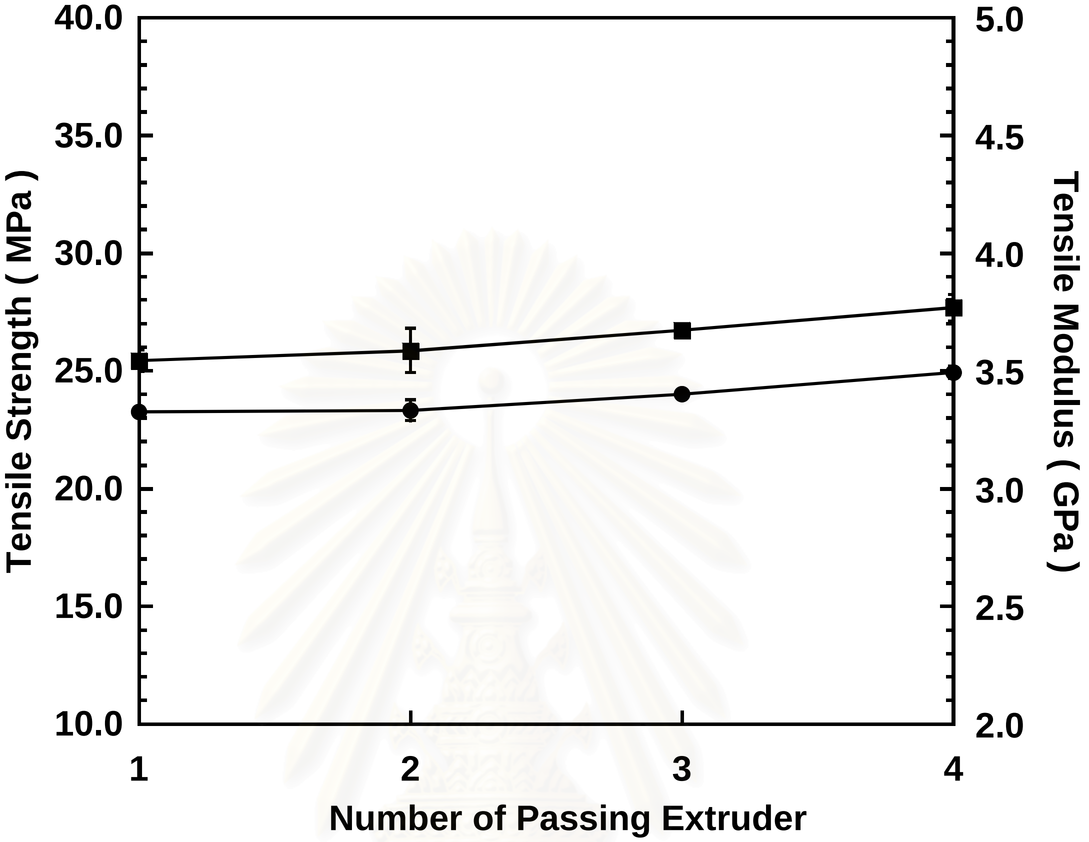


Figure 5.17: Tensile properties of polypropylene woodflour composites (60 wt%, 49 μm) at various numbers of passing extruder: (■) tensile modulus, (●) tensile strength

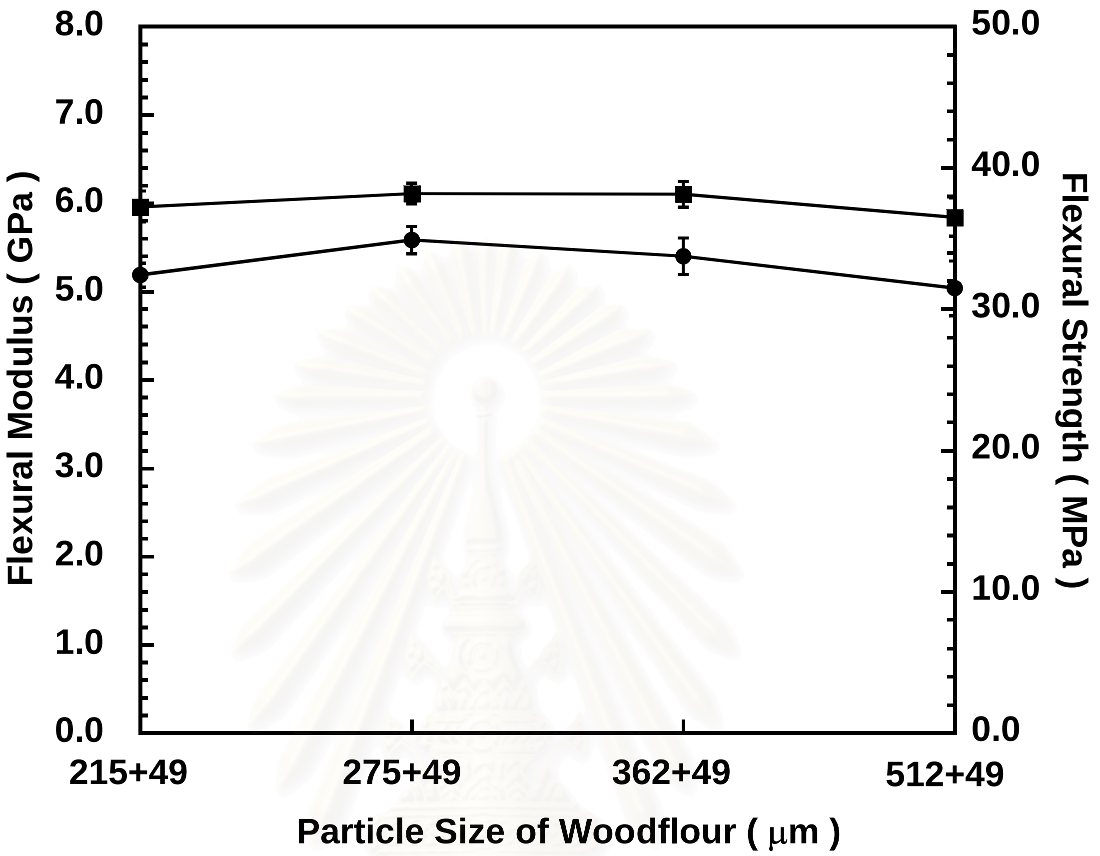


Figure 5.18: The flexural properties of woodflour filled polypropylene composites (bimodal particle size) : (■) flexural strength, (●) flexural modulus

