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THESIS

CELLULOSE-BASED FIBER FROM RICE STRAW REINFORCEMENT OF POLYLACTIC ACID BIOCOMPOSITES

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A Thesis Submitted in Partial Fulfillment of
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A series of biocomposites from combination of biodegradable poly(lactic acid) (PLA) matrix and biodegradable lignocellulosic rice straw varying from PLA/rice straw = 95:5, 90:10, 85:15 and 80:20 wt% were prepared. Two particle sizes of rice straw were used in this study which are STL (particle size ≥425 µm) and STP (particle size ≤250 µm). From the morphological studies by scanning electron microscopy (SEM) showed that both PLA/rice straw biocomposites still remain as single fiber and no voids around PLA matrix, but only STL rice straw pullout was oberved. These indicated that there is an adhesion between PLA matrix and STP rice straw but no adhesion between PLA matrix and STL rice straw. The impacts of the rice straw content and particle size on the mechanical properties of the biocomposites were investigated. It was found that tensile modulus and elongation at maximum load of both PLA/STL and PLA/STP biocomposites was increase, whereas the tensile strength of PLA/STL was slightly decrease and PLA/STP was increase by adding the rice straw. Thermal stabilities of both biocomposites were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimeter (DSC). Both PLA/STL (T_g = 60-62°C and T_m = 149-150°C) and PLA/STP (T_g = 60°C and T_m = 150-152°C) biocomposites had the same trend of glass transition (T_g) and melt temperature (T_m) as pure PLA (T_g = 61.9°C and T_m = 152°C) but slightly lower than melt temperature of pure STL (T_m = 173.5°C) and STP (T_m = 165.9°C) rice straw. In addition, an exothermic crystallization temperature (T_c) peak at about 106-116°C for both PLA/rice straw (STL and STP) showed that rice straw fibers can act as nucleating agent and attribute for the crystalline reorganization during heating on the PLA matrix. TGA thermogram showed that the PLA matrix degradation temperature and the corresponding onset temperature decrease when the rice straw content increase. Although the weight loss of both biocomposites decreases with an increase of both rice straw fiber content. However, the degradation temperatures of both PLA/rice straw biocomposites are in between the values of both PLA (345°C) and rice straw (STL= 286°C and STP = 311°C) components.

Student's signature Thesis Advisor's signature

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Thanainun Soonthornwatanasiri
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LIST OF ABBREVIATIONS

DSC = Differential Scanning Calorimeter

LCF = Lignocellulosic Filler

MPa = Mega Pascal

PLA = Poly Lactic Acid

SEM = Scanning Electron Microscope

STL = Rice Straw Long

STP = Rice Straw Powder

T_c = Crystallization temperature

T_g = Glass transition temperature

TGA = Thermal Gravimetric Analysis

T_m = Melting temperature

CELLULOSE-BASED FIBER FROM RICE STRAW REINFORCEMENT OF POLYLACTIC ACID BIOCOMPOSITES

INTRODUCTION

Over the last two decades, polymers from renewable resources or bio-based polymers have attracted an increasing amount of attention predominantly due to two major reasons: firstly environmental concerns, and secondly the realization those petroleum resources are finite. Generally, polymers from renewable resources can be classified into three groups: (1) natural polymers, such as starch, protein and cellulose; (2) synthetic polymers from natural monomers, such as polylactic acid (PLA); and (3) polymers from microbial fermentation, such as polyhydroxyalkanoate (PHA). A large numbers of these biodegradable polymers are commercially available. They show a large range of properties and at present, they can compete with non-biodegradable polymers in different industrial fields (e.g., packaging, agriculture, hygiene, and cutlery).

