การพัฒนาสารประกอบแต่งของพอลิไวนิลคลอไรด์กับเส้นใยทางการเกษตร

นางสาวสาวิตรี มุสาลี

วิทยานิพนธ์นี้เป็นส่วนหนึ่งของการศึกษาตามหลักสูตรปริญญาวิศวกรรมศาสตรมหาบัณฑิต
สาขาวิชาวิศวกรรมเคมี ภาควิชาวิศวกรรมเคมี
คณะวิศวกรรมศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย
ปีการศึกษา 2550

DEVELOPMENT OF POLY(VINYL CHLORIDE)/AGRICULTURAL FIBER COMPOSITES

Miss Sawittree Mulalee

A Thesis Submitted in Partial Fulfillment of the Requirements
for the Degree of Master of Engineering Program in Chemical Engineering
Department of Chemical Engineering
Faculty of Engineering
Chulalongkorn University
Academic Year 2007

Thesis Title DEVELOPMENT OF POLY(VINYL CHLORIDE)/AGRICULTURAL FIBER COMPOSITES

By Miss Sawittree Mulalee
Field of Study Chemical Engineering
Thesis Advisor Anongnat Somwangthanaroj, Ph.D.
Thesis Co-advisor Varun Taepaisitphongse, Ph.D.

Accepted by the Faculty of Engineering, Chulalongkorn University in Partial Fulfillment of the Requirements for the Master's Degree

....Dean of the Faculty of Engineering
(Associate Professor Boonsom Lerdhirunwong, Dr.Ing.)

THESIS COMMITTEE

Chirakarn Muangnapoh Chairman
(Associate Professor Chirakarn Muangnapoh, Dr. Ing.)

.... Thesis Advisor
(Anongnat Somwangthanaroj, Ph.D.)

Varun .... Thesis Co-advisor
(Varun Taepaisitphongse, Ph.D.)

.... Member
(Associate Professor Siriporn Damrongsakkul, Ph.D.)

.... Member
(Associate Professor Somsak Woramongconchai, D.Eng)

สาวิตรี มุลาลี: การพัฒนาสารประกอบแต่งของพอลิไวนิลคลอไรด์กับเส้นใยทางการเกษตร (DEVELOPMENT OF POLY(VINYL CHLORIDE)/AGRICULTURAL FIBER COMPOSITES) อ. ที่ปรึกษา : อ.ดร.อนงค์นาฎ สมหวังธนโรจน์, อ. ที่ปรึกษาร่วม : อ.ดร. วรัญ แต้ไพสิฐพงษ์, 73 หน้า.

ในงานวิจัยนี้ได้ทำการศึกษาถึงวัสดุทดแทนไม้ โดยใช้สารผสมระหว่างพอลิไวนิลคลอไรด์กับเส้นใยทางการเกษตร โดยทำการขึ้นรูปด้วยเครื่องบดผสมชนิดสองลูกกลิ้ง และเครื่องกดอัด โดยเส้นใยที่ใช้มีสามชนิดคือ ซังข้าวโพด ชานอ้อย และฟางข้าว และแบ่งออกเป็นสองขนาดคือ ขนาดเล็ก อยู่ในช่วง 106-180 ไมโครเมตร ขนาดใหญ่ อยู่ในช่วง 250-425 ไมโครเมตร พร้อมทั้งได้ศึกษาถึงผลของปริมาณ ขนาด และ ชนิดของเส้นใยที่ใช้ ที่มีผลต่อสมบัติทางกล ทางความร้อน และสมบัติการดูดซับน้ำของวัสดุผสมที่สร้างขึ้น จากผลการทดลองพบว่าวัสดุผสมจะให้ค่าความแข็งแรงที่สูงกว่าพอลิไวนิลคลอไรด์ นอกจากนั้นในวัสดุผสมที่มีปริมาณของเส้นใยผสมอยู่จำนวนมาก จะมีค่าความแข็งแรงสูงกว่าวัสดุผสมที่มีปริมาณของเส้นใยอยู่จำนวนน้อยกว่า ซึ่งจะสังเกตได้ว่าค่าความแข็งแรงของวัสดุผสมที่มีเส้นใยผสมอยู่ 60 phr จะเพิ่มขึ้น 45-52% เมื่อเปรียบเทียบค่าความแข็งแรงกับพอลิไวนิลคลอไรด์ อย่างไรก็ตาม การเพิ่มปริมาณของเส้นใยเพื่อที่จะผสมกับพอลิไวนิลคลอไรด์ที่มากขึ้น จะทำให้ปริมาณการดูดซับน้ำของวัสดุผสมเพิ่มมากขึ้นด้วย โดยวัสดุผสมที่มีเส้นใยอยู่ 60 phr จะมีค่าการดูดซับน้ำอยู่ในช่วง 6-9 เปอร์เซนต์โดยน้ำหนัก สำหรับผลของขนาดเส้นใยจะพบว่าเส้นใยที่มีขนาดเล็ก (106-180 ไมโครเมตร) จะให้สมบัติทางกลของวัสดุผสมมีค่าที่สูงขึ้นและยังให้ผลของการดูดซับน้ำในวัสดุที่มีค่าน้อยกว่าวัสดุผสมที่ผสมด้วยเส้นใยที่มีขนาดใหญ่ (250-425 ไมโครเมตร) อย่างไรก็ตาม ขนาดของเส้นใยไม่ได้ส่งผลเด่นชัดต่อสมบัติทางความร้อนของวัสดุผสม นอกจากนั้นเมื่อเปรียบเทียบชนิดของเส้นใยทางการเกษตรทั้งสามชนิด พบว่า วัสดุที่ผสมด้วยฟางข้าวเป็นสารประกอบแต่งจะให้ค่าความแข็งแรงและสมบัติทางความร้อนที่สูงขึ้น แต่วัสดุชนิดนี้จะให้ค่าปริมาณการดูดซับน้ำที่มากขึ้นด้วยเช่นกัน

ภาควิชา วิศวกรรมเคมี	ลายมือชื่อนิสิต......สาวิตรี มุลาลี......
สาขาวิชา วิศวกรรมเคมี	ลายมือชื่ออาจารย์ที่ปรึกษา......................
ปีการศึกษา 2550	ลายมือชื่ออาจารย์ที่ปรึกษาร่วม......................

4970627021 : MAJOR CHEMICAL ENGINEERING
KEY WORD: AGRICULTURAL FIBER PLASTIC COMPOSITE / POLY(VINYL CHLORIDE)

SAWITTREE MULALEE : DEVELOPMENT OF POLY (VINYL CHLORIDE)/AGRICULTURAL FIBER COMOPOSITES. THESIS ADVISOR: ANONGNAT SOMWANGTHANAROJ, Ph.D., THESIS COADVISOR : VARUN TAEPAISITPHONGSE, Ph.D., 73 pp.

In this research, wood substituted composites were produced by the usage of poly (vinyl chloride) and agricultural fiber. Moreover, this research were studied the effects of content, size, and type of agricultural fiber on mechanical, thermal, and water absorption properties of composites by the usage of agricultural fiber as corncob (CC), bagasse (BG), and rice straw (RS) as fillers of PVC with different fiber contents (20, 40, 60 phr) and fiber size (small (S), large (L)). PVC with other additives (PVC dry blend) and agricultural fiber were mixed in a two-roll mill followed by compression molding. The results showed high content and small size of fiber can increase the modulus, heat distortion temperature (HDT), and vicat softening temperature of composites. It showed tensile and flexural modulus of these composites increased between 45-52%, and 30-73%, respectively compared to PVC dry blend value. However, these composites also showed high amount of water absorption. The amount of water absorption of composites with 60 phr of fiber shows value between 6-9 wt%. Small-sized fiber increases the stiffness of composite better than that with large-sized fiber. Moreover, these composites adsorb less amount of water than that with large-sized fiber. However, size of fiber did not show significant effect on thermal properties of PVC/Agricultural fiber composites. Among three types of agricultural fiber, the composites with rice straw as filler showed the best results in modulus and thermal properties and they also showed the highest amount of water absorption.

Department ...Chemical Engineering……Student's signature……………………………..
Field of study ...Chemical Engineering ….Advisor'signature…………………………..
Academic Year 2007 Co-advisor's signature…………………………

ACKNOWLEDGEMENTS

I wish to express my sincerest gratitude and deep appreciation to my advisor, Dr. Anongnat Somwangthanaroj, and my co-advisor, Dr. Varun Taepaisitphongse, for their kindness, invaluable supervision, guidance, advice, and encouragement throughout the course of this study and editing of this thesis.

Gratefully thanks to Vinythai Public Co. Ltd., Thailand for providing financial support, raw materials and equipments, such as PVC dry blend resin, two-rolls mill machine, cutting mill, sieve analyzer, HDT/vicat tester, used in this work. Moreover, I would like to thank for all the assistances and conveniences provided by everyone at this company. Without these supports from Vinythai PCL, this work will not be possible.

Thanks to B&C Pulaski Corporation, Ltd., Thailand, Saraburi Sugar, Co. Ltd., Thailand, and Rice Research Center, Thailand, for providing raw materials, i.e. ground corncob, bagasse, and rice straw, used in this work. Thanks to the Center of Excellence in Particle Technology, Chulalongkorn University, Thailand, for providing ball mill and sieves.

Additionally, many thanks are extended to everyone in the Polymer Engineering Laboratory, Chulalongkorn University, for their discussion and friendly encouragement. I feel so fortunate having a chance to learn here.

Finally, I would like to affectionately give all gratitude to the members of my family for their wholehearted understanding, encouragement, and patiently support throughout my entire study.

CONTENTS

PAGE

CHAPTER

CHAPTER **PAGE**

CHAPTER **PAGE**

LIST OF TABLES

LIST OF FIGURES

FIGURE **PAGE**

CHAPTER I

INTRODUCTIONS

1.1 General Introduction

The term wood-plastic composite (WPC) refers to any composites that contain wood as filler and thermosets or thermoplastics as matrix. The woods used in composites are most often in particulate form or very short fibers, rather than long individual wood fibers. Filler particles are often incorporated into a polymer to modify properties to meet performance requirements. For certain applications, high filler content are needed to achieve the desired property modification.

Thermoplastic and thermosetting wood composites are the two major classes of plastic-wood products. Typically, useful properties of conventional thermoplastic wood composites compared to thermosetting wood composites include high cost-competitiveness, ease of processing, and recyclability. There are many thermoplastic polymers which could be compounded with agricultural fibers such as polypropylene (PP), low-density polyethylene (LDPE), high-density polyethylene (HDPE) and polystyrene (PS) (Haihong and Kamdem, 2004).

One of the most interesting thermoplastic polymers is poly(vinyl chloride) (PVC) due to its attractiveness of ease of processing, high productivity, and low cost (Georgopoulos et al., 2005). Furthermore, PVC wood composites have been proven to exhibit superior ultraviolet light resistance and weathering dimensional stability to those of natural wood besides their inherent fire-resistant characteristics with a limiting oxygen index (LOI) as high as 50 (LOI>26 is classified as self-extinguishable). Fiber composite is very attractive for the construction or home decoration purposes. Typically, the PVC/wood composites are used to produce door/window profiles, decking, railing, and siding.

The PVC compounding based on conical counter-rotating intermeshing twin-screw extruder is demonstrated to be one effective way to get well dispersed wood composite products. To obtain the enhanced PVC/wood composites' performance, heat stabilizers, processing aids, impact modifiers, lubricants, and pigments are also incorporated in the materials.

In recent years, there have been many researches on PVC/wood composites with many natural fibers such as bagasse, jute, hemp and rice straw as filler to reinforce the polymer. These are due to several advantages of natural fibers such as renewable and biodegradable raw materials, low abrasive nature, low cost, low density and acceptable strength properties (Yu-Tao et al., 2007 and Georgopoulos et al., 2005). The use of several types of agricultural fibers as well as the use of natural fiber with mica or glass fiber to form hybrid reinforcements is proved to help enhance the mechanical properties of the final products.

In Thailand, several kinds of agricultural fiber such as rice straw, flax, jute, bagasse, ground corncob are available and some are highly attractive as reinforcing filler as well as an extender for wood composites. The purpose of this study was to develop replacement for natural woods with composite materials made from poly(vinyl chloride) as the matrix and the agricultural waste as filler such as ground corncob, bagasse, and rice straw. Specifically, this work focused on the effects of content, size, and type of agricultural fiber on mechanical and thermal properties especially for heat distortion temperature and vicat softening temperature of PVC/agricultural fiber composites. Moreover, water absorption property of PVC/agricultural fiber composites was also investigated.

1.2 Objectives of the Present Study

This research aimed to generate the technical knowledge and formulations for production of PVC/agricultural fiber composites by combining PVC resin and natural fibers available locally, i.e. ground corncob, bagasse and rice straw, as alternatives for natural wood. The objectives were

1. To study the effect of agricultural fiber types, fiber particle sizes, and fiber loading on the properties of the resulting PVC/agricultural fiber composites.
2. To study the morphology of PVC/agricultural fiber composite.

1.3 Scopes of the Present Study

1. The following parameters were studied:
    - A. Types of agricultural fiber
        - Ground Corncob
        - Bagasse
        - Rice Straw
    - B. Agricultural fiber size: Small (106-180 μm), Large (250-425 μm).
    - C. Agricultural fiber loading: 20, 40, 60 phr.
2. The following properties will be studied:
    - A. Mechanical Properties
        - Tensile Property
        - Flexural Property
        - Impact Strength
    - B. Thermal Properties
        - Glass Transition Temperature (T_g)
        - Heat Distortion Temperature
        - Vicat Softening Temperature
    - C. Water Absorption

CHAPTER II

THEORY

2.1 PVC and Properties

Poly(vinyl chloride) (PVC) is one of the major thermoplastic materials because it is a polymer which is relatively cheap and versatile. PVC is produced by polymerization of vinyl chloride monomer (VCM). Most of VCM is obtained from ethylene (C_2H_4). The producing reactions of VCM were shown in Figure 2.1 and the molecular structure of PVC was shown in Figure 2.2.

$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$ (Direct Chlorination Reaction)
$C_2H_4Cl_2 + \text{Heat} \rightarrow C_2H_3Cl^{*} + HCl$ (Ethylene Dichloride Cracking)
(*C_2H_3Cl = Vinyl Chloride Monomer (VCM))

Figure 2.1: Vinyl Chloride Monomer Producing Process (http://www.vitythai.co.th)

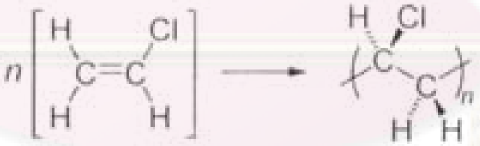


Figure 2.2: Molecular Structure of PVC
(http://en.wikipedia.org/wiki/Polyvinyl_chloride)

Due to poor properties of PVC such as hard, tough and poor heat stability, PVC is never used without compounding with additives such as plasticizers, stabilizers, modifiers, lubricants, flame retardant, and colorants. When PVC is compounded with additives, the physical properties of the compounded material depend on PVC resin, types and composition of additives. Compounded PVC burns slowly, tends to be self-extinguishing, and has high flash ignition temperature. Weathering resistance, excellent clarity and good flexural strength are other advantages of PVC. However, there are some limitations on using PVC because PVC is degradable at elevated temperatures and can be corrosive to processing equipments. Plasticized PVC is one of the most versatile plastic materials available. Compounding gives a very wide range of applications to PVC which approaches to that of rubbers and engineering plastics. Table 2.1 gives typical values of PVC properties.