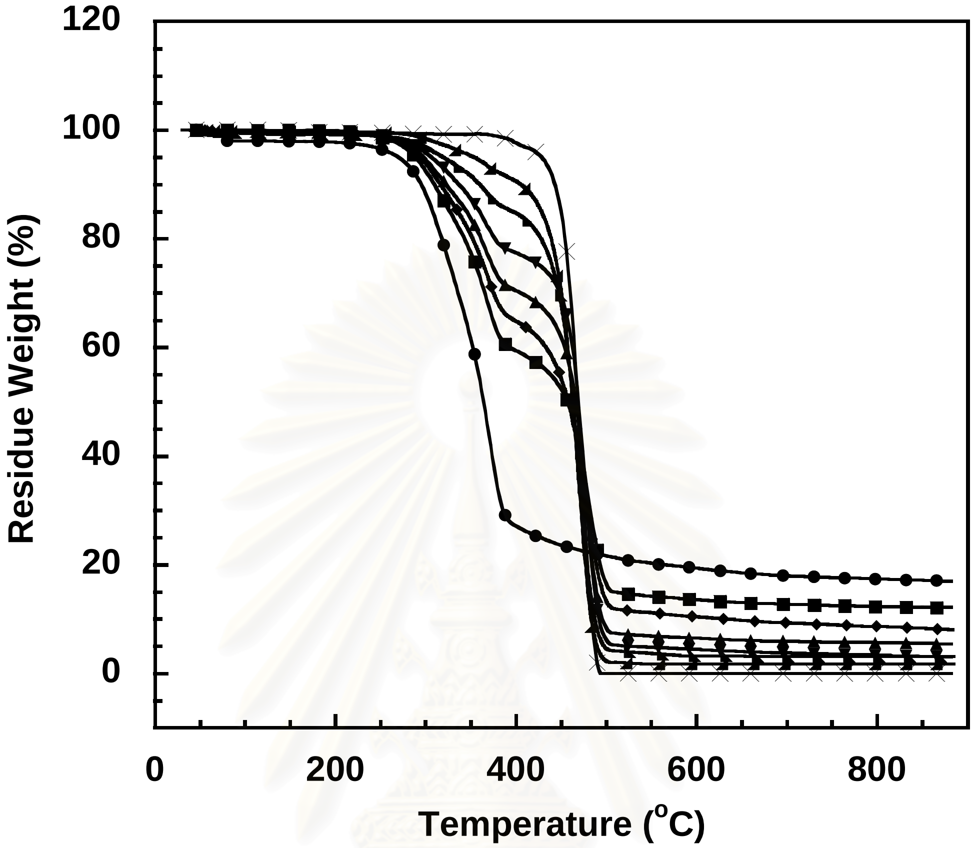


Figure 5.19: TGA thermograms of polypropylene, woodflour and woodflour filled polypropylene composites at various woodflour contents: (x) neat polypropylene, (◢) 10 wt% WF, (◣) 20 wt% WF, (▼) 30 wt% WF, (▲) 40 wt% WF, (♦) 50 wt% WF, (■) 60 wt% WF, (●) woodflour

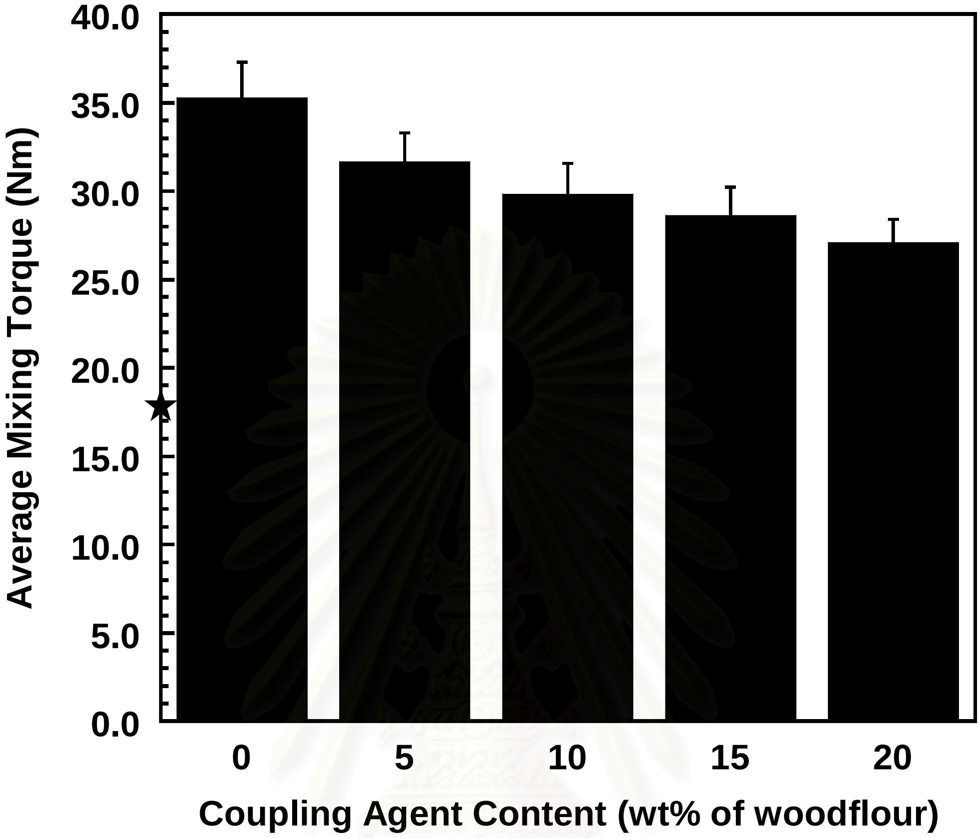


Figure 5.20: Average mixing toque of woodflour filled polypropylene composites at various coupling agent contents:★ Pure PP,