Biodegradable polymers are rarely used by themselves. Generally, fibers, such as carbon fibers and glass fibers are widely used to improve their mechanical properties. However, these fiber-reinforced polymeric composites cause environmental problems upon disposal. Reinforcements of biodegradable polymers by utilizing renewability, environmentally friendly, low cost and low density natural lignocellulosic fibers are required to obtain fully biodegradable composites together with to improve mechanical properties. Since both components are biodegradable, the biocomposites (biodegradable composites) are also expected to be biodegradable. A large number of biocomposites have been investigated in association with diverse lignocellulosic fibers from various origins such as bleached cellulose fibers, bamboo fibers or flax, oil palm, jute or ramie fibers.

Thailand has a total area of about 321 million rais or about 51.4 million hectares, of which about 133 million rais or 41% is under cultivation. The four main agricultural products are sugarcane, rice, cassava and palm oil. The annual production of these products from crop year 2000/2001 to 2005/2006 has been reported by the Office of Agricultural Economics of Thailand as shown in Table 1 (Office of Agricultural Economics, 2005). As the result, large quantities of agricultural crop residues are also left behind annually and are vastly underutilized as shown in Table 2. For example, in 2005/2006 crop year, from the crop-to-residues ratios (CRR) about 12,124,000 tons of rice straw residues which contains the top portion of the rice stem with three to five leaves were generated from the total 26,493,000 tons rice production in Thailand, of which about 9,457,000 tons was available unused rice straw residues. Rice straw is principally used as animal feed, and as raw material for fiber in paper industry. Burning is still the most common practice for rice straw disposal resulting in emissions to air that have a deleterious effect on air quality and human health (Gadde *et al*., 2009; DEDE, 2003). Utilization of rice straw as an alternate for reinforcements of biocomposites is not only reducing greenhouse gas emission from open burning the rice straw but also gaining monetary value of these agricultural wastes.

Table 1 Annual production of agricultural products (Unit: 1,000 tons per year).

Products	**00/01**	**01/02**	**02/03**	**03/04**	**04/05**	**05/06**
Sugarcane	49,563	60,013	74,263	70,101	67,900	63,621
Rice	25,844	26,523	26,057	26,841	24,977	26,493
Cassava	19,064	18,396	16,868	19,718	16,977	18,246
Palm oil	3,256	4,089	4,001	4,903	5,192	5,513

Table 2 CRR, SAF and biomass potential of four main agricultural products in 2005/2006.

Source	Production (1,000 tons)	Agricultural residues	CRR	Residues (1,000 tons)	SAF	Available unused residues (1,000 tons)
Sugarcane	63,621	Bagasse	0.29	18,450	0.01	185
		Trash	0.30	19,086	0.98	18,705
Rice	26,493	Rice husk	0.23	6,093	0.45	2,742
		Rice straw	0.45	12,124	0.78	9,457
Cassava	18,246	Cassava Rhizome	0.46	8,393	0.98	8,225
		Stalk	0.09	1,642	0.70	1,149
Palm oil	5,513	Fiber	0.15	827	0.13	108
		EFB	0.25	1,378	0.58	799
		Shell	0.05	275	0.04	11

CRR = Crop-to-residue ratios, SAF = Surplus Availability Factor,
EFB = Empty Fruit Bunches

Among biodegradable polymers, polylactic acid (PLA) has a great potential to replace petroleum-based plastics because of its high stiffness and strength. Thailand is the world’s top producer and exporter of tapioca, derived from cassava, and its second biggest sugar exporter, two crops in demand for the production of lactic acid, the precursor for production of polylactic acid. The world market for lactic acid is projected to reach 259 thousand metric tons by the year 2012. Given the low toxicity and biodegradability advantages of lactic acid as a raw material, demand for lactic acid in biodegradable polymers is forecast to post healthy gains. Biodegradable plastics end-use market growth is the strongest in the North America, Japan, and Europe, setting the pace of growth with a robust CAGR (Compound Annual Growth Rate) in excess of 6% over the period 2011 through 2015, for example, consumption in the biodegradable plastics end-use industry in Europe is projected to reach 6.7 thousand metric tons by the year 2015. As Thailand is an agricultural country, it is a potential base to produce biomass plastic material and this would be a new business opportunity for the country. Development of new technologies, emergence of new end-use applications, and evolution of new markets are all expected to offer opportunities for future growth.