Table 2.1: Properties of Rigid and Plasticized PVC (Garvin, 1956)

Properties	Rigid PVC	Plasticized PVC
Density (g/cm^3)	1.3-1.4	1.1-1.7
Specific Heat Capacity (cal/g °C)	0.25	-
Sag Temperature (°C)	78	-
Milling Temperature (°C)	150	20-140
Power Factor (%)	1.25	-
Shore Hardness (D)	-	47
Tear Resistance (kg/m)	-	8500

2.2Natural Fibers and Their Compositions (Bledzki, 1999)

Natural fibers or fillers such as ground corncob, bagasse and jute are renewable materials with very attractive mechanical properties. A growing awareness of environmental problems and the importance of energy conservation have made such renewable reinforcing materials of great importance.

The basic components of natural fibers are cellulose, hemicellulose, lignin, pectin, and waxes with regard to the physical properties of the fibers. The percentage composition for each of these components varies for different fibers.

2.2.1. Cellulose is the essential component of all plant-fibers. It is generally accepted that cellulose is a linear condensation polymer consisting of D-anhydroglucopyranose units which are joined together by 1,4-β-D-glucan. The pyranose rings are in the $^4C_1$ conformation, which means that the -CH$_2$OH, -OH groups, and the glycosidic bonds are equatorial with respect to the mean plane of the rings. The characteristic of cellulose is the presence of both crystalline and amorphous regions within their microfibrils that single cellulose chain may run through several crystalline regions and amorphous zones. Cellulose, as the skeletal substance, contributes its high tensile strength to the complex of fiber structure. Generally, the fibers contain 60-80 wt% of cellulose. However, hard fibers contain more cellulose than soft fibers do.

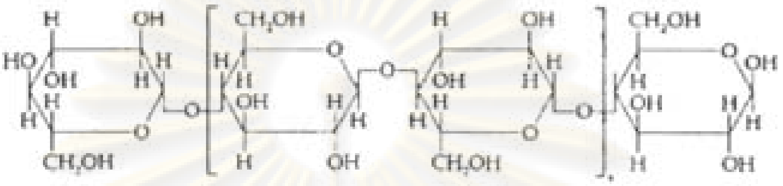


Figure 2.3: Structure of Cellulose (Bledzki, 1999)

2.2.2. Hemicellulose is not a form of cellulose at all and the name is an unfortunate one. They comprise a group of polysaccharides (excluding pectin) that remains associated with the cellulose after lignin has been removed. The constituents of hemicellulose differ from plant to plant. The function of hemicellulose is less clear; there is some possibility that they serve as a temporary matrix before lignification. The hemicellulose differs from cellulose in three important aspects. In the first place they contain several different sugar units whereas cellulose contains only 1,4-β-D-glucopyranose units. Secondly, they exhibit a considerable degree of chain branching, whereas cellulose is a strictly linear polymer. Thirdly, the degree of polymerization of native cellulose is ten to one hundred times which is higher than that of hemicellulose. Hemicellulose is responsible for the biodegradation, moisture absorption, and thermal degradation of the fiber as it shows the least resistance. Fiber contains the hemicellulose about of 5 to 20 wt%.

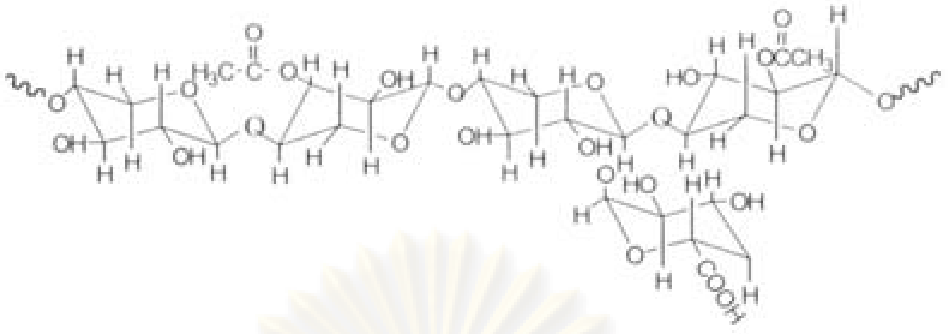


Figure 2.4: Structure of Hemicellulose (Bledzki, 1999)

2.2.3. Lignin is a complex hydrocarbon polymer with both aliphatic and aromatic constituents. Their chief monomer units are various ring-substituted phenyl-propanes with C-O-C and C-C linkages. However, these links are not fully understood. Structural details differ from one source to another. The mechanical properties of lignin are lower than those of cellulose. Although the lignin is thermally stable, it is responsible for the UV degradation. Composition of lignin in fiber is about 2 to 14 wt%.

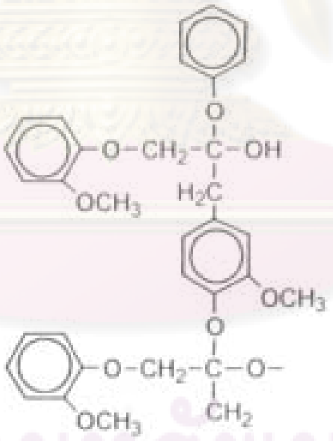


Figure 2.5: Structure of Lignin (Bledzki, 1999)

2.2.4. Pectin is a collective name for heteropolysaccharides, which consist essentially of polygalacturon acid. Pectin is soluble in water only after a partial neutralization with alkali or ammonium hydroxide.

2.2.5. Waxes make up the part of the fiber which can be extracted with organic solutions. These waxy materials consist of different types of alcohols, which are insoluble in water as well as several acids.

2.3 Composites

Composite material can be defined as a macroscopic combination of two or more distinct materials, having a recognizable interface between them. However, because composites are usually used for their structural properties, the definition can be restricted to include only those materials that contain reinforcement (such as fibers or particles) supported by a binder (matrix) material. The constituents can be organic, inorganic or metallic (synthetic and naturally occurring) in from of the particles, rods, fibers, plates, foams, etc. Compared with homogeneous materials, these additional variables often provide greater latitude in optimizing, for a given application, such physically uncorrelated parameters as strength, density, electrical properties, and cost. Further, the composite may be the only effective vehicle for exploiting the unique properties of certain special material (Reinhart, et al., 1989; Hillig et al., 1981).

2.3.1 Classification of Composite Materials

Most polymer-based composites do not have a formal nomenclature at this time. Figure 1 provides a polymer composite classification scheme. There are three major types of polymer composites: those where the matrix is non-polymeric (although wood, clearly polymeric, plays a matrix role here); those with the polymer as the matrix, usually being reinforced or filled with another material, such as fibers, plates, or particulates; and those where some degree of dual-phase continuity prevails, as in laminates foams. (Birley et al., 1988)

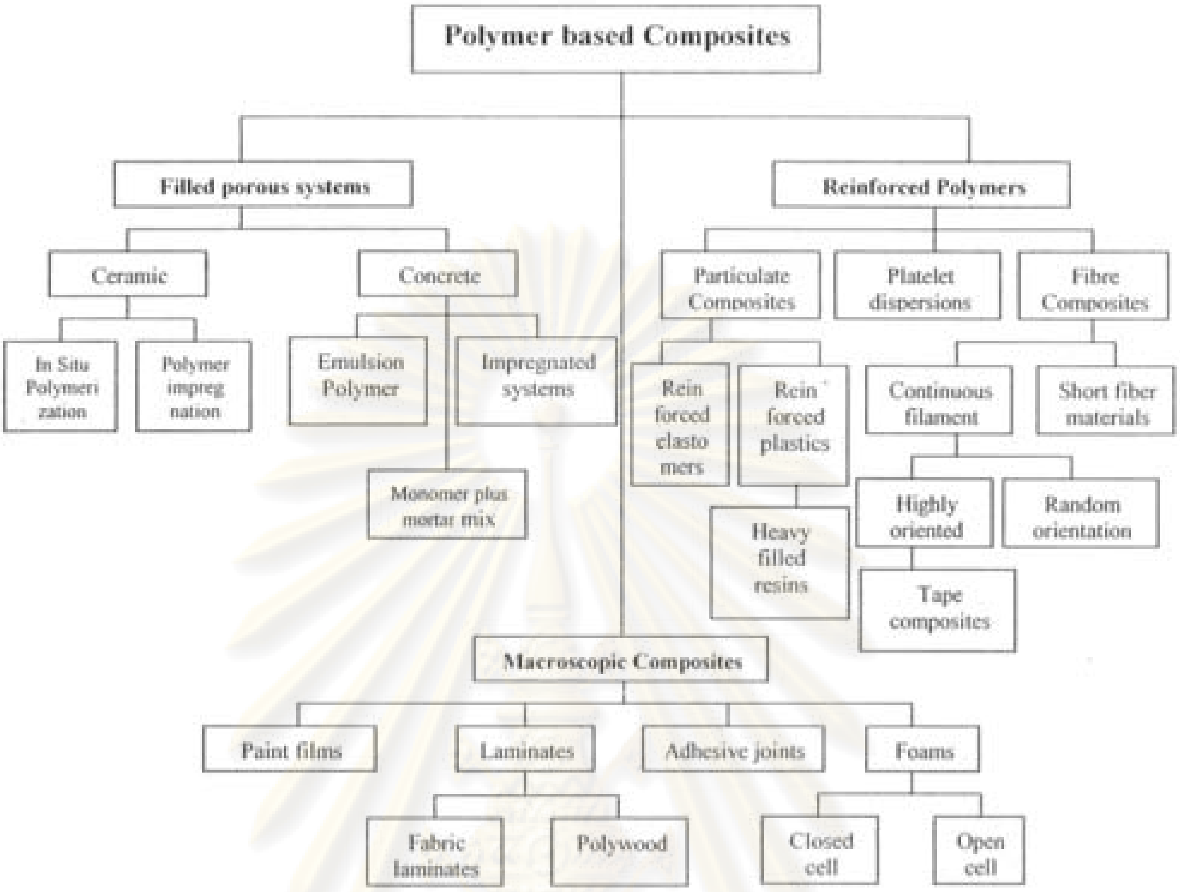


Figure 2.6: Classifications of Polymer based Composites (Birley et al., 1988)

2.3.2 Theory of the Action of Filler and Reinforcements

The action of active filler can be attributed to several mechanisms (Gachter and Muller, 1987). Some fillers form chemical bond with the material to be reinforced, such as carbon black produces crosslink in elastomers by means of radical reaction.

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

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

2.4 Wood Fiber Composite Matrices

A role of a matrix in a fiber-reinforced composite is to transfer stresses between the fibers, to provide a barrier against an adverse environment, and to protect the surface of the fibers from mechanical abrasion. The matrix plays a minor role in the tensile load-carrying capacity of a composite structure. However, selection of a matrix has a major influence on the interlaminar shear as well as on in-plane shear properties of the composite material. The interlaminar shear strength is an important design consideration for structures under bending loads, whereas the in-plane shear strength is important for structures under torsional loads. The matrix provides lateral support against the possibility of fiber buckling under compression loading, thus influencing to some extent the compressive strength of the composite material. The interaction between fibers and matrix is also essential in designing damage-tolerant structure. Finally, the processability and defects in a composite material depend strongly on the physical and thermal characteristics, such as viscosity, melting point, and curing temperature of the matrix. Other desirable properties of a matrix are: minimize moisture absorption, wet and bond to fiber, and eliminate voids during the compacting and curing processes. Moreover a matrix could have these properties i.e. have strength at elevated temperature (depending on the application), have low shrinkage, and have dimensional stability.

CHAPTER III

LITERATURE REVIEW

There were many researches on the effect of parameters such as pretreatment of fibers, size of fibers, loading of fibers, and coupling agents on the mechanical and other properties of PVC/agricultural fiber composites.

3.1 The Effect of Pretreatment of Fibers

Many studies showed enhancement of mechanical properties when rice straw (Kamel, 2004), sawdust pulp (Aspen) (Maldas et al., 1989), and sawdust particle (Sombatsompop and Chaochanchaikul, 2005) were pretreated before they were blended with PVC.

By treating rice straw with 5% NaOH solution at 80 °C for an hour, the maximum bending strength of PVC/rice straw composites was increased by 60%, and tensile strength was increased by 5% in comparison with PVC/untreated rice straw composite (Kamel, 2004).

The increment of the mechanical properties of PVC/sawdust (Aspen) composite was observed with the improved compatibility between hydrophobic PVC matrix and hydrophilic fibers with cyclohexanone. Tensile strength, elongation at break, and impact energy were increased by 12%, 35%, and 20% from PVC/untreated sawdust (Aspen) composite, respectively (Maldas et al., 1989).

The use of silanes such as *N*-2 (aminoethyl) 3-aminopropylmethyldimethoxysilane (KBM602), *N*-2 (aminoethyl) 3-aminopropyltrimethoxysilane (KBM603), and *N*-2 (aminoethyl) 3-aminopropyltriethoxysilane (KBE603) for the surface treatment of wood sawdust particle had been reported (Sombatsompop and Chaochanchaikul, 2005). Tensile strength of PVC/wood saw sawdust composite treated with *N*-2 (aminoethyl) 3-aminopropylmethyldimethoxysilane (KBM602) was increased by 16% when compared with PVC/untreated wood sawdust composite. To improve the impact properties, the most suitable silane was 1.5 wt% KBE603. The impact strength was increased by 20% from untreated wood sawdust composite. These effects can be seen from Figure 3.1.

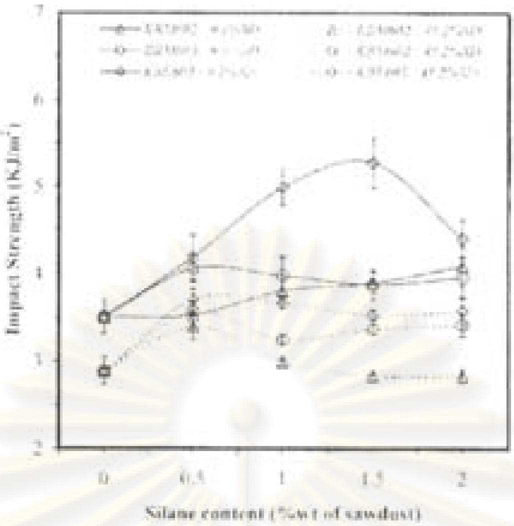


Figure 3.1: Plots of impact strength against the silane coupling agent content for the PVC/wood sawdust composites: (–) 9.1 and (- -) 41.2 wt % sawdust. (Sombatsompop and Chaochanchaikul, 2005)

3.2 The Effect of Size of Fibers

The size of agricultural fiber is one of the significant factors on the mechanical properties of PVC/agricultural fiber composites. It was reported that the strength PVC/ wood composite with Aspen sawdust mesh size 60 was 50% higher than that with aspen sawdust mesh size 40 (Maldas et al., 1989).

The reasons are that a short fiber (mesh size 60) are homogeneous, have critical length, and prevents entanglement while all fiber characteristics are maintained. Short fiber length also provides better dimensional stability as well as resistance to break during fabrication. Therefore, sawdust (Aspen) with a smaller particle size is more compatible with polymer than those with larger one. However, the tensile strengths of PVC/sawdust (Spruce), and PVC/sawdust (Birch) composites with sawdust mesh 60 were not much different from those with sawdust mesh 40.