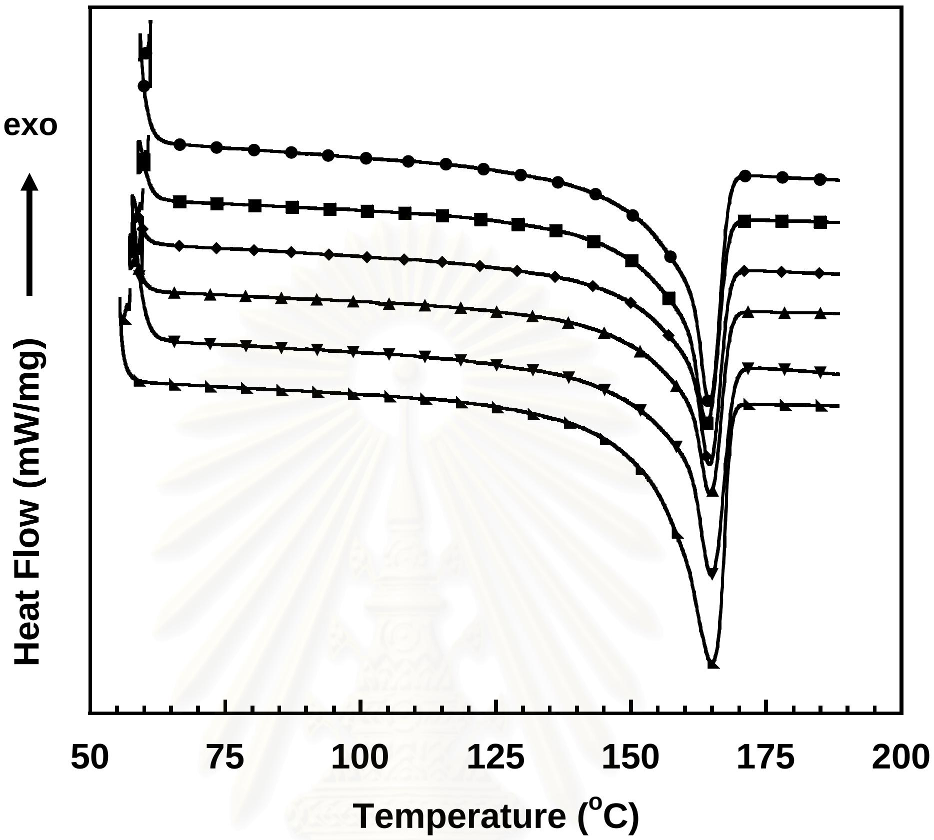


Figure 5.21: DSC thermograms of polypropylene and woodflour filled polypropylene composites at various coupling agent contents: (◣) neat polypropylene, (▼) MAPP 0 %, (▲) MAPP 5 %,(♦) MAPP 10 %, (■) MAPP 15 %, (●) MAPP 20 %

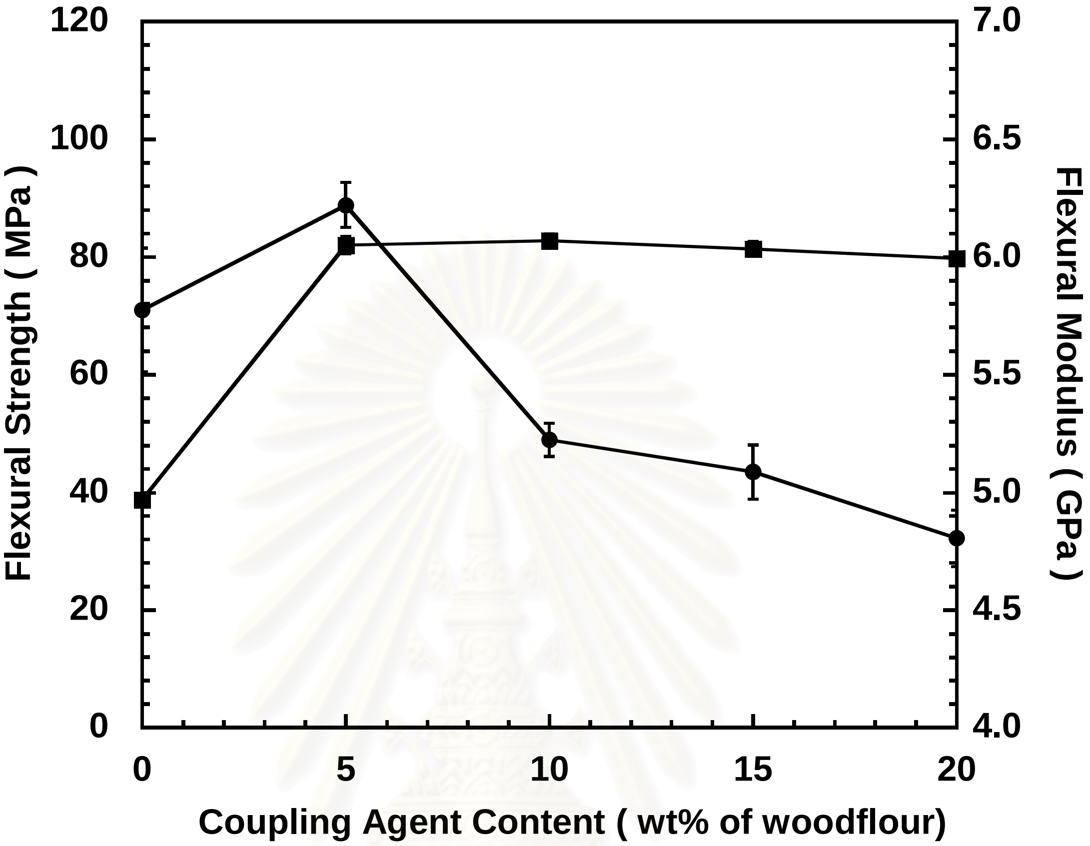


Figure 5.22: Flexural properties woodflour filled polypropylene composites at various coupling agent contents: (■) Flexural strength, (●) Flexural modulus