The objectives of this thesis are focused on the processing and on the characterization of biocomposites based on biodegradable polyester, polylactic acid (PLA) and rice straw lignocellulosic fibers (LCF) with the goal to obtain fully biodegradable composites together with to improve mechanical properties. Three main approaches are used to investigate the “fiber-matrix” interaction; (i) the mechanical properties through the evolution of the modulus with the fibers content, (ii) the glass temperature shift with the increase of fiber content and then (iii) the morphology of the composites.

OBJECTIVES

1. To process lignocellulosic-based fiber from rice straw reinforced polylactic acid biocomposites using two-roll mill with two particle sizes: STL, particle size ≥ 425 µm and STP, particle size ≤250 µm.

2. To characterize the mechanical properties of the obtained biocomposites: tensile strength, elongation, modulus, hardness etc.

3. To characterize the thermal properties of the obtained biocomposites by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

4. To study the morphology of the biocomposites by scanning electron microscopy (SEM).

LITERATURE REVIEW

Fiber reinforced polymeric composites have been used for a variety of structural applications because of their high specific strength and modulus compared to metals. Initially developed for aerospace industry, high performance or advanced composites are now found in applications from automotive parts to circuit boards, and from building materials to specialty sporting goods (Bledzki and Gassan, 1999; Netravali and Chabba, 2003). The push now is to use composites in place of common plastics in consumer products to improve performance and reduce weight cost. Most composites currently available on the market are designed with long term durability in mind and are made from nondegradable polymeric resins, such as epoxies and polyurethane, and high strength fibers, such as graphite, aramids and glass. Since many of these polymeric resins and fibers are derived from nondegradable, mostly petroleum-based materials, once discarded they do not degrade for several decades under normal environmental conditions and end up in landfills while some are incinerated after use. In addition, landfills are decreasing in number, making less space available to discard waste. As a result, disposal of composites after their intended life is already becoming ecological and environmental problems. Although there are some efforts to recycle and/or reuse those composites, it is found that both of these disposal alternatives are expensive and wasteful because most composites are generally made from two dissimilar materials, as a consequent they cannot be easily recycled or reused.

In recent years, the ever-growing worldwide litter problem has raised environmental consciousness among consumers, manufactures, and governments. The growing global environmental awareness and societal concern, high rate of depletion of petroleum resources, concepts of sustainability, and new environmental regulations have together triggered the search for new products and processes that are compatible with the environment. It is estimated that we currently consuming petroleum at an “unsustainable” rate, about 100,000 times faster than nature can create it. To alleviate these problems, governments in many countries have established laws to encourage the use of recycled and/or bio-based “green” products.

Composite materials are no exception to this paradigm. For these reasons, environmental friendly, fully biodegradable reinforced plastics or biocomposites from natural fibers and biodegradable polymers will play a major role in greening the products of the future (Yu *et al.*, 2006).

Biodegradable and environmental friendly plant based lignocellulosic fibers are the most widely used for reinforcing (or filling) polymers (plastics). Natural fibers (lignocellulosics) are degraded by biological organisms since they can recognize the carbohydrate polymers in cell wall. Lignocellulosics exposed outdoors undergo photochemical degradation caused by ultraviolet light. The availability of inexpensive plant-based fibers in every part of the world has, in part, fueled their use in the past few years (Table 3). These renewable fibers present strong variations according to the botanical origin and offer several other advantages as well. They are nonabrasive to processing equipment, can be incinerated, are CO_2 neutral (when burned), and the hollow tabular structure also reduces their bulk density, making them lightweight.

Table 3 World production of natural fibers, annual average (2003-2005).

Natural fibers	Thousand tons
Cotton	23,733
Jute	2,664
Flax fiber	777
Kenaf	500
Coir	450
Sisal, Henequen, and other Agaves	299
Ramie	249
Abaca	87
Hemp	68

Source: FAO Statistics, December 2006.