3.3 The Effect of Loading of Fibers

Adding small amount of fiber into PVC matrix can enhance the mechanical properties of wood composite. However, too much fiber would decay the composite's properties. When loading of rice straw was increased from 80 to 95 wt% based on the total weight of composite sample, it was found that the tensile strength of PVC/rice straw composite was decreased by 85% (Kamel, 2004). Other study showed that when loading of coconut shell powder was increased from 60 to 80 phr, tear strength of PVC/coconut shell powder composite decreased by 57% and when loading of tea leaves was reduced from 100 phr to 50 phr, the tear strength of PVC/tea leave composite was increased by nearly to 2.4 times (Zurale et al., 1998). The higher tear strength could be related to the vein structure of tea leaves. The other research found that tensile strength and tensile modulus of PVC/eucalyptus composite weredecreased by 2% and 50%, respectively, when there was an increase of eucalyptus from 10 to 20 phr. It was found that the loading of bagasse in PVC/bagasse composite was the significant parameter of tensile and impact properties (Yu-Tao et al., 2007). When loading of bagasse was doubled, tensile strength and tensile modulus increased by 8%. However, elongation at break was decreased by 26%. Impact strength was decreased 2 times. The decrease of elongation at break might be due to the higher brittleness introduced by blending bagasse with the PVC matrix. The decay on impact strength of the composites could be explained in terms of molecular motion of bagasse in PVC matrix. From these results, the optimum bagasse loading can improve the mechanical properties of PVC/fiber composite. However a large proportion of fibers did not show any desirable impact on the properties of the composites.

3.4 The Effect of Coupling Agents

The development of PVC/agricultural fiber composites was limited by a compatibility issue of poor interphase adhesion between the hydrophobic PVC matrix and the hydrophilic fibers. Many efforts have been carried out on the improvement of the interfacial adhesion between fiber and PVC by combining composites with coupling agents such as maleated polypropylene (MAPP), aminopropyltriethoxysilane (A-1100), dichlorodiethylsilane (DCS), phthalic anhydride (PA), benzoic acid, chitin, chitosan, and lignin.

Silane is an important coupling agent in the filled-plastic industry since it has the –OH side group that can connect to the wood surface through hydrogen bonds formed between the hydroxyl groups of silanols and wood. The other side of silanols is the functional group which adheres to PVC matrix through the weak van der Waals force such that strong interfacial adhesion cannot be established between wood and PVC.

It was found that aminopropyltriethoxysilane (A-1100) was a suitable adhesion promoter for PVC/newsprint composite (Matuana et al., 1998) and tensile strength of the composites was improved significantly up to 34% from PVC/untreated fiber composites. The other coupling agents had no effect on tensile strength when compared with the composite with untreated newsprint. This effect could be seen from Table 3.1.

Table 3.1: Effect of Coupling Agents on Tensile Properties on PVC/Newsprint-Fiber composite. (Matuana et al., 1998)

Samples	Strength (MPa)	Modulus (GPa)	Elongation at break (%)
Plasticized PVC	37.4±2.7	1.9±0.2	5.26±0.1
Composites with			
Untreated Fiber	28.5±0.8	3.2±0.1	1.4±0.1
Treated Fibers with			
A-1100	38.3±3.1	3.6±0.1	1.3±0.2
DCS	30.0±1.9	2.7±0.1	1.8±0.2
PA	29.4±0.8	2.8±0.2	1.8±0.2
E-43	29.3±2.2	2.1±0.1	1.2±0.2

There was suggestion that lignin could improve the surface adhesion between bagasse fiber and PVC matrix (Kamel, 2004). The experimental result showed that the bending strength of the composite was increased by 2.5 times with the addition of 7 wt% lignin. This might be due to the attachment of lignin to the hydroxyl surface of lignocelluloses materials.

Chitin and chitosan had a positive effect on the flexural strength of PVC/wood flour composites. Flexural strength of PVC/woodflour composite was increased by 20% when 6.67 wt% chitin or 0.5 wt% chitosan was added to the composite. These could be related with the better interaction between woodflour and matrix (Shah and Matuana, 2005).

CHAPTER IV

EXPERIMENT

4.1 Materials

4.1.1 PVC Resin

Suspension PVC resin (Siamvic 258 RB, K-value 58), stabilizer, processing aid, external lubricant, and internal lubricant are supplied by Vinythai Public Company Limited. Table 4.1 shows characteristics of suspension PVC resin

Suspension PVC resin with K-value 58 is a low K value resin suitable for rigid PVC processing. It produces very low dust during transportation. It can be processed easily at low temperature. It has good thermal stability, good initial color, no tendency to stick on hot metal surface, and very low level of fish-eyes.

Table 4.1: Characteristics of Suspension PVC Resin

Characteristics	Units	Values (*)	Standards
K-value (cyclohexanone)		58	DIN 53726
Polymerization Degree		680	JIS K6721
Apparent Bulk Density	kg/l	0.56	ISO 60
Volatile Matter	%	0.3	ISO 1269

(*) In the case of certain characteristics the values given in this are means based on a large number of individual measurements distributed around the means in a range corresponding to the normal manufacture and measurement tolerances. These values should not be considered as specifications.

4.1.2 Agricultural fibers

Three types of natural fibers were used in this research, namely corncob, bagasse and rice straw.

Corncob

Corncob is the central wooden core of a cornear. Young cornears, also called baby corn, can be consumed raw. But as the plant matures the cob becomes tougher until only the kernels are edible. When harvesting corn the corncob is collected as part of the cornear, leaving the corn stover in the field. Ground corncob used in this research was obtained from B&C Pulaski Corporation, Ltd, Thailand. The proximate composition of corncob received from B&C Pulaski Corporation, LTD, Thailand, is shown in Table 4.2.

Figure 4.1: Corncob

Table 4.2: Proximate Composition of Corncob

Composition	wt %
Cellulose	34
Nitrogen-Free Extract (NFE)	55
Ash Content	1
Moisture	10

Bagasse

Bagasse is the biomass remaining after sugarcane stalks are crushed to extract their juice. In this research, bagasse was received from Saraburi sugar, Co. Ltd., Thailand. The composition of bagasse is shown in Table 4.3

Figure 4.2: Bagasse

Table 4.3: Average Composition of Bagasse (HUFA, 2001)

Composition	Percentage base on Dry Weight
Ash	1.50
Lignin	18.29
Hemicellulose	35.84
Alphacellulose	41.00
Other	3.37

Rice Straw

Rice straw is an agricultural by product, the dry stalk of a cereal plant, after the nutrient grain or seed has been removed. Rice straw makes up about half of the yield of rice. In times gone by, it was regarded as a useful by-product of the harvest such as animal food, roof, and natural fertilizer. Rice straw in this research was obtained from rice research center, Pathumthani, Thailand. The composition of rice straw has shown in Table 4.4.

Figure 4.3: Rice Straw

Table 4.4: Average Composition of Rice Straw (Linko, 1997)

Composition	Wt%
Cellulose	43.92
Hemicellulose	25.00
Lignin	12.00
Ash	17.00
Other	2.08

4.2 Preparation of PVC Dry Blend

PVC dry blend for PVC/agricultural fiber composites in this research was prepared from the formula given in Table 4.5 which was received from Vinythai PCL, Thailand. Ingredients of PVC dry blend were expressed in parts per hundred parts of pure PVC resin (phr). PVC and additives were mixed in dry blend machine at the temperature of 130 °C for 15 minutes and then cooled with the temperature of 30 °C for 5 minutes.

Table 4.5: PVC Dry Blend Formulation

Ingredients	Concentration (phr)
PVC	100
Stabilizer	4
Processing aid	6
External Lubricant	2
Internal Lubricant	0.5

4.3 Preparation of PVC/Agricultural Fiber Composites

PVC dry blend and agricultural fiber such as ground corncob, bagasse, and rice straw were mixed together in the two-roll mills as shown in Figure 4.4 (Labtech) for 10 min with temperature of both front and back rolls at 175°C and the roll gap was 0.3 mm. The contents and sizes of agricultural fiber in each formulation were varied following Table 4.6. After mixing, the mixtures were compression molded into rectangular sheets (20x20 cm) of about 4 mm thickness using steel mold (flash type) and heated with hydraulic press for 8 min at 170 °C under pressure of 10 MPa, and followed by cooling to room temperature in another press for 4 min. The obtained sheets were cut into appropriate samples for mechanical and thermal properties testing.

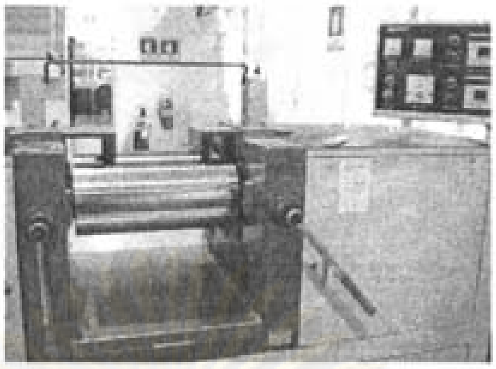


Figure 4.4: Two Rolls Mill Machine

Table 4.6: Size and Content of Agricultural Fiber Used

Type	Particle Size			Content (phr)
	size	µm	mesh	
Corncob (CC)				20
	S	106-180	140-80	
Bagasse (BG)				40
	L	250-425	60-40	
Rice Straw (RS)				60

4.4 Characterizations

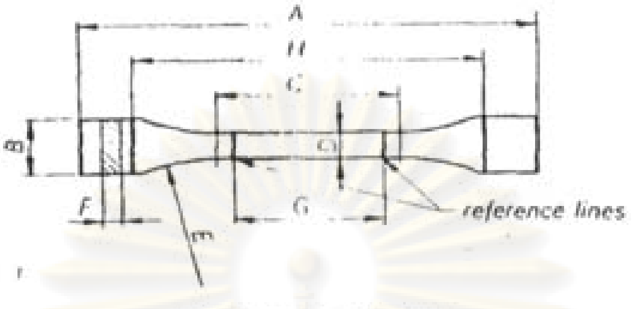
4.4.1. Mechanical Properties

Tensile Property

Tensile test measures the force required to break a specimen and the extent to which the specimen stretches or elongates to that breaking point. Tensile test produces a stress-strain diagram, which is used to determine tensile modulus.

The dog-bone shape specimens were prepared for tensile testing following ASTM D638 (or ISO 527). The dimension of the specimen was shown in Figure 4.5. At least five measurements were taken using Instron Universal Testing Machine

(Instron 5567, NY, USA) and statistically averaged to obtain an average value and a standard deviation. The crosshead speed was 50 mm/min.



Dimensions in millimetres

A : Overall length, minimum	150 mm.
B : Width at ends	20 ± 0.5 mm.
C : Length of narrow parallel portion	60 ± 0.5 mm.
D : Width of narrow parallel portion	10 ± 0.5 mm.
E : Radius, minimum	60 mm.
F : Thickness	4 ± 1 mm.
G : Distance between reference lines	50 ± 0.5 mm.
H : Initial distance between grips	115 ± 5 mm.

Figure 4.5: Dimensions of Dog-bone Shape Specimen (ASTM D638 or ISO 527)

Flexural Property

In engineering mechanics, flexure (also known as bending) characterizes the behavior of a structural element subjected to a lateral load. A structural element subjected to bending is known as a beam. A closet rod sagging under the weight of clothes on clothes hangers is an example of a beam experiencing bending.

The bar shape specimens (10×4×80 mm) are prepared for flexural testing following ASTM D790. At least seven measurements are taken using Instron Universal Testing Machine (Instron 5567, NY, USA) as shown in Figure 4.6 and statistically averaged to obtain an average value and a standard deviation. The set up value for flexural testing follow by ASTM D790 are standard speed 1.2 mm/min, span 48 mm, and load cell 1 kN.

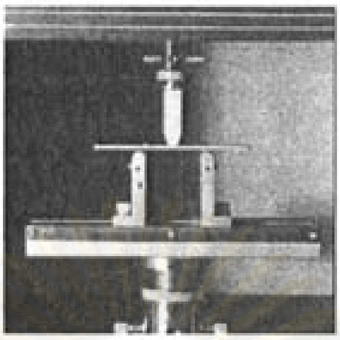


Figure 4.6: Flexural Testing (http://www.ptli.com)

Izod Impact Property

Notched Izod Impact is a single point test that measures a resistance of material to impact from a swinging pendulum. Izod impact is defined as the kinetic energy needed to initiate fracture and continue the fracture until the specimen is broken. Izod specimen is notched to prevent deformation of the specimen upon impact. The specimen is clamped into the pendulum impact test fixture with the notched side facing the striking edge of the pendulum. The pendulum is released and allowed to strike through the specimen. If breakage does not occur, a heavier hammer is used until failure occurs. ASTM impact energy is expressed in J/m or ft-lb/in. ISO impact strength is expressed in kJ/m^2. Impact strength is calculated by dividing impact energy in J (or ft-lb) by the thickness of the specimen. The test result is typically the average of 10 specimens. The bar shape specimens were prepared for Izod impact strength testing following ASTM D256 (or ISO 180). The dimension of the standard specimen was $64\times12.7\times3.2$ mm^3. The depth under notch of the specimen was 10.2 mm. The impact tester (Yasuda Seiki. Seisakushi Ltd., Japan) was shown in Figure 4.7.

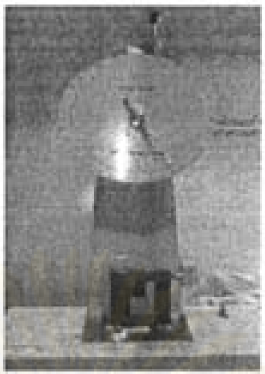


Figure 4.7: Impact Tester (Yasuda)

4.4.2. Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) as shown in Figure 4.8 is a type of electron microscope capable of producing high-resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample.

Test specimens are sputter coated with gold, then placed in a vacuum chamber for viewing on the computer monitor at up to 10,000x magnification.

Figure 4.8: Scanning Electron Microscope (SEM)

4.4.3. Thermal Properties

Differential Scanning Calorimeter (DSC)

Differential scanning calorimetry or DSC is a thermoanalytical technique in which the difference in the amount of heat required to increase the temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at very nearly the same temperature throughout the experiment. Thermal transitions of PVC/agricultural composites were determined by means of differential scanning calorimeter (DSC) as shown in Figure 4.10. A sample of 10 to 20 mg. in an aluminum sample pan is placed into the differential scanning calorimeter. The sample was heated at a controlled rate (usually 10°/min) and a plot of heat flow versus temperature was produced. The resulting thermogram was then analyzed for Tg, T_m, ΔH_m or ΔH_c as shown in Figure 4.9 (as an example).