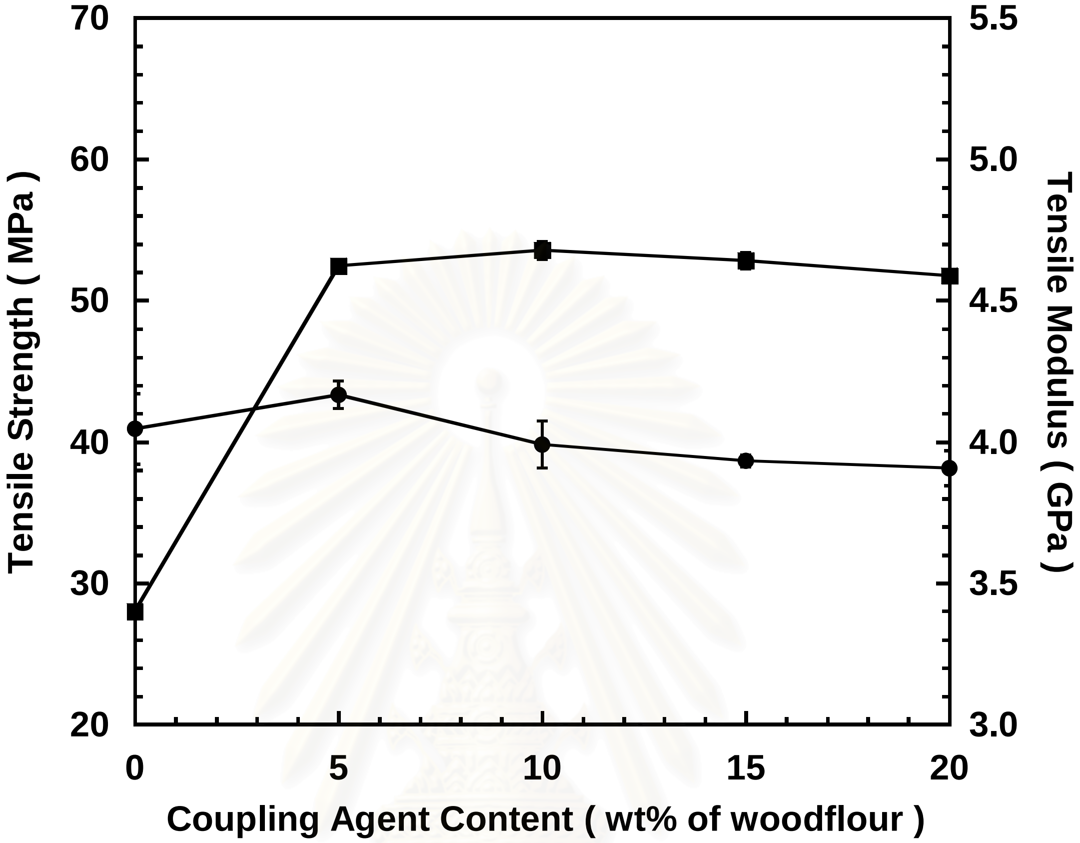
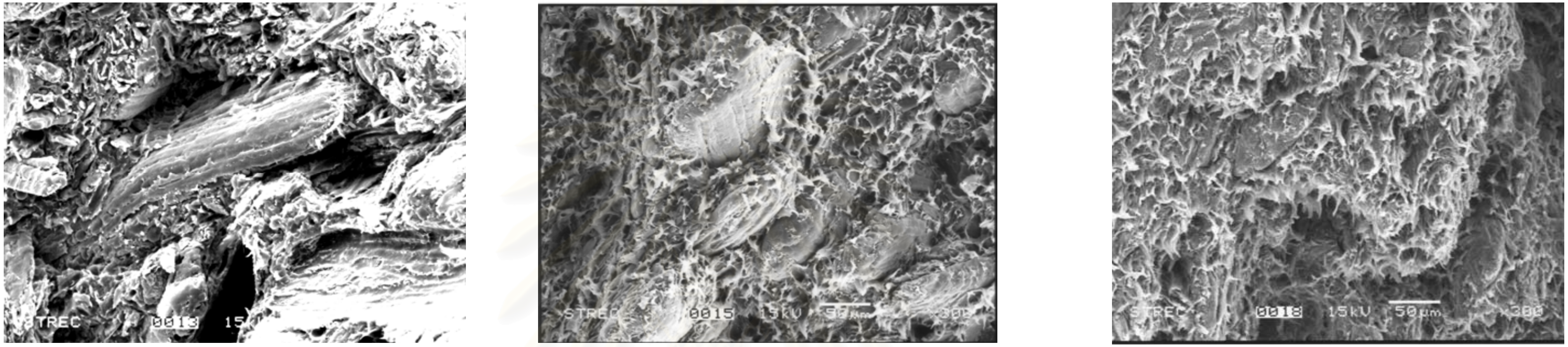


Figure 5.23: Tensile properties woodflour filled polypropylene composites at various coupling agent contents: (■) Tensile strength, (●) Tensile modulus



(a) MAPP 0 %

(b) MAPP 5 %

(c) MAPP 20 %

Figure 5.24: SEM micrographs of the fracture surface of woodflour filled polypropylene composites at various coupling agent contents: (a) MAPP 0 %, (b) MAPP 5 %, (C) MAPP 20 %

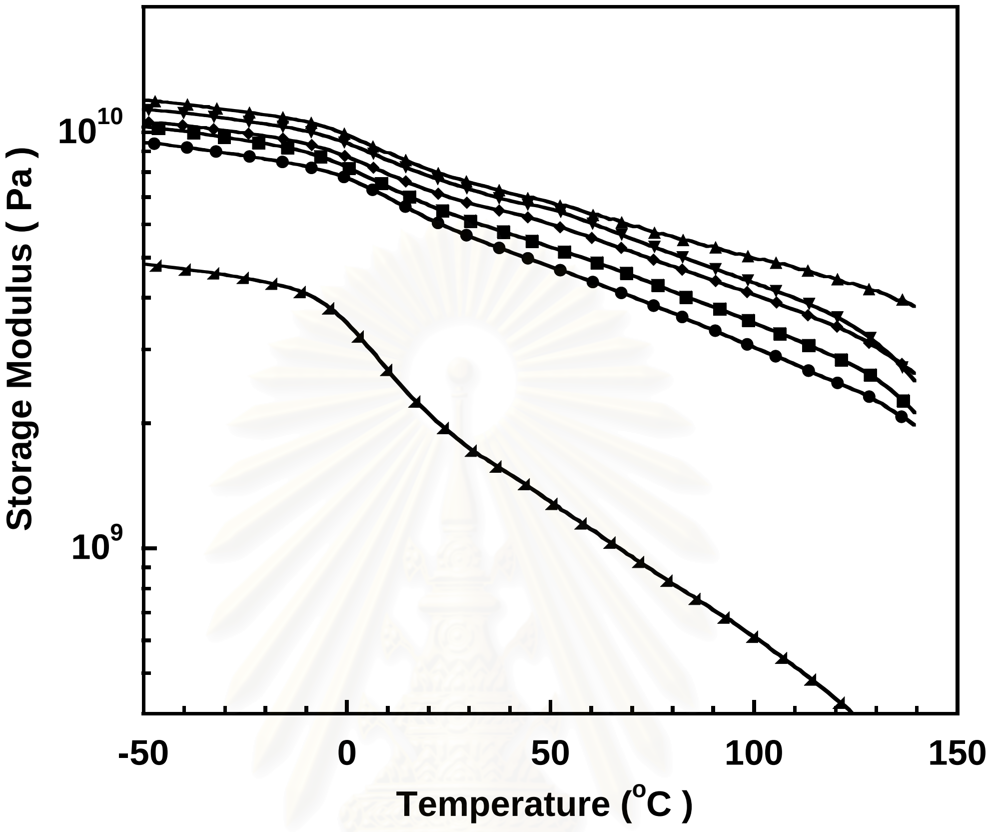


Figure 5.25: Storage modulus of woodflour filled polypropylene composites at various coupling agent contents: (▼) MAPP 0 %, (▲) MAPP 5 %,(♦) MAPP 10 %, (■) MAPP 15 %, (●) MAPP 20 %,(◢)neat PP