Natural fibers are subdivided based on their origins, coming from plants, animals (silk, wool) or minerals (asbestos). Generally, plant or vegetable fibers are used. Plants fibers may include seed hair, fiber sheafs of dicotylic plants or vessel sheafs of monocotylic plants or bast fibers and hard fibers or leaf fibers, depending upon the sources. Some examples are cotton (seed hairs), ramie, jute, and flax (bast fibers), and sisal and abaca (leaf fibers). Of these fibers, jute, ramie, flax and sisal are the most commonly used fibers for polymer composites. Natural fibers in the form of wood flour have also been often used for preparation of natural fiber composites. Fibers obtained from the plant stems or leaves, are renewable annually as compared to wood, which takes 20-25 years to grow before it can be cut and used. Some plants such as bamboo grow so fast that they can be harvested every few months. As a result, their supply could be virtually endless. The mechanical properties of some natural fibers are presented in Table 4 (Bledzki and Gassan, 1999; Saheb and Jog, 1999). The tensile strength of glass fibers (graphite or aramids such as Kevlar fibers used in advanced composites), is substantially higher than that of natural fibers, however, when the specific modulus of natural fibers (modulus/specific gravity) is considered, the natural fibers show values that are comparable to or better than those of glass fibers. With their environmental friendly character and some techno-economical advantages, these fibers motivate more and more different industrial sectors to replace common fiberglass since these higher specific properties are one of the major advantages of using natural fiber composites for applications wherein the desired properties also include weight reduction.

Table 4 Mechanical properties of natural fibers as compared to conventional reinforced fibers.

Fiber type	**Density (g/cm^3)**	**Young's modulus (GPa)**	**Specific modulus (Young's modulus/ density)**
E-Glass	2.55	73	29
Hemp	1.48	70	47
Flax	1.4	60-80	43-57
Jute	1.46	10-30	7-21
Sisal	1.33	38	29
Coir	1.25	6	5
Cotton	1.51	12	8

Primarily, fibers contained cellulose, hemicelluloses, pectin, and lignin (Figure 1 and Table 5). Cellulose is derived from D-glucose units, which condense through β(1→4)-glycosidic bonds and it can be broken down chemically into its glucose units by treating it with concentrated acids at high temperature. Cellulose is a straight chain polymer, no coiling or branching occurs, and the molecule adopts an extended and rather stiff rod-like conformation, aided by the equatorial conformation of the glucose residues. The multiple hydroxyl groups on the glucose from one chain form hydrogen bonds with oxygen molecules on the same or on a neighbor chain, holding the chains firmly together side-by-side and forming microfibrils with high tensile strength (Figure 2). This strength is important in cell walls, where the microfibrils are meshed into a carbohydrate matrix, conferring rigidity to plant cells.