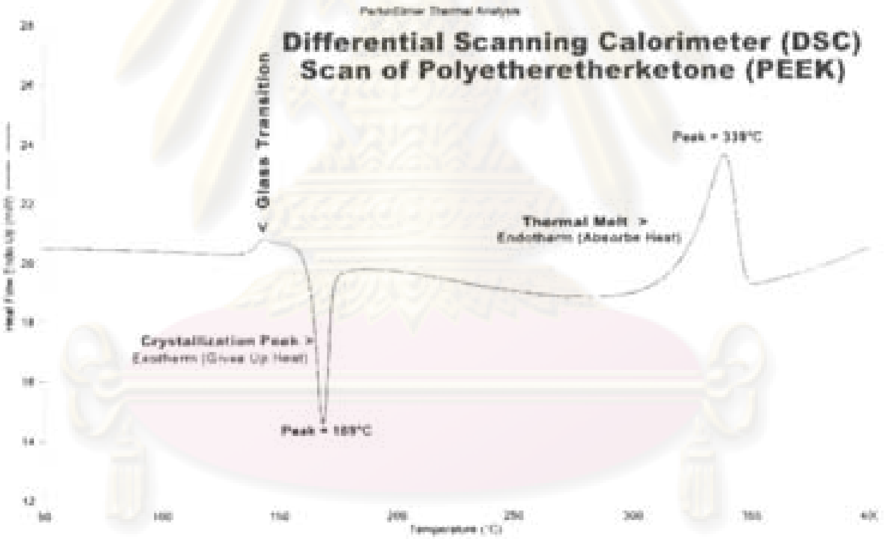


Figure 4.9: The Resulting Thermogram of DSC

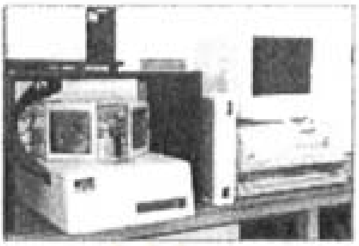


Figure 4.10: Differential Scanning Calorimeter (DSC)

Heat Distortion Temperature and Vicat Softening Temperature

Heat distortion temperature is defined as the temperature at which a standard test bar deflects a specified distance under a load as shown in Figure 4.11. It is used to determine short-term heat resistance. It distinguishes between materials that are able to sustain light loads at high temperatures and those that lose their rigidity over a narrow temperature range. The specimen was placed under the deflection measuring device. The specimen was then lowered into a silicone oil bath where the temperature was raised at 120°C per hour until they deflected 0.25 mm.

Figure 4.11: Heat Distortion Temperature Tester (http://www.ptli.com)

The vicat softening temperature is the temperature at which a flat-ended needle penetrates the specimen to the depth of 1 mm under a specific load as shown in Figure 4.12. The temperature reflects the point of softening to be expected when a material is used in an elevated temperature application. A test specimen was placed in the testing apparatus so that the penetrating needle rested on its surface at least 1 mm from the edge. A load of 10N was applied to the specimen. The specimen was then lowered into a silicon bath at 23 °C. The bath was raised at a rate of 50 °C per hour until the needle penetrated 1 mm.

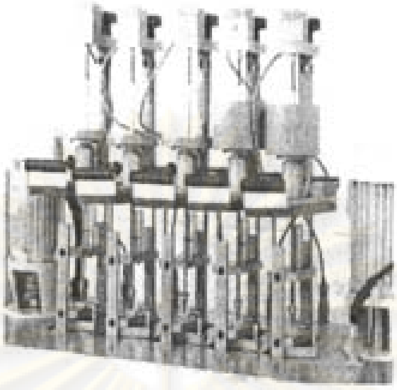


Figure 4.12: Vicat Tester (http://www.ptli.com)

4.4.4. Water Absorption

Water absorption is used to determine the amount of water absorbed under specified conditions. Factors affecting water absorption include type of plastic, additives used, temperature and length of exposure. The data sheds light on the performance of the materials in water or humid environments. For the water absorption test, the specimen is dried in an oven for a specified time and temperature and then placed in a desiccator to cool. Immediately upon cooling, the specimens are weighed. The material is then emerged in water at agreed upon conditions, often 23°C for 24 hours or until equilibrium. Specimens are removed, patted dry with a lint free cloth, and weighed every week. The dimension of sample is 4 mm thick. Water absorption is expressed as increase in weight percent. As given in eqn. (1)

$$\text{Percent Water Absorption} = [(\text{Wet weight} - \text{Dry weight})/\ \text{Dry weight}] \times 100 \qquad (1)$$

Figure 4.13: Water absorption testing (http://www.ptli.com)

4.4.5. Aspect Ratio

The aspect ratio (which is defined as the ratio of length to with) of agricultural fiber can be determined by measuring the length and with of the fiber from SEM micrograph of agricultural fiber. One hundred samples of agricultural fiber were measured.

CHAPTER V

RESULTS AND DISCUSSION

The effects of fiber loading, fiber size, and fiber type on the mechanical, thermal, water absorption, and morphological properties were studied. The wood composite samples were prepared by two rolls mill at 175°C and compression molding at 170 °C and 10 MPa. The PVC/agricultural fiber composites were tested for the following properties: tension and flexural properties were tested by Universal testing machine (Instron, 5567), impact property was tested by impact tester (Yasuda, Japan). Thermal properties such as glass transition temperature (Tg) were tested by differential scanning calorimeter, heat distortion temperature and vicat softening temperature were test by vicat/HDT tester (Ceast, USA). Moreover, the microstructure of impact fracture of the composites was observed by a scanning electron microscope (SEM) (Joel, JSM 5410, LV).

It can be note that the abbreviation in this chapter refers to full name of PVC/agricultural fiber composites as follow:

Full name	Abbreviation
Corncob	CC
Bagasse	BG
Rice Straw	RS
Small Size (106-180 μm)	S
Large Size (250-425μm)	L

For example, PVC/CC-S refers to PVC dry blend filled with small sized-corncob.

5.1 Mechanical Properties

The mechanical properties measured in this research consisted of tensile properties, flexural properties and impact strength. It can be observed from the results that fiber size and fiber loading affected properties of the composites.

5.1.1 Tensile Property Measurement

Tensile Strength and Elongation at break

The effect of fiber loading on tensile strength of composites was shown in Figures 5.1-5.2. It would be seen that these values generally decreased when the agricultural fiber were added into PVC matrix. It would be clearly seen at composites with high fiber content. At 40 phr of CC-S, tensile strength of PVC/corncob composite was 38 MPa while tensile strength of PVC dry blend is 46 MPa and elongation at break of these composites decreased almost 18 times compared to that of PVC dry blend. Moreover, the composites with higher fiber content show lower values of tensile strength and elongation at break. In addition, at 60 phr of CC-S, tensile strength and elongation at break of PVC/corncob composite slightly decreased by 7% and 13% compared to composites with 20 phr of CC-S. It could be explained that the addition of fiber in PVC dry blend made the composites more brittle due to the increment of interfacial defects causing more debonding between polymer and fibers and the agricultural fibers themselves have lower elongation at break than PVC matrix (Yu-Tao et al., 2007). Moreover, these results were caused by poor dispersion of fibers in the matrix.

The effect of fiber size on tensile property of PVC/agricultural fiber composites were also shown in Figure 5.1-5.2. It showed the addition of small-sized fiber in PVC dry blend reduced the tensile strength of composites less than larged-sized fiber when these 2 figures were compared. Composite with 60 phr of small-sized rice straw showed 27 % higher tensile strength than that with large-sized rice straw because the small-sized fiber had higher specific area than that of large-sized fiber. Moreover, small-sized fibers could be better dispersed in PVC matrix; hence, the composites with small-sized fibers showed less voids between fibers and PVC matrix than composites with large-sized fibers. Therefore, the small-sized fibers could better reinforce composites. However, size of fiber did not significantly affect the elongation at break of composites as could be seen in Figure 5.3-5.4. Elongation at break of composite with 60 phr of CC-S was 1.58% while that of composite with 60 phr of CC-L is 1.47%. It could be concluded that sizes of fiber used in this research were not significantly different enough from each other to have different effect on the brittleness of composites.

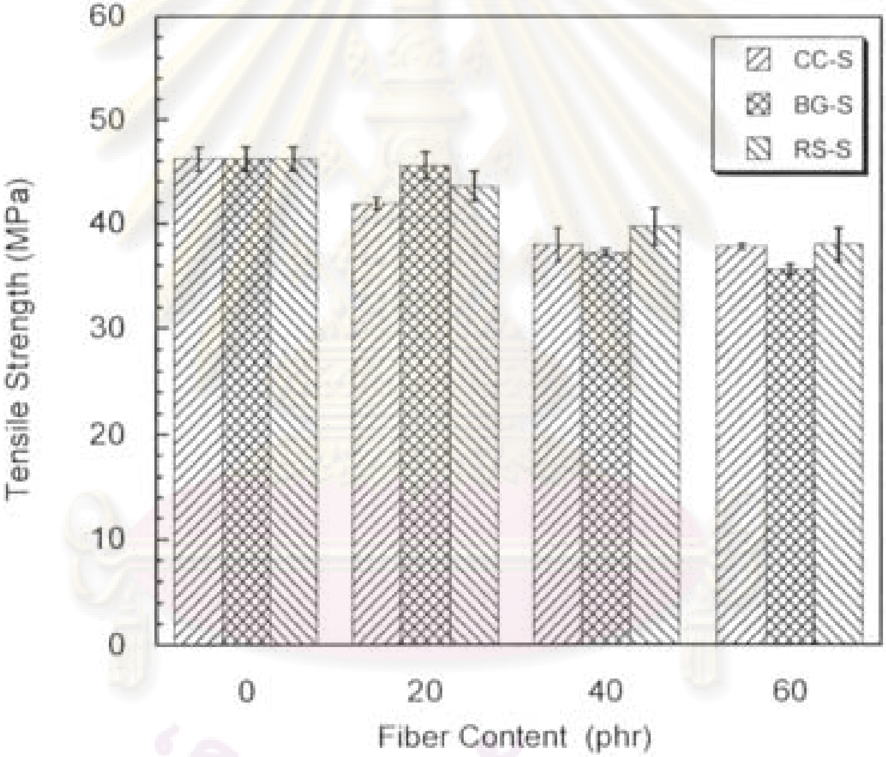


Figure 5.1: Tensile Strength of PVC/Agricultural Fiber Composites with Fiber Size of 106-180 μm (S)

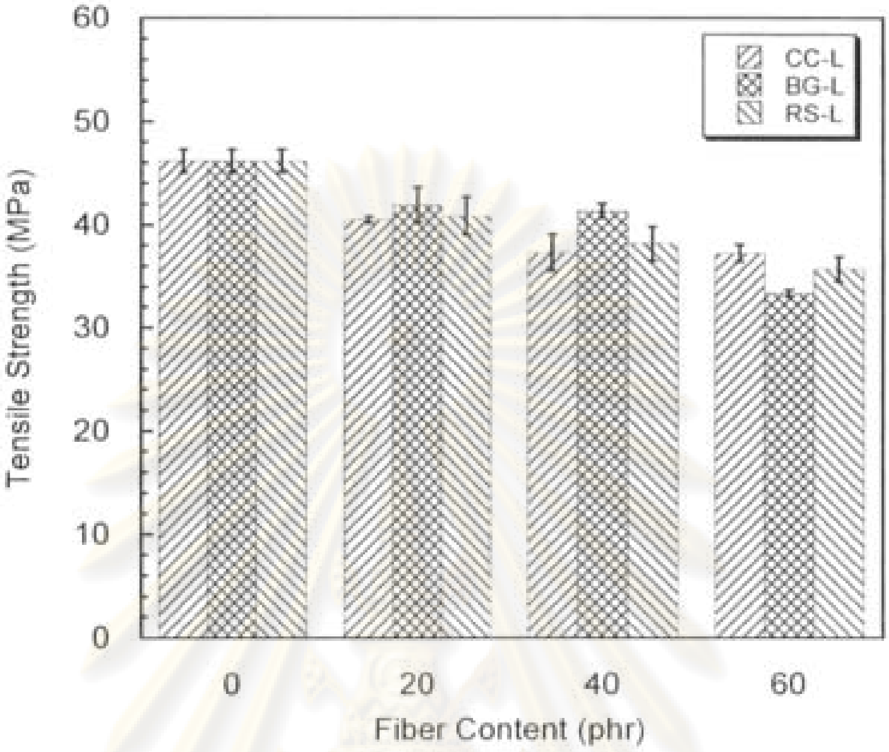


Figure 5.2: Tensile Strength of PVC/Agricultural Fiber Composites with Fiber Size of 250-425 μm (L)

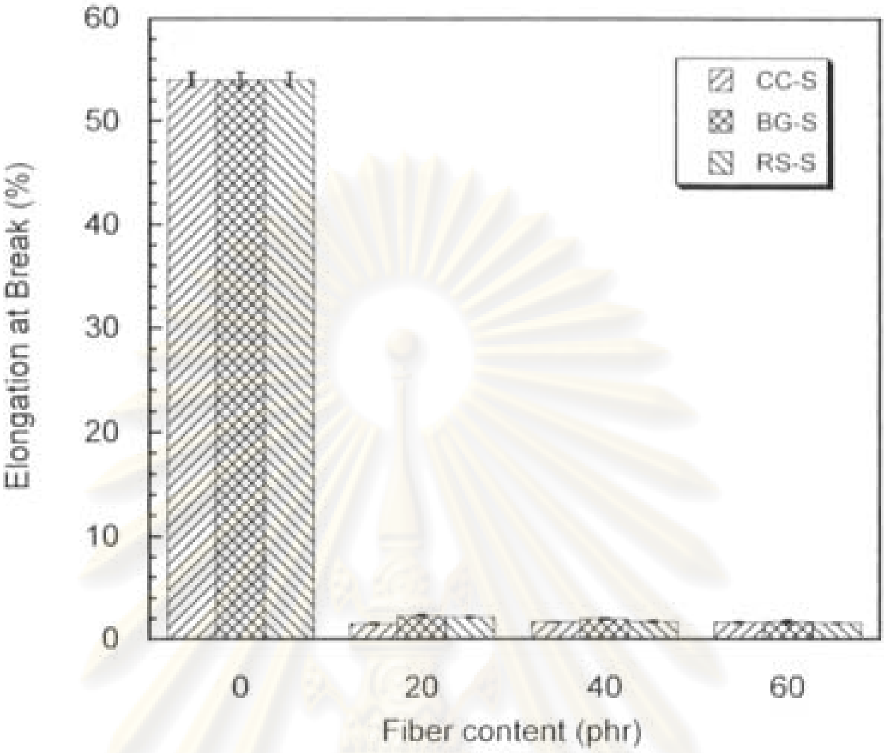


Figure 5.3: Elongation at Break of of PVC/Agricultural Fiber Composites with Fiber Size of 106-180 μm (S)

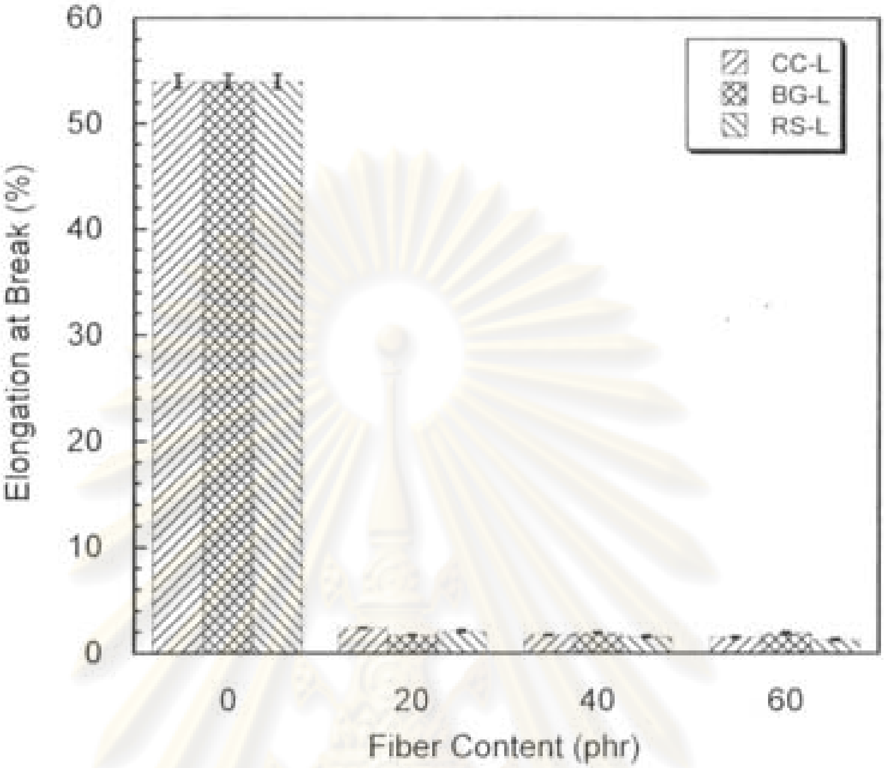


Figure 5.4: Elongation at Break of of PVC/Agricultural Fiber Composites with Fiber Size of 250-425 μm (L)

Tensile Modulus

The addition of fibers in PVC caused the composite to be stiffer than PVC dry blend because fiber was reinforcing filler so the increase of tensile modulus of composite is occurred. These results were shown in Figure 5.6-5.7. They showed that the addition of fiber in PVC could increase the tensile modulus. At 20 phr of PVC/BG-L composite, tensile modulus of composite was 2.9 GPa while tensile modulus of PVC dry blend was 2.5 GPa. Moreover, composites with high fiber contents showed higher tensile modulus than that with low fiber contents. For example, composite with 60 phr of BG-L showed tensile modulus 25% higher value than that with 20 phr of BG-L.