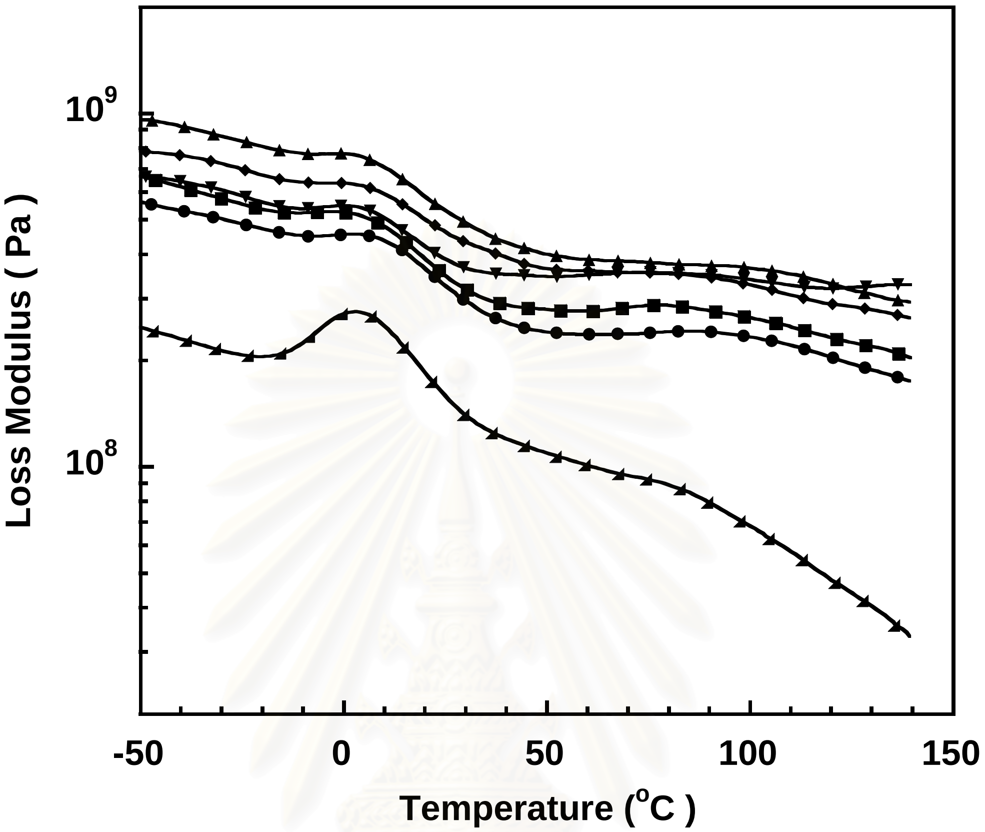


Figure 5.26: Loss modulus of woodflour filled polypropylene composites at various coupling agent contents: (▼) MAPP 0 %, (▲) MAPP 5 %,(♦) MAPP 10 %, (■) MAPP 15 %, (●) MAPP 20 %,(◢)neat PP

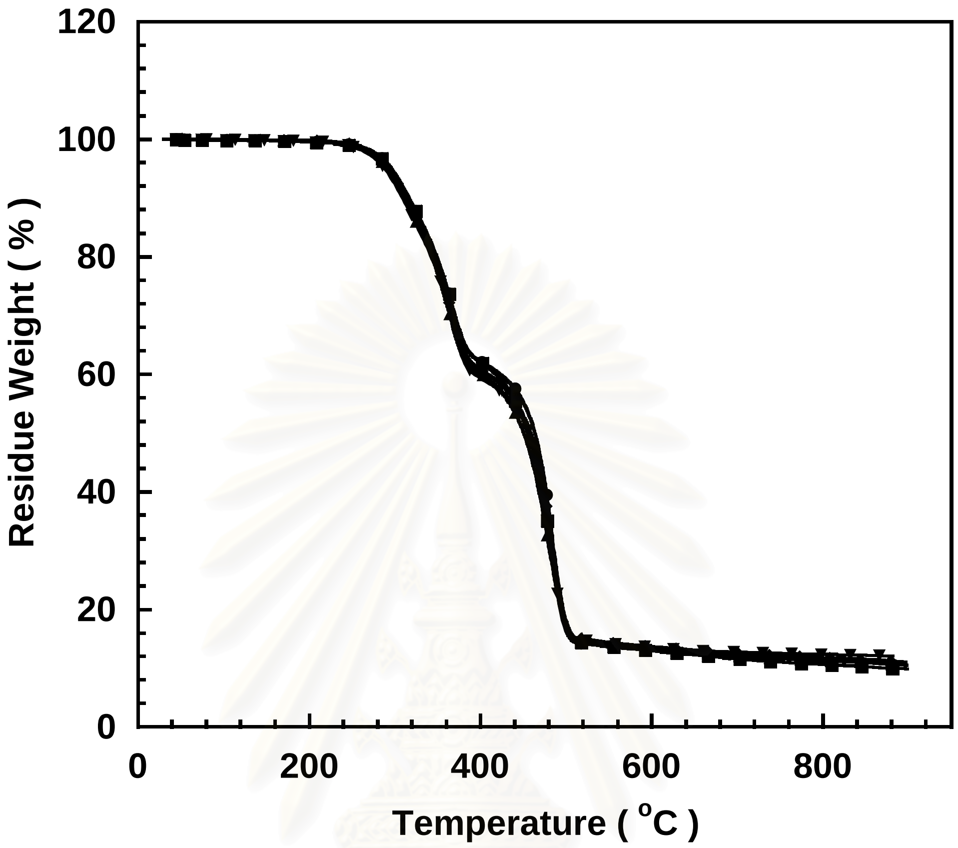


Figure 5.27: TGA thermograms of woodflour filled polypropylene composites at various coupling agent contents: (▼) MAPP 0 %, (▲) MAPP 5 %,(♦) MAPP 10 %, (■) MAPP 15 %, (●) MAPP 20 %

CHAPTER VI

CONCLUSIONS

In this study, the effects of polypropylene types with different melt flow rates, average particle sizes, filler contents, size distributions of filler and coupling agent (MAPP) contents on the mechanical, thermal and some related physical properties of woodflour filled polypropylene composites were examined. In comparison of the composites processed from three types of polymers matrix with similar mechanical properties, the woodflour composites based on high melt flow rate polymer matrix (PP-HP644T) rendered higher flexural and tensile properties than those of wood flour composites with PP-HP648N and PP-HP740H.

It was found that the particle sizes and woodflour contents played a significant role in the mechanical properties of wood flour composites. Flexural and tensile modulus increased, while flexural and tensile strength decreased with increasing woodflour contents. Furthermore, the average particle size of woodflour that was suitable for improving the mechanical properties of the composite was about 200-300 μm. The optimal bimodal particle sizes that rendered the greatest packing density of wood flour were the combination of the particles of 275 μm and 49 μm at a mass ratio of 73:27. The thermal stability and degradation temperature (at 5% weight loss) of wood flour composites decreased with increasing woodflour mass fraction.