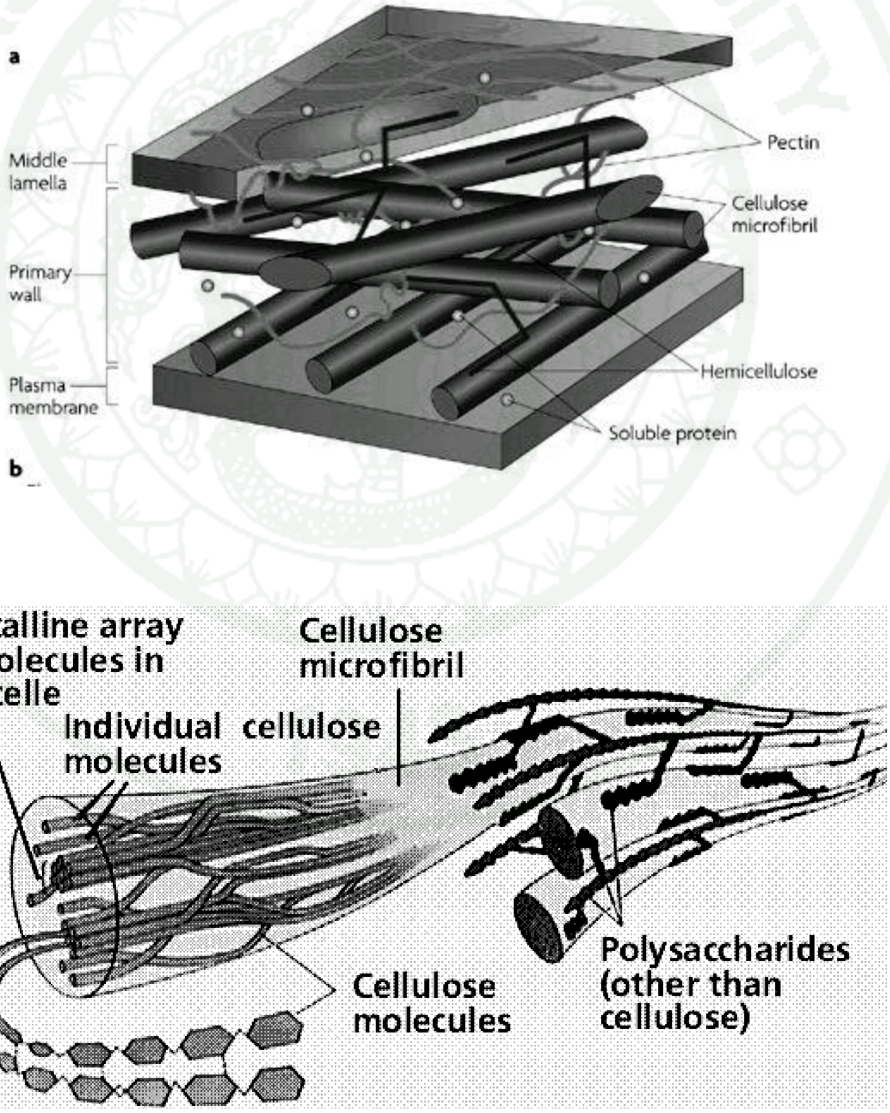
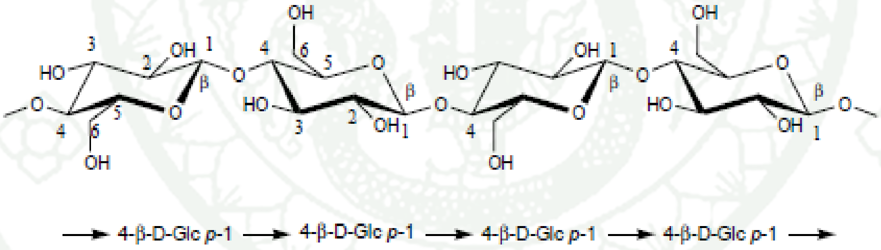


Figure 1 Image of arrangement of cellulose microfibrils of natural fiber.

Table 5 Chemical composition (wt%) of vegetable fibers.

Fiber	Cellulose	Hemicellulose	Pectin	Lignin	Ash
Bast fibers					
Flax	71	19	2	2	1-2
Hemp	75	18	1	4	1-2
Jute	72	13	>1	13	8
Ramie	76	15	2	1	5
Leaf fibers					
Abaca	70	22	1	6	1
Sisal	73	13	1	11	7
Seed-hair fibers					
Cotton	93	3	3	-	1
Wheat straw	51	26	-	16	7
Lignocellulosic fillers*					
LCF$_{0\text{-}1}$	58	8	-	31	3
LCF$_{0\text{-}0.1}$	56	7	-	31	6
LCF$_{0.1\text{-}1}$	59	8	-	31	2