However, tensile modulus of composites with different fiber size were slightly different as compared between Figure 5.6 and 5.7 (when standard deviation was taken in the account). For example, tensile modulus of composites with 60 phr of small-sized bagasse was 3.83 GPa while this value of composites with 60 phr of large-sized bagasse was 3.48 GPa.

Moreover, Figure 5.7 showed that composites with bagasse and rice straw as fillers had higher values of tensile modulus than that with corncob. At 60 phr of fiber content, tensile modulus of composites with BG-L and RS-L were 3.48 and 3.72 GPa, respectively, while tensile modulus of composites with CC-L was 3.39 GPa. The composites with other contents and sizes of fibers showd the same trends of results. These effects could be explained in term of amount of cellulose of agricultural fiber. Table 5.1 showed that amounts of fiber (cellulose and hemicellulose together) of bagasse and rice straw were slightly higher than that of corncob (Yu Tao, 2007).

(a) 20 phr (b) 40 phr (c) 60 phr

Figure 5.5: SEM Micrograph of PVC/ Large-Sized Bagasse Composites at Various Bagasse Loading (a) 20 phr, (b) 40 phr, (c) 60 phr

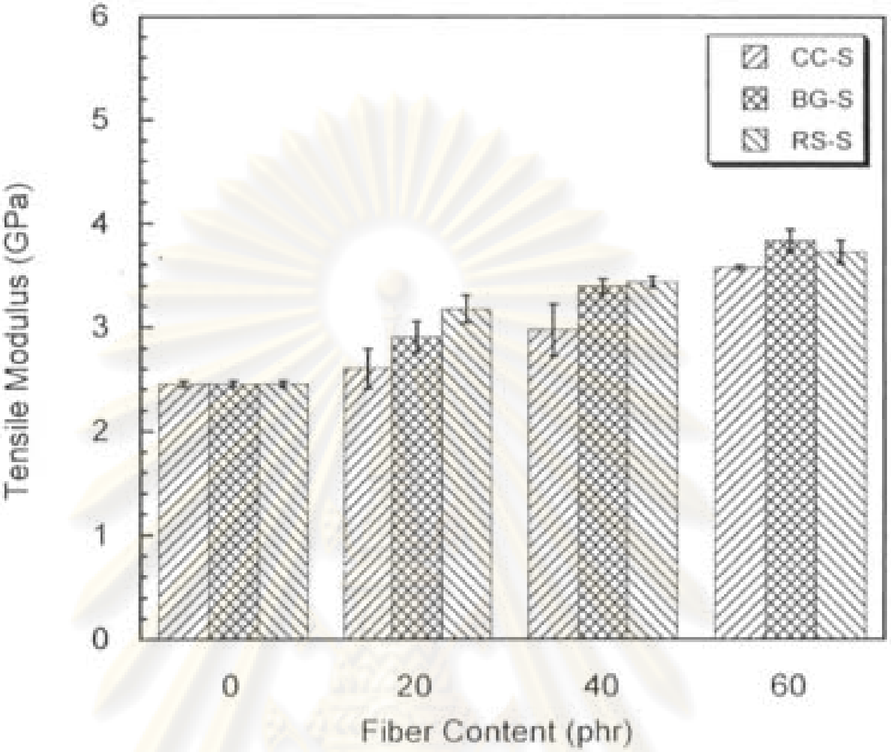


Figure 5.6: Tensile Modulus of PVC/Agricultural Fiber Composites with Fiber Size of 106-180 μm (S)

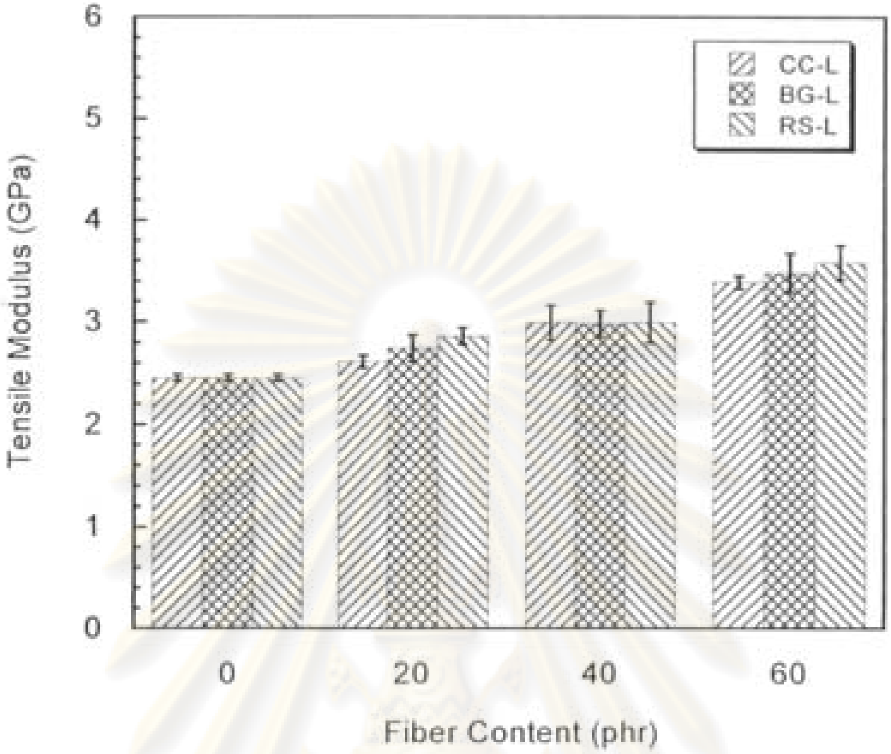
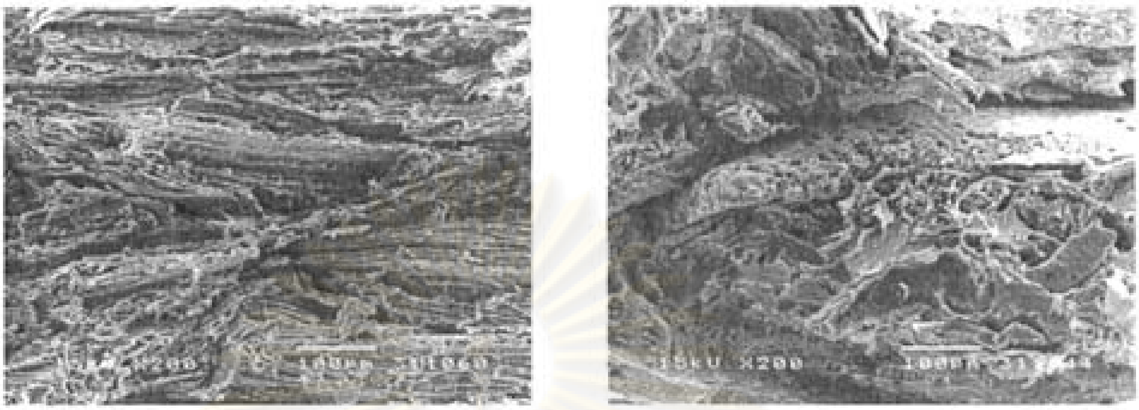


Figure 5.7: Tensile Modulus of PVC/Agricultural Fiber Composites with Fiber size of 250-425 μm (L)

Table 5.1: Chemical Composition of Agricultural fiber

Fiber composition (wt%)	Corncob	Bagasse	Rice Straw
Cellulose	34	41	43.92
Hemicellulose	40	35.84	35
Lignin	23	18.29	12
Ash	1.50	1.50	7
Other	1.5	3.37	2.08



(a) 106-180 μm

(b) 250-425 μm

Figure 5.8: SEM Micrograph of PVC/Rice Straw Composites with Rice Straw Content of 60 phr at Various Size: (a) 106-180μm, (b) 250-425 μm

5.1.2 Flexural Property Measurement

Flexural Strength and Flexural Modulus

The results of flexural property of PVC/agricultural fiber composites show the same trend as the results of tensile property. The composites showed the decrease of flexural strength as shown in Figures 5.9-5.10 and also show the increment of flexural modulus as shown in Figures 5.11-5.12. From Figure 5.9, at 60 phr of CC-S, flexural strength of PVC/CC-S composite was 60 MPa while flexural strength of PVC dry blend was 74 MPa.

The effects of fiber size on flexural property of PVC/agricultural fiber composites were also shown in Figures 5.9-5.12. It could be seen from Figures 5.9 and 5.10 that flexural strength of composites with small-sized fiber has higher value than that with large-sized fiber. Composite with 60 phr of small-sized bagasse shows 12% higher flexural strength than that with large-sized bagasse.

Similarly, the small-sized rice straw improved flexural modulus of composites more than large-sized rice straw. Flexural modulus of PVC/RS-S composites at 60 phr of rice straw was 4.82 GPa while PVC/RS-L was at 4.23 GPa as shown in Figure 5.11 and 5.12. This could be due to higher specific area of RS-S than that of RS-L. Moreover, small-sized rice straw could be dispersed in PVC matrix better; hence, the composites with small- sized rice straw showed lower void between fiber and PVC matrix than composites with large-sized rice straw. Therefore, the small size fiber could reinforce composites better. This effect was supported by SEM micrographs as shown in Figure 5.8. The SEM micrograph of the composite filled with RS-L (Figure 5.8 (b)) exhibited poorer interface between filler and polymer matrix. As a result, the tensile and flexural modulus of PVC/agricultural fiber composites were decreased with increasing fiber size. However, size of corncob and bagasse used in this work did not significantly affect the flexural modulus of composites.

PVC/rice straw composites showed the highest value of flexural modulus. Especially at 60 phr of small-sized rice straw, flexural modulus of composite almost doubled as compared to that of PVC dry blend (2.79 GPa). These results could be due to different amount of cellulose in fiber, since the cellulose and hemicellulose had a significant effect on the stiffness of material (Bledzki, 1999). When data in Table 5.1, were considered, it could be expected that the composites with rice straw as fillers would be stiffer than the composites with corncob and bagasse.

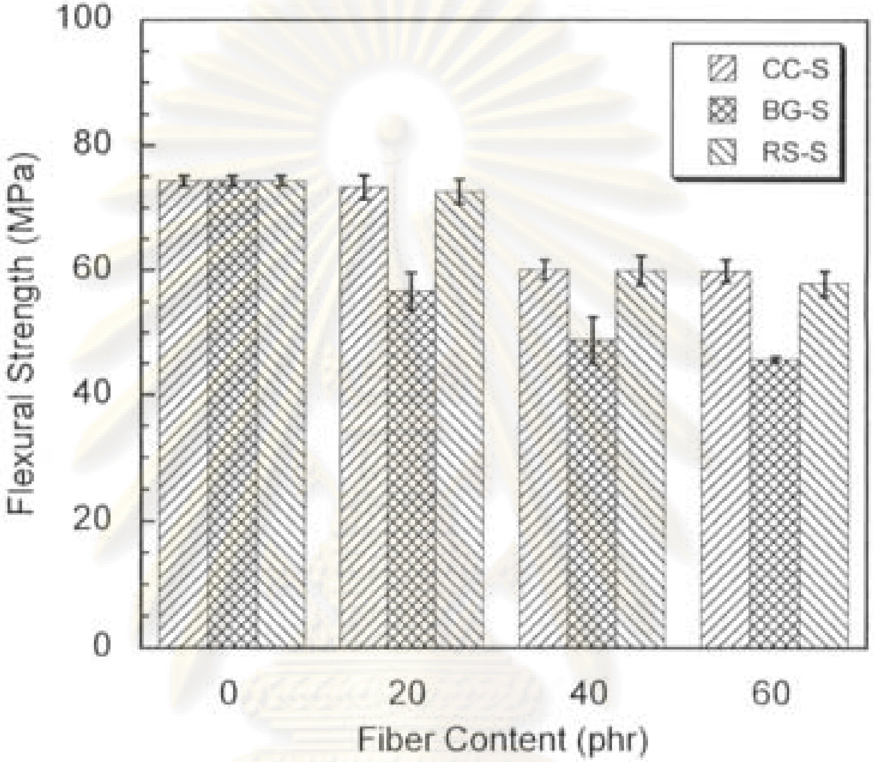


Figure 5.9: Flexural Strength of PVC/Agricultural Fiber Composites with Fiber Size of 106-180 μm (S)

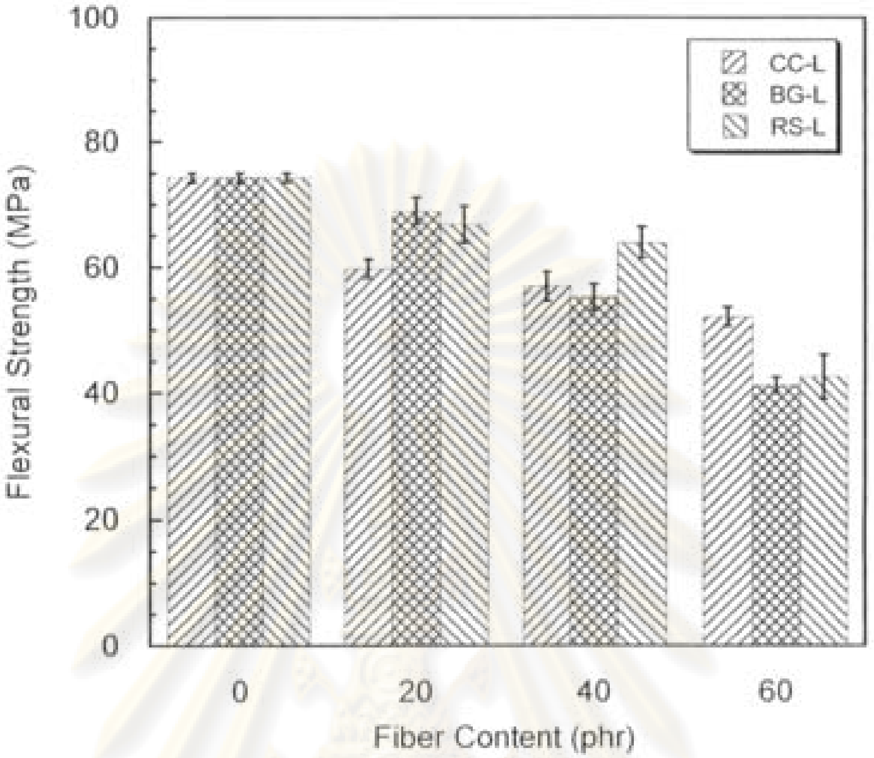


Figure 5.10: Flexural Strength of PVC/Agricultural Fiber Composites with Fiber Size of 250-425 μm (L)