The influence of MAPP contents on the mechanical and thermal properties of woodflour composites was investigated. This work recommends MAPP content of 5 wt% (of woodflour) to be introduced into the woodflour composites for optimization of the composite mechanical properties. It was reported that the flexural strength and tensile strength were 110% and 87% higher than those of the woodflour composite without MAPP. The thermal stability and degradation temperature of woodflour composites containing the coupling agent were slightly increased with increasing coupling agent content.

REFERENCES

Arbelaiz, A., Fernandez, B., Ramos, J.A., Retegi, A., Llano-Ponte, R., and Mondragon, I. Mechanical properties of short flax fibre bundle/polypropylene composites: Influence of matrix/fibre modification, fibre content, water uptake and recycling. Compos. Sci. and Tech. 65 (2005): 1582–1592.

Balasuriya, P.W., Ye, L., and Ma,i Y.W. Mechanical properties of wood flake-polyethylene composites.Part I: effect of processing methods and matrix melt flow behaviour. Composites: Part A. 32 (2001): 619–629.

Bledzki, A.K., and Gassan, J. Composites reinforced with cellulose based fibres. Prog. Polym. Sci. 24 (1999): 221–274.

Bledzki, A.K., Letman, M., Viksne, A., and Rence, L. A comparison of compounding processes and wood tye for wood fibre-PP composites. Composites: Part A. 36 (2005): 789-797.

Brydson, J.A., Plastics materials 4th edition, London: Butterworth scientific, 1982

Coutinho, F.M.B., and Costa, T.H.S. Performance of polypropylene–wood fiber composites. Polym. Test. 18 (1999): 581–587.

Danyadi, L., Janecska, T., Szaboc, Z., Nagyc, G., Moczo, J., and Pukanszky, B. Wood flour filled PP composites: Compatibilization and adhesion. Compos. Sci. and Tech. 67 (2007): 2838–2846.

Department of Argriculture. Area of rubber wood grown in Thailand. Available from: http://www.doa.go.th [2005 December 15]

Doh, G., Lee, S., Kang, I., and Kong, Y. Thermal behavior of liquefied wood polymer composites (LWPC). Comp. Struct. 68 (2005): 103–108.

Fried, J.R., Polymer Science and Technology, New Jersey: Prentice - Hall International, Inc., 1995.

Friedrich, K., Fakirov, S., and Zhang, Z. Polymer composites from nano-to macro scale. New York: Springer Science+Business Media. Inc., 2005.

Gauthier, R., July, C., Coupas, A.C., Gauthier, H., and Escoubes, M. Interfaces in Polyolefin/Cellulosic Fiber Composites: Chemical Coupling, Morphology, Correlation with Adhesion and Aging in Moisture. Polym. Compos. 19, (1998): 287-300.

German, R.M. Powder Metallurgy Science, 2nd edition, New Jersey: MPIF, 1994.

Harper, C.A., Hand Book of Plastics and Elastomers, New York : McGraw-Hill, Inc., 1975.

Keener, T.J., Stuart, R.K., and Brown, T.K. Maleated coupling agents for natural fibre composites. Composites: Part A. 35 (2004): 357–362.

Kim, H., Kim, S., Kim, H., and Yang, H. Thermal properties of bio-flour-filled polyolefin composites with different compatibilizing agent type and content. Thermochim. Acta 451 (2006): 181–188.

Kim, H., Lee, B., Choi, S., Kim, S., and Kim, H. The effect of types of maleic anhydride-grafted polypropylene (MAPP) on the interfacial adhesion properties of bio-flour-filled polypropylene composites. Composites: Part A. 38 (2007): 1473–1482

Kroschwitch, J.I. Concise Encyclopedia of Polymer Science and Engineering, New York: John Wiley & Son, Inc., 1990.

Ichazo, M.N., Albano, C., Gonzalez, J., Perera, R., and Candal, M.V. Polypropylene / Wood flour composites: treatments and properties. Comp. Struct. 54, (2001): 207- 214.

Li, S., Jarvela, P.K., and Jarvela, P. A. Melt Rheological Properties of Polypropylene–Maleated Polypropylene Blends. I. Steady Flow by Capillary. J. Appl. Polym. Sci. 71 (1999): 1641–1648.

Low, I.M. Ceramic matrix composites. New York: CRC Press, 2006.

Maier, C., and Calafut T., Polypropylene The Definitive User’s Guide and Data Book, New York: William Andrew Inc., 1998.

Mantia, F.P.L., Morreale, M., and Mohd Ishak, Z. A. Processing and Mechanical Properties of Organic Filler–Polypropylene Composites. J. Appl. Polym. Sci. 96 (2005): 1906–1913.

Matthews, F.L., and Rawlings, R.D. Composite Materials: Engineering and Science, 1st edition, London: Chapman & Hill, 1994.

Nachtigall, S.M.B., Cerveira, G.S., and Rosa, S.M.L. New polymeric coupling agent for polypropylene/wood-flour. Polym. Test. 26 (2007): 619-628.

Nielsen, L.E. and Landel, R.F. Mechanical properties of polymers and composites, 2nd edition, New York: Marcel Deker, inc., 1994.

Nitz, H., Reichert, P., Romling, H., and Mulhaupt, R. Influence of compatibilizers on the surface hardness, water uptake and the mechanical properties of poly(propylene) wood flour composites prepared by reactive extrusion. Macromol. Mater. Eng. 276/277 (2000): 51–58.

Nunez, A.J., Kenny, J.M., Reboredo, M.M., Aranguren, M.I., and Macovich, N.E. Thermal and Dynamic Mechanical Characterization of Polypropylene-Woodflour Composites. Polym. Eng. Sci, 42 (2002): 733-742.

Nunez, A.J., Sturm, P.C., Kenny, J. M., Aranguren, M. I., Marcovich, N.E., and Reboredo, M.M. Mechanical Characterization of Polypropylene–Wood Flour Composites. J. Appl. Polym. Sci. 88 (2003): 1420-1428.

Pracella, M., Chionna, D., Anguillesi, I., Kulinski, Z., and Piorkowska, E. Functionalization, compatibilization and properties of polypropylene composites with Hemp fibres. Compos. Sci. and Tech. 66 (2006): 2218–2230.

Premalal, H.G.B., Ismail, H., and Baharin, A. Comparison of the mechanical properties of rice husk powder filled polypropylene composites with talc filled polypropylene composites. Polym. Test. 21 (2002): 833–839.

Qiu, W., Endo, T., and Hirotsu, T. Structure and properties of composites of highly crystalline cellulose with polypropylene: Effects of polypropylene molecular weight. Eur. Polym J. 42 (2006): 1059–1068.