cellulose

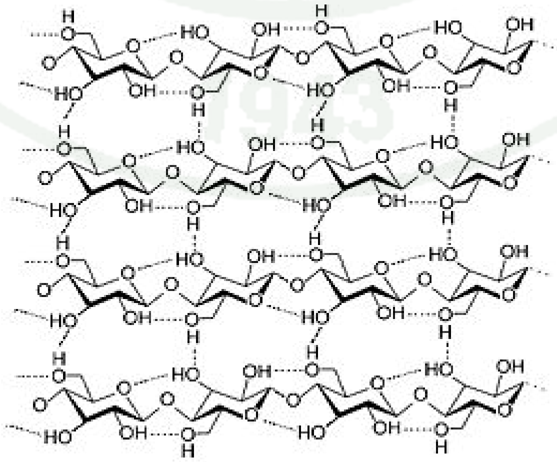


Figure 2 A strand of cellulose showing the hydrogen bonds (dashed) within and between cellulose molecules.

While cellulose is crystalline, strong, and resistant to hydrolysis, hemicellulose has a random, amorphous structure with little strength (Table 6). It is easily hydrolyzed by dilute acid or base as well as myriad hemicellulase enzymes. Hemicellulose is classified as a mixed glycan polymer of several sugars including xylose, arabinose, glucose, mannose and galactose. The major hemicelluloses in coniferous wood (softwood) are galactoglucomannan or glucomannan and arabinoglucuronoxylan or xylan. Other softwood hemicelluloses are arabinogalactan, xyloglucan and other glucans. Galactoglucomannan backbone is a linear or slightly branched chain of β(1→4)-glycosidic bonds of D-mannopyranose and D-glucopyranose units; and of α(1→6)-bonds of D-galactopyrasnose residues as single unit on the side chains (Figure 3). Galactoglucomannan can be roughly divided into two types: one with a low galactose content, sometimes referred to simply as glucomannan; and the other with a high galactose content. The ratio of galactose to glucose to mannose are 0.1-0.2:1:3-4 and 1:1:3 in the two types respectively. The hydroxyl groups at position C2 and C3 in the backbone units are partly substituted by O-acetyl groups, on average one group per 3-4 hexose units. Softwood arabinoglucuronoxylan (referred to as xylan) has a backbone of β(1→4)-glycosidic bonds of xylopyranose units. Single unit side chains are 4-O-methyl-D-glucoronic acid units attached by α(1→2)-bonds, on average one unit per 5-6 xylose units (Figure 3). Some branching of the otherwise linear backbone at C2 of the xylose units has been reported. No substitution by acetyl groups has been found. Hardwood also contains glucomannan with a backbone of β(1→4)-glycosidic bonds of D-mannopyranose and D-glucopyranose units without side chain units. The ratio of mannose to glucose units is 1:1 to 2.3:1 (Figure 4).

Pectin is a polysaccharide that acts as a cementing material in the cell walls of all plant tissues. Pectin is the methylated ester of polygalacturonic acid, which consists of chains of 300 to 1000 galacturonic acid units joined with α (1→4)-linkages (Figure 5). The degree of esterification (DE) or methylation affects the gelling properties of pectin. The structure shown here has three methyl ester forms (-$COOCH_3$) for every two carboxyl groups (-COOH), hence it has a 60% degree of esterification, normally called a DE-60 pectin. Commercially pectins are categorised according to their methoxy content and whether they from gels quickly or slowly. Roughly speaking pectins can be split in to high methoxy pectins (>50% esterified) and low methoxy pectins (<50% esterified).

Table 6 Principal structural difference between cellulose and hemicelluloses.