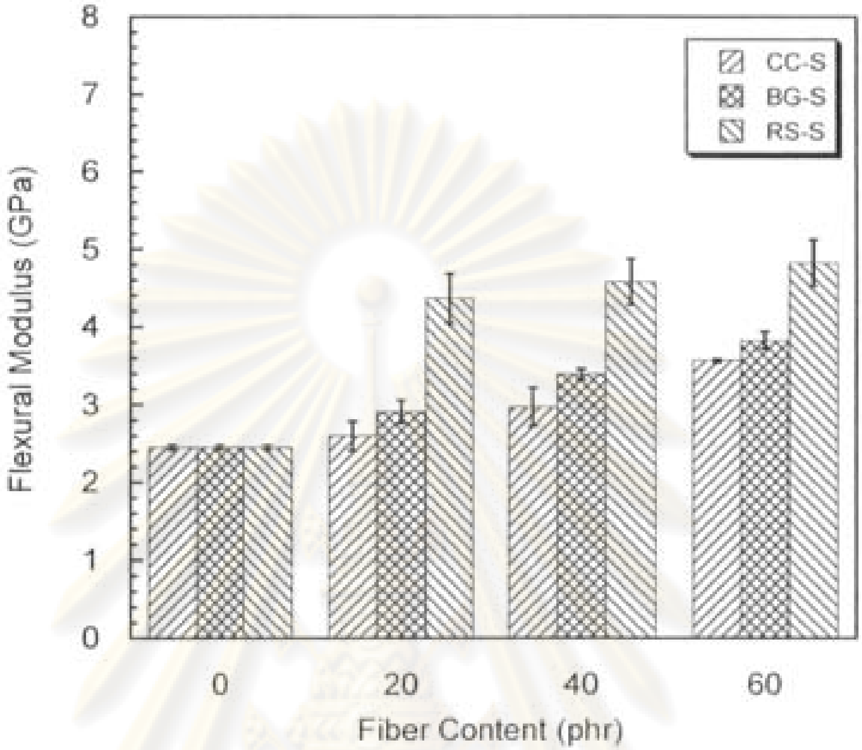


Figure 5.11: Flexural Modulus of PVC/Agricultural Fiber Composites with Fiber Size of 106-180 μm (S)

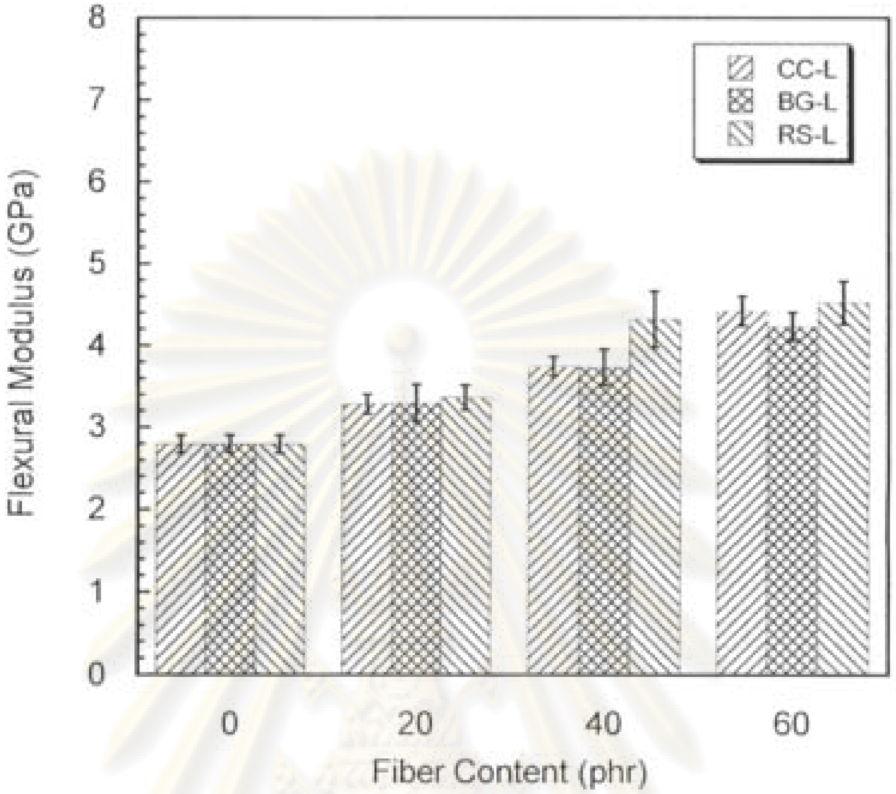


Figure 5.12: Flexural Modulus of PVC/Agricultural Fiber Composites with Fiber Size of 250-425 μm (L)

5.1.3 Impact Property Measurement

From Figures 5.13-5.14, the impact strength of PVC/agricultural fiber composites were lower than that of PVC dry blend. Moreover, the composites with the highest fiber content showed the lowest values of impact strength. At 60 phr of CC-S, impact strength of PVC/corncob composite was 4.04 kJ/m^2 while impact strength of PVC dry blend is 8.80 kJ/m^2. As the fiber reinforced the matrix causing the composites to be stiffer, the ductile portion of PVC was reduced; thus, the composite toughness was decreased. Moreover, the composites showed more pores than pure PVC so it took less energy to break composites.

The effect of fiber size on impact property of PVC/agricultural fiber composites was also shown in Figures 5.13-5.14. They showed that size of fiber did not have significant effect on this property. Impact strength of composites with 60 phr of small-sized corncob was 4.04 kJ/m^2 while this value of composites with 60 phr of large-sized corncob was 4.02 kJ/m^2. This might be due to sizes of fiber were not different enough to change the energy that composites absorbed before breaking (Maldas et al., 1989).

In addition, it shows that type of fiber do not affect impact strength of PVC/agricultural fiber composites. It can be seen that impact strength of composites with 60 phr of CC-S, BG-S, and RS-S are 4.04, 4.00, and 4.01 kJ/m^2, respectively. It could be concluded that type of fiber did not increase or decrease the energy that composites absorbed before breaking.

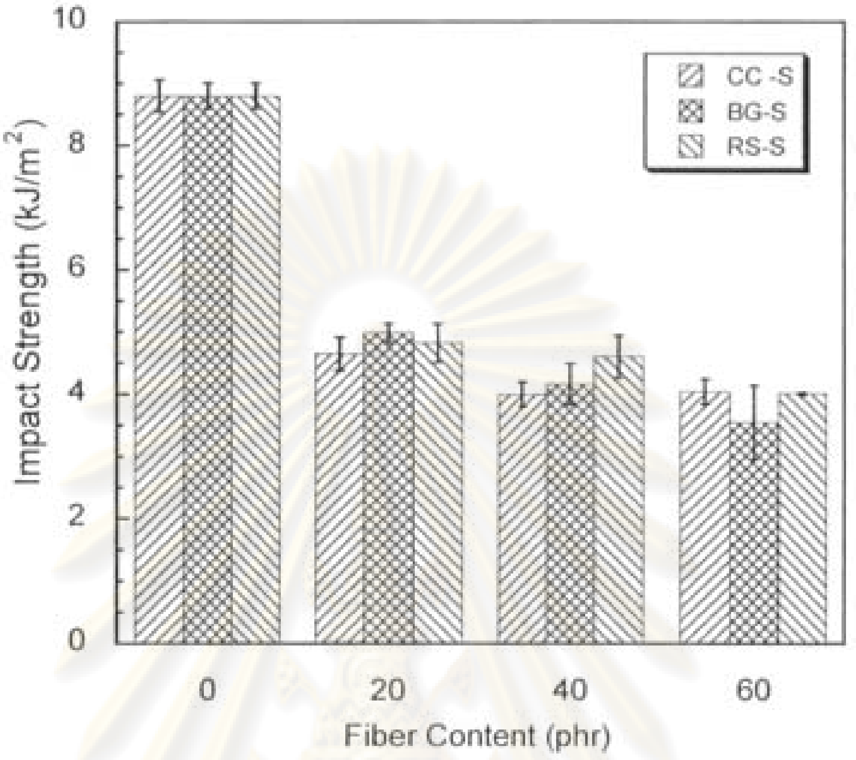


Figure 5.13: Impact Strength of PVC/Agricultural Fiber Composites with Fiber Size of 106-180 μm (S)

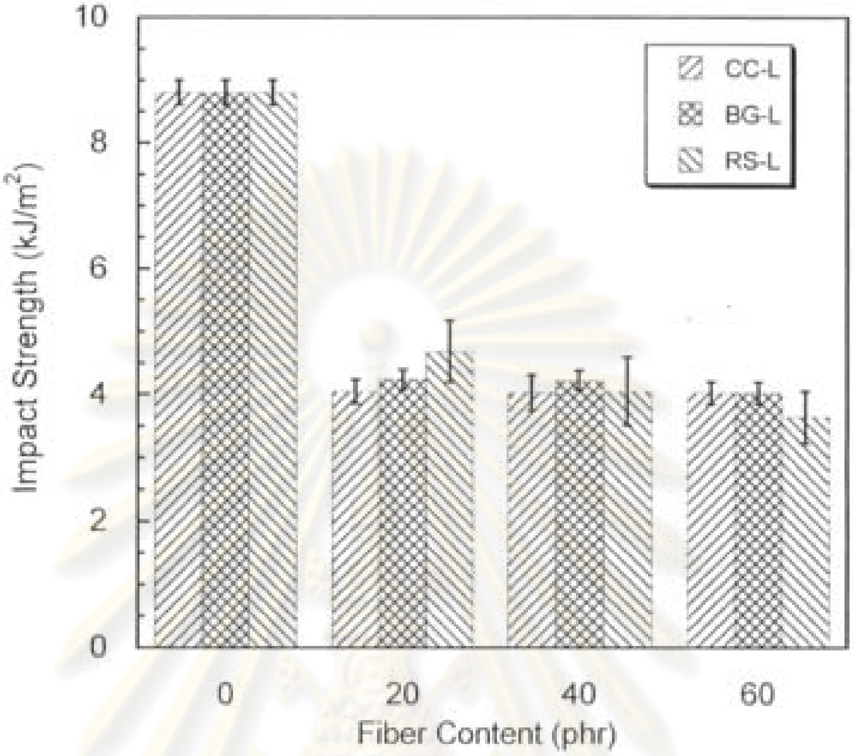


Figure 5.14: Impact Strength of PVC/Agricultural Fiber Composites with Fiber Size of 250-425 μm (L)

5.2 Thermal Properties

The thermal properties measured in this research consisted of glass transition temperature (T_g), heat distortion temperature and vicat softening temperature. It can be observed from the results that fiber loading, fiber size and fiber loading affected these properties of the composites.

5.2.1 Glass Transition Temperature (T_g) Measurement

The effect of agricultural fiber content on the glass transition temperature of PVC/agricultural fiber composites was shown in Table 5.2. It showed that the addition of fiber in PVC dry blend does not change T_g of composites compared to that of PVC dry blend. T_g of composite with 20 phr of CC-S showed the same value of PVC dry blend. Table 5.1 shows values of T_g as increased the fiber content. It showed that T_g of 60 phr of CC-S was 82 °C. This might imply that the hydrogen bonds between agricultural fiber and PVC matrix were not strong enough to have an effect on this property of the composites.

The effect of fiber size on glass transition temperature of composites was also shown in Table 5.1. It was found that size of fiber also did not affect T_g of PVC/agricultural fiber composites. For example, T_g of composite with 40 phr of small-sized rice straw was 81 °C while T_g of composite with 60 phr of larged-sized rice straw is 82 °C.

From Table 5.2, it could be seen that glass transition temperature of composites with different type of fiber also showed nearly the same values. As can be seen in PVC/rice straw composites, T_g of composites with 60 phr of large-sized rice straw and bagasse were 82.7 °C while T_g of composite with 60 phr of large-sized corncob was 81.3 °C.

Table 5.2: Glass Transition Temperature of PVC/Agricultural Fiber Composites

Filler	Fiber Size	Fiber Content (phr)	T_g (°C)
PVC dry blend	-	-	81
Corncob	S (106-180 µm)	20	81
		40	81
		60	82
	L (250-425 µm)	20	81
		40	81
		60	81
Bagasse	S (106-180 µm)	20	81
		40	82
		60	82
	L (250-425 µm)	20	81
		40	82
		60	82
Rice Straw	S (106-180 µm)	20	81
		40	81
		60	82
	L (250-425 µm)	20	81
		40	82
		60	82

5.2.2 Heat Distortion Temperature (HDT) Measurement

The addition of fiber in PVC matrix slightly increased the heat distortion temperature (HDT) of composites as shown in Figures 5.15-5.16. As shown in Figure 5.15, HDT of composite with 20 phr of RS-S was 73 °C while this value of PVC dry blend was 71 °C. Moreover, composites with high fiber content also show high value of HDT. As shown in Figure 5.16, at 60 phr of BG-L, HDT of PVC/bagasse composite was 74.5 °C while HDT of composite with 20 phr of BG-L was 71 °C. The reason for these effects was the same as given for glass transition temperature of composites. As fiber reinforced the composites and made them stiffer than PVC dry blend (Yu-Tao et al., 2007), therefore, the more fiber content in PVC matrix, the better the composites could withstand heat before distortion.

Figure 5.15 and 5.16 also showed that fiber size slightly affected the heat distortion temperature of composites. HDT of composites with 60 phr of large-sized rice straw increased 12% compared to small-sized rice straw composites. This effect could be supported by SEM micrograph as shown in Figure 5.8. It could be seen that the large-sized fiber (aspect ratio=5) has higher aspect ratio than that of small-sized fiber (aspect ratio=3), and it could improve thermal properties of composite better than small-sized fiber (Matuana et al., 1998).

The comparison of three types of fiber showed that type of fiber slightly affected HDT of composites. Figure 5.15 showed that composite with bagasse as filler had the highest value of HDT. For example, HDT of PVC/bagasse composite with 60 phr of large-sized bagasse was 79 °C while this value of composite with 60 phr of large-sized corncob and rice straw was 74 and 78 °C, respectively. It could be seen that the amount of cellulose in fiber improved the stiffness of composites such that the HDT of composites increased.