Qiu, W. Effect of maleated polypropylene on the performance of polypropylene/cellulose composite. Polym. Compos. (2005): 448-453.

Qiu, W., Zhang, F., Endo, T., and Hirotsu, T. Preparation and Characteristics of Composites of High-Crystalline Cellulose with Polypropylene: Effects of Maleated Polypropylene and Cellulose Content. J. Appl. Polym. Sci. 87 (2003): 337–345.

Rozman, H.D., Saad, M.J., and Mohd Ishak, Z.A., Flexural and impact properties of oil palm empty fruit bunch (EFB)-polypropylene composites the effect of maleic anhydride chemical modification of EFB. Polym. Test. 22 (2003): 335–341.

Rimdusit, S., Tanthapanichakoon, Wiwat., and Jubsilp, C. High performance wood composites from highly filled polybenzoxazine. J. Appl. Polym. Sci. 99 (2006): 1240-1253.

Simpson, W., and Tenwolde, A. Wood Handbook., Madison: U.S. Department of Agriculture, 1999.

Sombatsompop, N., Yotinwattanakumtorn, C., and Thongpin, C. Influence of type and concentration of maleic anhydride grafted polypropylene and impact modifiers on mechanical properties of PP/wood sawdust composites. J. Appl. Polym. Sci. 97 (2005): 475-484.

Stark, N.M., and Berger, J.M. Effect of Species and Particle Size on Properties of Wood-Flour-Filled Polypropylene Composites., The Forest Product Laboratory, Chemical Engineering, University of Wisconsin, 1997.

Xanthos M., Functional fillers for plastics, Weinheim : Wiley-VCH, 2005.

Yang, H.S., Wolcott, M. P., Kim, H.S., Kim, S., and Kim, H.J. Effect of different compatibilizing agents on the mechanical properties of lignocellulosic material filled polyethylene bio-composites. Comp. Struct. 79 (2007): 369–375.

APPENDICES

Appendix A

Theoretical Density Calculation

Theoretical density calculation of a filler-reinforced composite is based on the filler volume fraction in the material. Experimentally, it is easier to determine the filler weight fraction, W_f, from which the filler volume fraction, V_f, and composite density, ρ_c can be calculated: (Jubsilp, C., 2002)

$$V_f = \frac{W_f / \rho_f}{(W_f / \rho_f) + (1 - W_f) / \rho_m}$$

$$\rho_c = \frac{1}{(W_f / \rho_f) + (1 - W_f) / \rho_m}$$

where W_f = Filler weight fraction

$(1-W_f)$ = Matrix weight fraction

ρ_f = Filler density

ρ_m = Matrix density

ρ_c = Composite density

In terms of filler volume fraction, V_f, the composite density, ρ_c, can be written as:

$$\rho_c = \rho_f V_f + \rho_m V_m$$

For example, the proportion of polypropylene to woodflour in this research was 60:40 by weight. The densities of woodflour filler and polypropylene matrix are 1.49 g/cm^3 and 0.90 g/cm^3, respectively, which we can calculate theoretical density of polypropylene woodflour composite showing as follows.

$$\rho_c = \frac{1}{(0.40/1.49) + (1-0.40)/0.90}$$

$$\rho_c = 1.069 \quad \text{g/cm}^3$$

Appendix B

Mechanical Characterizations

Appendix B-1 Tensile Modulus of Woodflour Filled Polypropylene Composites (40wt%, 215µm) as a Function of Polypropylene Types and Numbers of Passing through an Extruder.

Number of Passing through an Extruder	**Tensile Modulus (GPa)**		
	HP740H	**HP648N**	**HP644T**
1	2.80±0.05	3.05±0.05	3.27±0.05
2	2.99±0.04	3.17±0.08	3.45±0.09
3	2.97±0.11	3.10±0.10	3.42±0.07
4	2.99±0.02	3.19±0.06	3.25±0.08

Appendix B-2 Tensile Strength of Woodflour Filled Polypropylene Composites (40 wt%, 215µm) as a Function of Polypropylene Types and Numbers of Passing through an Extruder.

Number of Passing through an Extruder	**Tensile Strength (MPa)**		
	HP740H	**HP648N**	**HP644T**
1	31.79±0.23	32.26±0.01	32.54±0.14
2	32.05±0.28	32.52±0.46	33.51±0.77
3	31.71±1.12	32.13±0.56	33.01±0.41
4	31.59±0.35	32.18±0.39	32.99±1.02

Appendix B-3 Flexural Modulus of Woodflour Filled Polypropylene Composites (40wt%, 215µm) as a Function of Polypropylene Types and Numbers of Passing through an Extruder.

Number of Passing through an Extruder	**Flexural Modulus (GPa)**		
	HP740H	**HP648N**	**HP644T**
1	3.33±0.69	3.56±0.18	4.02±0.26
2	3.34±0.26	3.46±0.08	3.82±0.18
3	3.33±0.68	3.59±0.07	3.85±0.12
4	3.28±0.45	3.49±0.12	3.84±0.02

Appendix B-4 Flexural Strength of Woodflour Filled Polypropylene Composites (40wt%, 215µm) as a Function of Polypropylene Types and Numbers of Passing through an Extruder

Number of Passing through an Extruder	**Flexural Strength (MPa)**		
	HP740H	**HP648N**	**HP644T**
1	52.30±0.69	52.56±0.64	52.99±1.37
2	52.71±0.26	53.15±0.41	54.87±1.44
3	53.19±0.68	53.42±0.73	54.87±0.78
4	52.76±0.45	53.39±0.50	54.43±0.50

Appendix B-5 Flexural Modulus of PP/Woodflour Composite as a Function of Average Particle Sizes and Woodflour Contents.

Average Particle Size (μm)	**Flexural Modulus (GPa)**					
	PP/Wood 10wt%	**PP/Wood 20wt%**	**PP/Wood 30wt%**	**PP/Wood 40wt%**	**PP/Wood 50wt%**	**PP/Wood 60wt%**
49	1.72±0.05	1.82±0.03	2.02±0.07	3.07±0.05	3.59±0.06	4.14±0.16
90	1.80±0.13	1.90±0.05	2.53±0.03	3.84±0.14	3.95±0.11	4.59±0.25
165	1.99±0.05	2.25±0.09	2.99±0.17	3.85±0.03	4.41±0.19	5.42±0.09
215	2.08±0.03	2.48±0.09	3.23±0.08	4.09±0.26	4.62±0.15	5.49±0.19
275	2.24±0.04	2.50±0.05	3.33±0.07	4.30±0.19	5.01±0.17	5.77±0.26
362	2.20±0.08	2.48±0.08	3.29±0.09	4.05±0.03	4.50±0.21	5.30±0.35
512	2.11±0.08	2.36±0.05	3.14±0.08	3.64±0.26	4.35±0.10	5.07±0.16

Appendix B-6 Flexural Strength of PP/Woodflour Composite as a Function of Average Particle Sizes and Woodflour Contents.