	Cellulose	**Hemicellulose**
Monomer	Pure glucose	Mixed sugars
Polymer chain length	Long (5µm)	Short
M.W.	High (10000 units)	Low (hundred units)
Polymer topology	Linear	Branched
Side groups substitution	No substitution	Substitution on C2, C3, and C6
Polymer morphology	Crystalline + amorphous	Amorphous
Solubility	Low	High
Reactivity	Less reactive	More reactive
Hydrolysis	Partial	Readily (susceptible)

Lignin is a complex chemical compound most commonly derived from wood, and an integral part of the secondary cell walls of plants. It is one of the most abundant organic polymers on Earth, exceeded only by cellulose, employing 30% of non-fossil organic carbon and constituting from a quarter to a third of the dry mass of wood. Lignin is composed of three monomers, each a carbon ring with different methoxy group configuration and a 3-carbon tail: *p*-coumaryl alcohol, coniferyl alcohol, and sinapyl alcohol (Figure 6). These subunits polymerize into lignin in the form of the phenylpropanoids: *p*-hydroxyphenyl (H), guaiacyl (G), and syringal (S) respectively (Figure 7). The proportions of phenylpropanoids differ with the botanical origin of the lignin such as many grasses have mostly G, while some palms have mainly S. The phenylpropaniod units are attached to each other by a series of C-O-C and C-C bonds such as β-O-4, β-5, α-O-4, β-β, and 5-5 (Figures 8-9). These lignin molecules fill the space between cellulose, hemicellulose and pectins as the plant ages and binds with the hemicellulose (Figure 10). Lignin coating the cellulose allows water to move up the plant stem without leakage but also reduces digestion of the cellulose in the rumen. Gymnosperms have a lignin that consists almost entirely of G with small quantities of H. That of dicotyledonous angiosperms is more often than not a mixture of G and S (with very little H), and monocotyledonous lignin is a mixture of all three. Many grasses have mostly G, while some palms have mainly S. All lignins contain small amounts of incomplete or modified monolignols, and other monomers are prominent in non-woody plants.