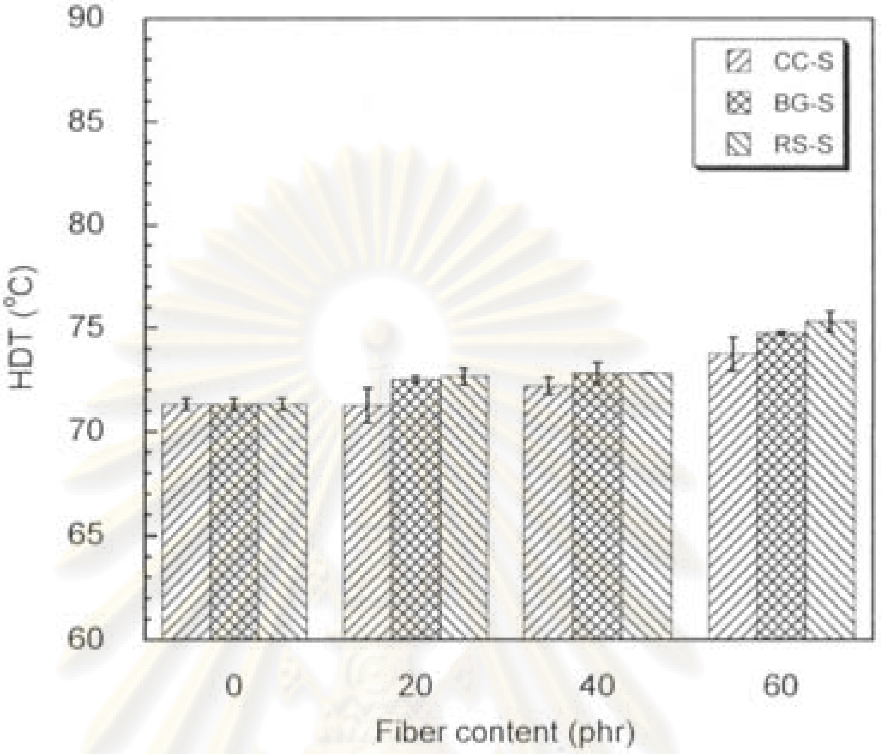


Figure 5.15: Heat Distortion Temperature of PVC/Agricultural Fiber Composites with Fiber Size of 106-180 μm (S)

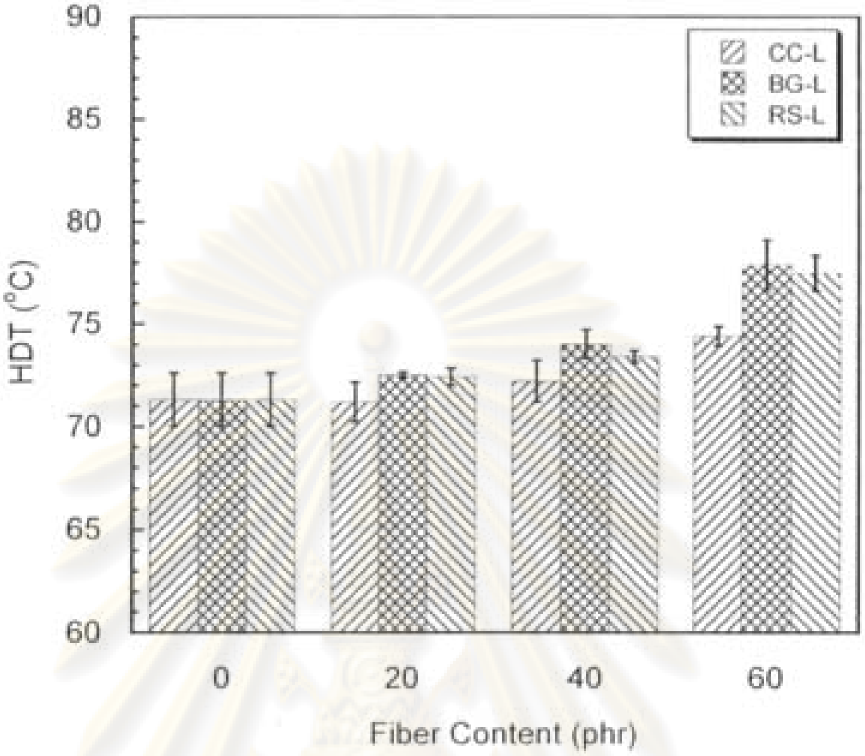


Figure 5.16: Heat Distortion Temperature of PVC/Agricultural Fiber Composites with Fiber Size of 250-425 μm (L)

5.2.3 Vicat Softening Temperature Measurement

The addition of fiber in PVC matrix slightly increased vicat softening temperature of composites as shown in Figures 5.17-5.18. For example, vicat softening temperature of composite with 20 phr of CC-L was 75.5 °C while this property of PVC dry blend was 74 °C. Moreover, high fiber content added in PVC matrix slightly increased vicat softening temperature of composites. When this property was compared between composites with 20 and 60 phr of CC-L, it was found that composite with 60 phr had 10% higher value than that with 20 phr. These effects could be explained that the addition of fiber increaseed the stiffness of composites due of cellulose and hemicellulose content of fiber and so the composite could resisted the penetration better than PVC dry blend (Bledzki et al.,1999).

Figures 5.17 and 5.18 showed vicat softening temperatue of PVC/agricultural fiber composites with different fiber size. It showed that composites with small-sized bagasse and rice straw had higher value of vicat softening temperature than that with larged-sized fiber. Vicat softening temperature of composite with 60 phr of small-sized rice straw was 87 °C while this value of composite with large-sized rice straw was 83 °C. This effect could be explained that composites with small-sized fiber could be dispersed in polymer matrix better than large-sized fiber. Therefore, both PVC and dispersed filler in the composite could better hinder the needle to penetrate into the composite than the composite with poor dispersion of fillers.

Moreover, these 2 figures showed that composites with bagasse (BG) and rice straw (RS) as filler showed higher values of vicat softening temperature than that of composites with corncob (CC). For example, vicat softening temperature of composite with 60 phr of small-sized bagasse and rice straw was 87 and 86 °C, respectively, while this value of composite with 60 phr of small-sized corncob was 82 °C. As shown in Table5.1, it could be seen that bagasse and rice straw have higher weight percentage of cellulose than corncob. Therefore, the composites with bagasse and rice straw were stiffer than that with corncob.

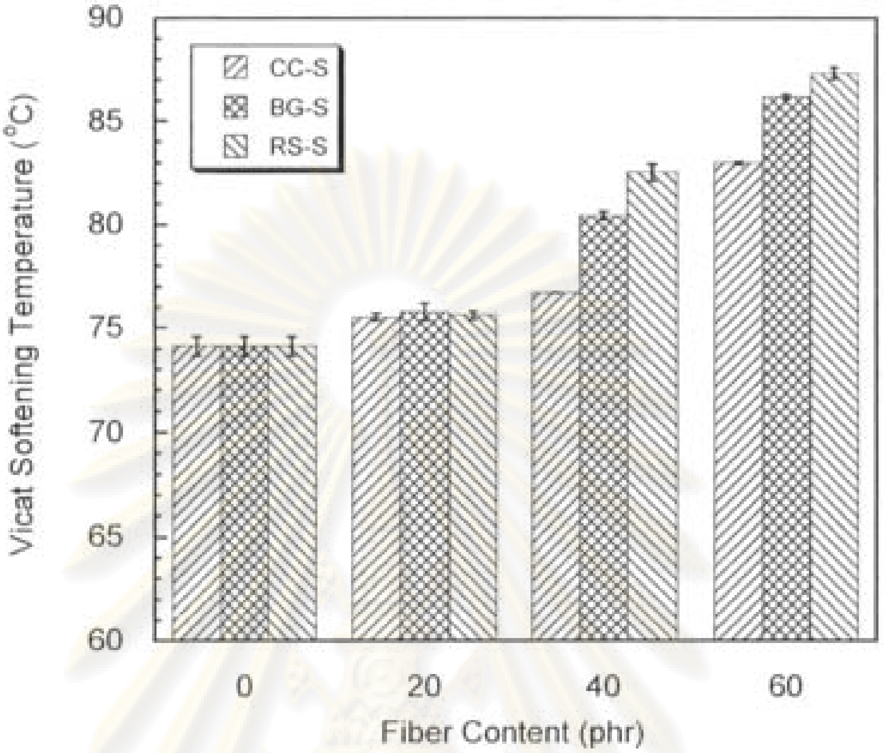


Figure 5.17: Vicat Softening Temperature of PVC/Agricultural Fiber Composites with Fiber Size of 106-180 μm (S)

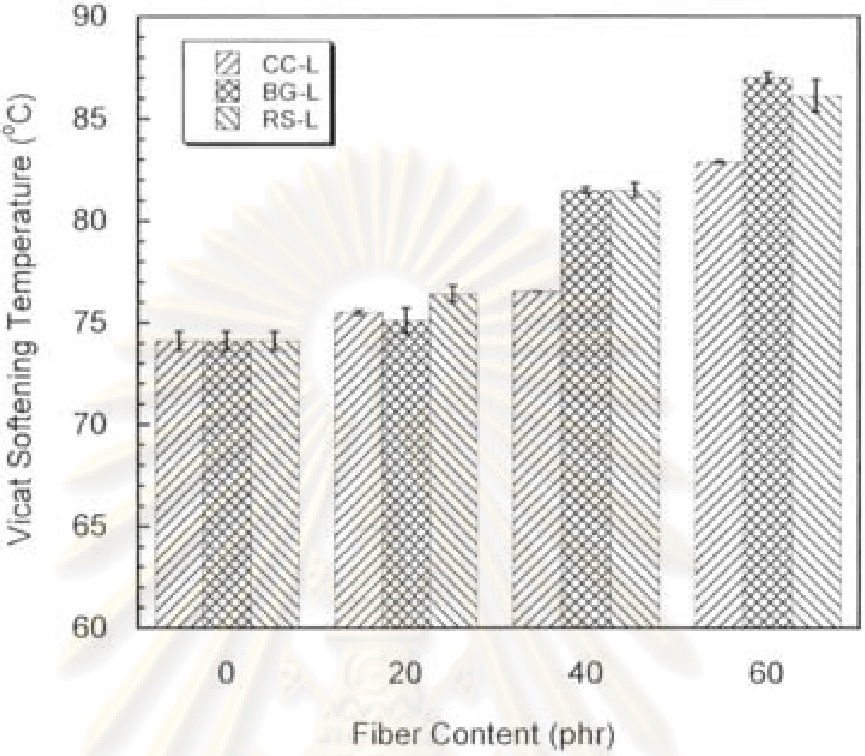


Figure 5.18: Vicat Softening Temperature of PVC/Agricultural Fiber Composites with Fiber Size of 250-425 μm (L)

5.3 Water Absorption

The amounts of water absorption after soaking for 4 months of PVC/agricultural fiber composites were shown in Figure 5.19-5.20. They showed that the addition of fiber increases water absorption of composites. The higher the fiber content, the higher the amount of water that can be absorbed by the composites. At 60 phr of small-sized rice straw, water absorption of PVC/rice straw composite was 5.9 wt% while water absorption of PVC dry blend was 0.32 wt%. This occurred because fiber is a hydrophilic material. Moreover, the addition of fiber into the PVC matrix made the composites to be more pores between particles of PVC and fibers; so water can also be stored in these pores. Moreover, Figure 5.19 showed that 60 phr of RS-S, PVC/RS-S composites had the highest water absorption content and was 37.5 % higher than that with 20 phr of RS-S.

Moreover, it showed that large-sized fiber could absorb water more than that of small-sized fiber. Water absorption of PVC/RS-S composite at 60 phr filler is 8.41 wt% while water absorption of PVC/RS-L composite at the same filler content is 9.47 wt%. It could be that the large-sized fiber which had more amount of void between PVC matrix and fiber to absorb water than that of small-sized fiber. This effect can be supported by SEM micrograph as shown in Figure 5.21.

Table 5.2 showed that rice straw had the highest percentage of cellulose so it could absorb more water than other fibers. It could be observed that water absorption of PVC/rice straw composites had the highest water absorption value. Water absorption of composite with 60 phr of large-sized rice straw was 9.47 wt% while this value of composite with 60 phr of large-sized corncob and bagasse were 7.29 and 7.55 wt%, respectively. Cellulose and hemicellulose were the significant factor of water absorption (Bledzki, 1999).

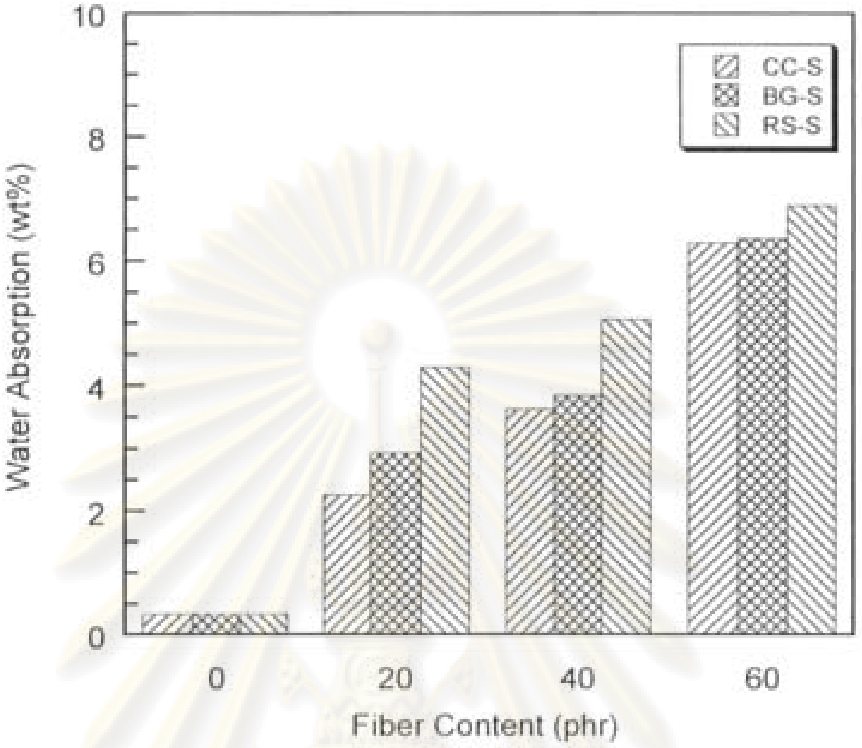


Figure 5.19: Water Absorption after Soaking in Water for 4 months of PVC/Agricultural Fiber Composites with Fiber Size of 106-180 μm (S)