Average Particle Size (μm)	**Flexural Strength (MPa)**					
	PP/Wood 10wt%	**PP/Wood 20wt%**	**PP/Wood 30wt%**	**PP/Wood 40wt%**	**PP/Wood 50wt%**	**PP/Wood 60wt%**
49	52.83±0.86	50.56±0.89	48.66±0.86	45.96±0.62	42.06±1.20	33.45±0.80
90	55.92±0.61	52.06±0.25	51.51±0.45	46.51±0.61	45.93±0.25	36.83±1.62
165	56.01±0.47	53.09±0.37	52.62±1.07	50.05±0.47	47.16±1.10	38.13±0.20
215	56.81±0.51	53.64±0.76	52.69±1.68	51.06±1.29	47.44±0.65	38.29±0.75
275	58.47±0.53	54.85±0.80	53.85±0.37	51.67±1.49	50.22±0.89	38.68±1.17
362	56.35±0.52	54.23±0.53	53.74±0.53	49.80±1.08	49.23±1.07	36.25±0.55
512	55.62±0.47	53.11±0.76	52.15±0.76	45.90±0.51	39.97±0.49	34.41±0.56

Appendix B-7 Tensile Modulus of PP/Woodflour Composite as a Function of Average Particle Sizes and Woodflour Contents.

Average Particle Size (μm)	**Tensile Modulus (GPa)**					
	PP/Wood 10wt%	**PP/Wood 20wt%**	**PP/Wood 30wt%**	**PP/Wood 40wt%**	**PP/Wood 50wt%**	**PP/Wood 60wt%**
49	1.68±0.05	1.72±0.02	1.99±0.03	2.62±0.04	2.79±0.04	3.31±0.08
90	1.73±0.04	1.93±0.03	2.36±0.05	2.79±0.05	3.21±0.13	3.59±0.13
165	1.76±0.03	1.96±0.05	2.39±0.05	2.97±0.03	3.29±0.04	3.68±0.12
215	1.82±0.04	1.98±0.03	2.45±0.04	3.03±0.08	3.36±0.03	3.91±0.09
275	1.86±0.04	2.07±0.04	2.53±0.02	3.09±0.07	3.62±0.07	4.05±0.13
362	1.79±0.03	2.03±0.04	2.48±0.03	2.73±0.05	3.31±0.04	3.87±0.09
512	1.77±0.03	1.97±0.06	2.41±0.02	2.70±0.07	3.00±0.05	3.39±0.12

Appendix B-8 Tensile Strength of PP/Woodflour Composite as a Function of Average Particle Sizes and Woodflour Contents.

Average particle size (μm)	**Tensile Strength (MPa)**					
	PP/Wood 10wt%	**PP/Wood 20wt%**	**PP/Wood 30wt%**	**PP/Wood 40wt%**	**PP/Wood 50wt%**	**PP/Wood 60wt%**
49	31.59±0.22	31.85±0.32	30.70±0.19	28.32±0.38	27.65±0.12	22.53±0.18
90	33.80±0.42	33.14±0.28	32.85±0.18	30.87±0.41	28.93±0.25	23.48±0.14
165	34.09±0.54	33.56±0.46	33.13±0.24	31.75±0.39	30.72±0.23	24.10±0.19
215	34.14±0.37	33.84±0.30	33.07±0.14	32.54±0.09	31.01±0.07	26.22±0.33
275	34.77±0.43	34.05±0.43	33.79±0.32	32.35±0.17	31.97±0.28	28.02±0.49
362	34.05±0.19	33.80±0.37	33.53±0.28	31.33±0.34	30.16±0.17	25.47±0.21
512	32.09±0.56	32.06±0.52	31.19±0.43	28.35±0.16	28.17±0.23	23.92±0.35

Appendix B-9 Flexural Properties of Polypropylene Woodflour Composites (60 wt%, Average Particle Size = 49 µm) at Various Numbers of Passing through an Extruder.

Number of Passing through an Extruder	**Flexural Modulus (GPa)**	**Flexural Strength (MPa)**
1	4.14 ± 0.20	33.45 ± 0.74
2	4.30 ± 0.11	34.27 ± 0.47
3	4.57 ± 0.07	34.65 ± 1.02
4	4.58 ± 0.12	35.64 ± 0.76

Appendix B-10 Tensile Properties of Polypropylene Woodflour Composites (60wt%, average particle size = 49 µm) at Various Number of Passing through an Extruder.

Number of Passing through an Extruder	**Tensile Modulus (GPa)**	**Tensile Strength (MPa)**
1	3.54 ± 0.05	23.24± 0.21
2	3.59± 0.09	23.32± 0.11
3	3.67 ± 0.02	24.00± 0.45
4	3.77 ± 0.06	24.93± 0.26

Appendix B-11 Flexural Properties of Woodflour Filled Polypropylene Composites (Bimodal Particle Size).

Average Particle Size	**Flexural Modulus (GPa)**	**Flexural Strength (MPa)**
215+49	5.19 ± 0.14	37.24 ± 1.11
275+49	5.58 ± 0.15	38.17 ± 0.72
362+49	5.40± 0.21	38.13 ± 0.92
512+49	5.04 ± 0.31	36.49 ± 1.36

Appendix B-12 Flexural Properties of Woodflour Filled Polypropylene Composites at Various Coupling Agent Contents.

Coupling Agent Content (wt% of woodflour)	**Flexural Modulus (GPa)**	**Flexural Strength (MPa)**
0	5.77 ± 0.26	38.68 ± 1.17
5	6.22 ± 0.09	81.98± 1.43
10	5.22 ± 0.07	82.75 ± 1.17
15	5.08 ± 0.11	81.33 ± 1.29
20	4.80± 0.12	79.75 ± 0.82
neat PP	1.63± 0.03	59.18± 0.36
neat MAPP	1.27± 0.02	46.19± 1.07

Appendix B-13 Tensile Properties of Woodflour Filled Polypropylene Composites at Various Coupling Agent Contents.

Coupling Agent Content (wt% of woodflour)	**Tensile Modulus (GPa)**	**Tensile Strength (MPa)**
0	4.04 ± 0.12	28.02 ± 0.49
5	4.16 ± 0.04	52.44 ± 0.32
10	3.99 ± 0.08	53.57 ± 0.65
15	3.93 ± 0.02	52.83 ± 0.56
20	3.90 ± 0.06	51.78 ± 0.39
neat PP	1.66 ± 0.04	39.33± 0.70
neat MAPP	1.10± 0.04	25.64 ±0.27

VITA

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