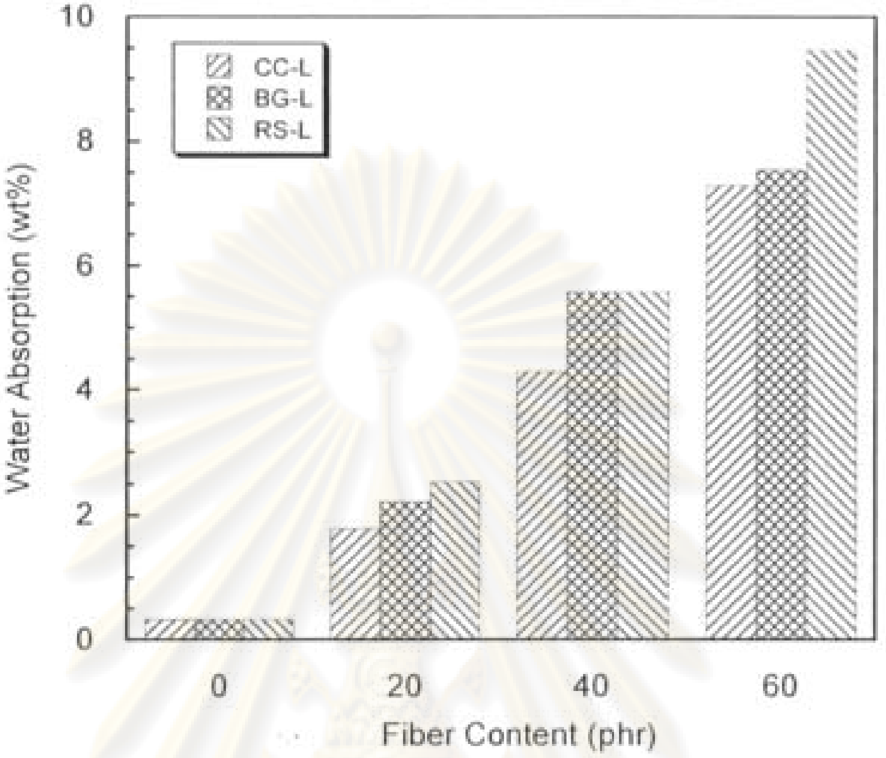
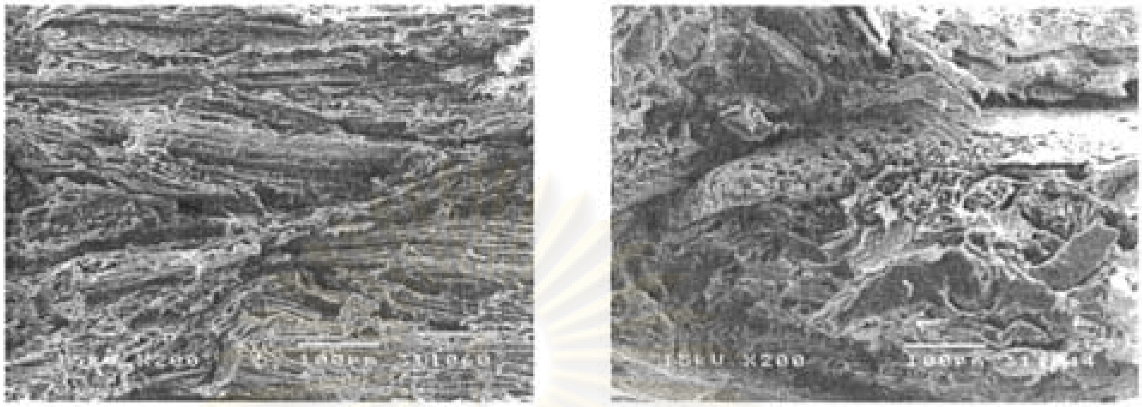


Figure 5.20: Water Absorption after Soaking in Water for 4 months of PVC/Agricultural Fiber Composites with Fiber Size of 250-425 μm (L)



(a) 106-180 μm (b) 250-425 μm

Figure 5.21: SEM Micrograph of PVC/Rice Straw Composites with Rice Straw Content of 60 phr at Various Size: (a) 106-180μm, (b) 250-425μm

CHAPTER VI

CONCLUSIONS

The addition of agricultural fibers into PVC dry blend resulted in stiff and brittle composites compared to PVC dry blend, as noticed from an increase in tensile modulus and flexural modulus of PVC/agricultural fiber composites. On the other hand, the strength properties of composite were decreased and PVC/agricultural fiber composites absorbed more water than PVC dry blend.

Small-sized fibers increased the stiffness of composites better than that with large-sized fiber. Moreover, these composites adsorbed less amount of water than that with large-sized fibers. However, size of fibers did not show significant effect on thermal properties of PVC/agricultural fiber composites.

Bagasse (BG) and rice straw (RS) enhanced the stiffness of composite higher than that of corncob when adding into PVC dry blend because these two fillers had higher amount of cellulose than that of corncob. However, types of fibers did not show any effect on thermal properties of PVC/agricultural fiber composites. Finally, it could be observed that PVC/rice straw composite absorbed more water than other PVC/agricultural fiber composites.

REFERENCES

Birley, A.W, Heath, R.J and Scott, M.J. Plastics Materials: Properties and Applications. New York: Chapman and Hall, 1988.

Bledzki, A.K, Gassan, J. Composites reinforced with cellulose based fibers. J. Appl. Polym. Sci. 24 (1999): 221-274.

Garvin, S. Polymer Processes. Interscience Publ, NY, Chap XVI ,1956.

Gachter, R and Muller, H. Plastics Additives Handbook. New York: Hanser Gardner Publications, (1987).

Georgopoulos, S. Th.; Tarantili, P.A.; Avgerinos, E.; Andreopoulos, A.G.; and Koukios, E.G. Thermoplastic polymers reinforced with fibrous agricultural residues. Polym. Degrad. Stabil. 90 (2005):303-311.

Haihong, J and Kamdem, D.P. Development of Poly (Vinylchloride)/Wood composites. J. Vinyl. Addit. Techn. 10 (2004):212-230.

Kamel, S. Preparation and properties of composites made from rice straw and poly(vinyl chloride) (PVC). Polym. Advan. Technol. 14 (2004): 611-615.

Linko, M. Advanced Biochemical Engineering. (1997): 251-252.

Maldas, D and Kokta, B.V. Studies on the preparation and properties of particle boards made from bagasse and PVC: II. Influence of the addition of coupling agents. Bioresource Technol. 35 (1991): 160-165.

Maldas, D, Kokta, B. V and Daneault, C. Composites of Polyvinyl chloride-agricultural fibers: IV. Effect of the nature of fibers. J. Vinyl. Addit. Techn. 10 (1989): 128-137.

Matuana, L.M, Kamdem, D.P and Jun, Z. Photoaging and stabilization of rigid PVC/wood-fiber composites. J. Appl. Polym. Sci. 80 (2001): 1943-1950.

Matuana, L.M., Woodhams, R.T.; Park, C.B and Balatinecz, J.J. Influence of interfacial interactions on the properties of PVC/cellulosic fiber composites. Polym. Composite. 19 (1998): 446-455.

Reinhart, T.J and Clements, L.L. Engineered Material Handbook. Ohio: ASM International, (1989).

Shah, B.L.; and Matuana, L.M.; Novel coupling agents for PVC/wood-flour composites. J Vinyl Addit Techn 10 (2005): 23-35.

Sombatsompop, N.; and Chaochanchaikul, K. Average mixing torque, tensile and impact properties, and thermal stability of Poly(vinyl chloride)/sawdust composites with different silane coupling agents. J Appl Polym Sci 96 (2005): 213-221.

Tulin, B. Processing of PVC. Petkim petrochemicals research center, Turkey.

Walten, B. Modern Plastics. (1963): 143-144.

Whelan, A.; and Craft, J.L. Development in PVC production and processing -I. Applied Science Publishers Ltd, (1997).

Yu-Tao, Z.; De-Rong, C.; Dong-Shan, W.; and Jiu-Ji, C. Study on the interface modification of bagasse fibre and the mechanical properties of its composite with PVC. Composites 38 (2007):20-25.

Zurale, M. M.; and Bhide, S. J. Properties of fillers and reinforcing fibers. Mech Compos Mater 34 (1998):651-663.

Final report the research project for higher utilization of forestry and agricultural plant materials in Thailand (HUFA) (2001), Kasetsart University. Available from: http:// posaa.kapi.ku.ac.th[2007 December 15]

http://en.wikipedia.org/wiki/Polyvinyl_chloride [2007 December 15]

www.vinythai.co.th [2007 December 15]

www.ptli.com [2007 December 15]

APPENDICES

Appendix A

Properties of PVC/Agricultural Fiber Composites

Appendix A-1 Properties of PVC/Corncob Composites.

Properties	Size of Fiber(μm)	Content of Fiber (phr)	Value of PVC$_{ref}$	Value of Composites
Tensile Strength (MPa)	106-180	20	46.2±1.1	41.8±0.5
		40		37.9±1.5
		60		37.7±0.2
	250-425	20		40.4±0.3
		40		37.2±1.7
		60		37.2±0.8
Tensile Modulus (GPa)	106-180	20	2.5±0.0	2.6±0.1
		40		2.9±0.2
		60		3.5±0.0
	250-425	20		2.6±0.0
		40		2.9±0.1
		60		3.3±0.0
Elongation at Break (%)	106-180	20	53.9±0.6	1.4±0.0
		40		1.6±0.0
		60		1.5±0.0
	250-425	20		2.3±0.0
		40		1.7±0.1
		60		1.4±0.1

Flexural Strength (MPa)	106-180	20	74.3±0.8	73.3±1.9
		40		60.0±1.5
		60		59.9±1.7
	250-425	20		59.1±1.5
		40		56.7±1.5
		60		52.9±2.3
Flexural Modulus (GPa)	106-180	20	2.8±0.1	3.5±0.2
		40		4.0±0.3
		60		4.2±0.2
	250-425	20		3.2±0.1
		40		3.7±0.1
		60		4.2±0.1
Impact Strength (kJ/m^2)	106-180	20	8.8±0.2	4.6±0.2
		40		3.9±0.1
		60		4.0±0.1
	250-425	20		4.0±0.1
		40		4.0±0.1
		60		4.02±0.1
Glass Transition Temperature (Tg) (^{o}C)	106-180	20	82	81.1
		40		81.2
		60		82.2
	250-425	20		81.4
		40		81.3
		60		81.3
Heat Distortion Temperature (^{o}C)	106-180	20	71.3±1.3	71.0±0.8
		40		72.1±0.4
		60		73.7±0.8
	250-425	20		71.2±0.9
		40		72.2±0.9
		60		74.4±0

Vicat Temperature (°C)	106-180	20		75.5±0.1
		40		76.7±0.0
		60		83.0±0.0
	250-425	20	74.1±0.5	75.5±0.1
		40		76.5±0.0
		60		82.9±0.0
Water absorption* (%)	106-180	20		2.34
		40		4.65
		60		6.96
	250-425	20	0.32	3.14
		40		5.21
		60		7.29

* The amounts of water absorption were measured after being submerged in water for 4 months.

Appendix A-2 Properties of PVC/Bagasse Composites.

Properties	**Size of Fiber**	**Content of Fiber**	**Value of PVC_{ref}**	**Value of Composite**
Tensile Strength (MPa)	106-180	20	46.2±1.1	47.5±1.3
		40		37.1±0.3
		60		35.6±0.4
	250-425	20		41.9±1.6
		40		33.3±0.7
		60		33.3±3.2
Tensile Modulus (GPa)	106-180	20	2.5±0.0	2.9±0.1
		40		3.3±0.0
		60		3.8±0.1
	250-425	20		2.7±0.1
		40		2.9±0.1
		60		3.4±0.1
Elongation at Break (%)	106-180	20	53.9±0.7	2.2±0.0
		40		1.9±0.0
		60		1.6±0.1
	250-425	20		1.7±0.0
		40		1.9±0.0
		60		1.8±0.1
Flexural Strength (MPa)	106-180	20	74.3±0.8	56.6±3.0
		40		68.7±3.7
		60		45.6±0.4
	250-425	20		68.9±2.1
		40		55.2±2.0
		60		41.2±3.2

Flexural Modulus (GPa)	106-180	20	2.7±0.1	3.4±0.1
		40		4.5±0.0
		60		4.2±0.2
	250-425	20		3.7±0.2
		40		3.8±0.1
		60		4.2±0.2
Impact Strength (kJ/m^2)	106-180	20	8.8±0.2	4.9±0.1
		40		4.1±0.3
		60		4.0±0.5
	250-425	20		4.2±0.1
		40		4.3±0.1
		60		4.0±0.1
Glass Transition Temperature (T_g) (^{o}C)	106-180	20	82	81.4
		40		82.6
		60		82.7
	250-425	20		81.8
		40		82.6
		60		82.7
Heat Distortion Temperature (^{o}C)	106-180	20	71.3±1.3	71.9±0.3
		40		72.8±0.5
		60		74.0±0.5
	250-425	20		72.5±0.1
		40		74.0±0.7
		60		77.9±1.2
Vicat Temperature (^{o}C)	106-180	20	74.1±0.5	75.7±0.4
		40		80.4±0.6
		60		87.1±0.1
	250-425	20		75.1±0.6
		40		81.5±0.1
		60		86.0±0.2

Water absorption* (%)	106-180	20	0.32	2.75
		40		4.45
		60		7.17
	250-425	20		2.95
		40		6.63
		60		7.55

* The amounts of water absorption were measured after being submerged in water for 4 months.

Appendix A-3 Properties of PVC/Rice Straw Composites.

Properties	Size of Fiber (μm)	Content of Fiber (phr)	Value of PVC_{ref}	Value of Composite
Tensile Strength (MPa)	106-180	20	46.2±1.1	43.5±1.4
		40		39.9±2.3
		60		38.6±1.5
	250-425	20		45.0±1.8
		40		44.0±2.0
		60		30.2±0.5
Tensile Modulus (GPa)	106-180	20	2.5±0.0	3.1±0.1
		40		3.4±0.0
		60		3.9±0.1
	250-425	20		2.8±0.0
		40		3.5±0.2
		60		2.7±0.1

Elongation at Break (%)	106-180	20	53.9±0.7	2.1±0.0
		40		1.6±0.0
		60		1.4±0.1
	250-425	20		2.0±0.1
		40		1.5±0.1
		60		1.2±0.1
Flexural Strength (MPa)	106-180	20		76.6±1.9
		40		56.9±2.3
		60		57.8±2.7
	250-425	20	74.3±0.8	66.8±7.9
		40		63.8±5.4
		60		42.5±3.5
Flexural Modulus (GPa)	106-180	20		4.3±0.3
		40		3.5±0.3
		60		4.8±0.2
	250-425	20	2.8±0.1	3.3±0.3
		40		4.3±0.2
		60		4.5±0.1
Impact Strength (kJ/m^2)	106-180	20		4.8±0.3
		40		4.6±0.3
		60		4.0± 0.2
	250-425	20	8.8±0.2	4.6±0.4
		40		5.0±05
		60		3.6±0.4
Glass Transition Temperature (T_g) (^oC)	106-180	20		81.3
		40		81.5
		60		82.7
	250-425	20	82	81.4
		40		82.1
		60		82.7

Heat Distortion Temperature (°C)	106-180	20	71.3±1.3	72.6±0.4
		40		73.8±0.2
		60		74.0±0.5
	250-425	20		73.4±0.2
		40		72.4±0.4
		60		77.5±0.8
Vicat Temperature (°C)	106-180	20	74.1±0.5	75.6±0.2
		40		82.5±0.4
		60		87.3±0.3
	250-425	20		76.5±0.3
		40		81.1±0.8
		60		83.0±0.4
Water absorption* (%)	106-180	20	0.32	3.56
		40		5.75
		60		8.41
	250-425	20		4.35
		40		7.14
		60		9.47

*The amounts of water absorption were measured after being submerged in water for 4 months

VITA

Miss Sawittree Mulalee was born in Udonthani, Thailand on September 14, 1983. She completed senior high school at Satrirachinuthit School of Udonthani, Thailand in 2001 and received Bachelor of engineering degree from the Department of Chemical Engineering, Faculty of Engineering, Thammasat University, Thailand in 2006. She began her study for Master degree in chemical engineering at Department of Chemical Engineering, Faculty of Engineering, Chulalongkorn University Bangkok, Thailand, in June 2006.

Part of this work was accepted for oral presentation at the Tenth Pacific Polymer Conference hold during December 4th-7th, 2007 at Kobe, Japan.