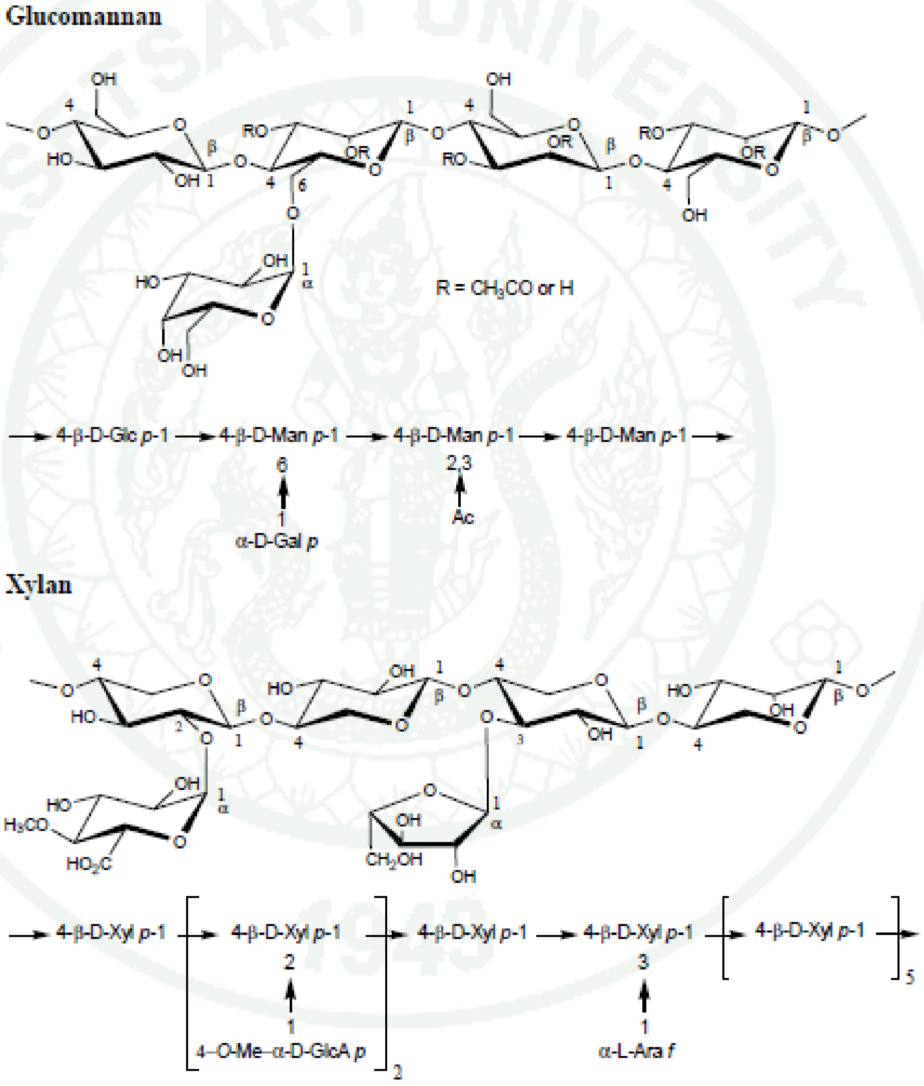


Figure 3 Structure of softwood hemicellulose.

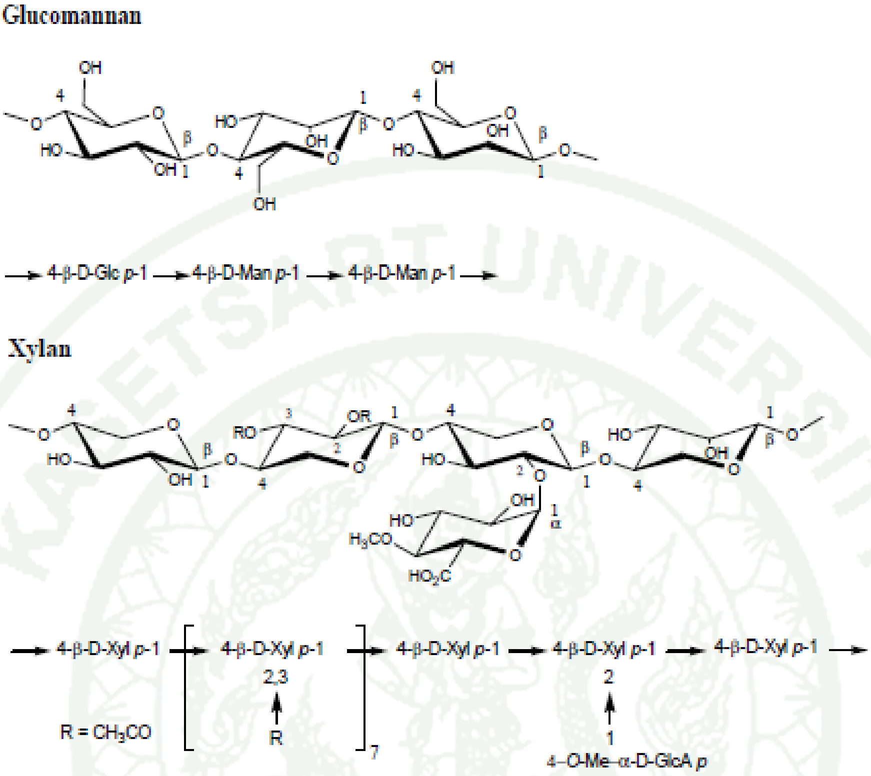


Figure 4 Structure of hardwood hemicellulose.

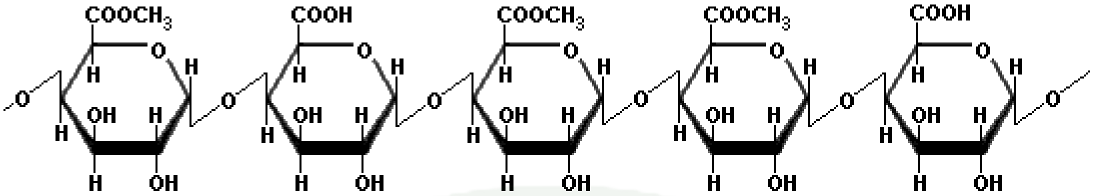


Figure 5 Structure of DE-60 pectin.

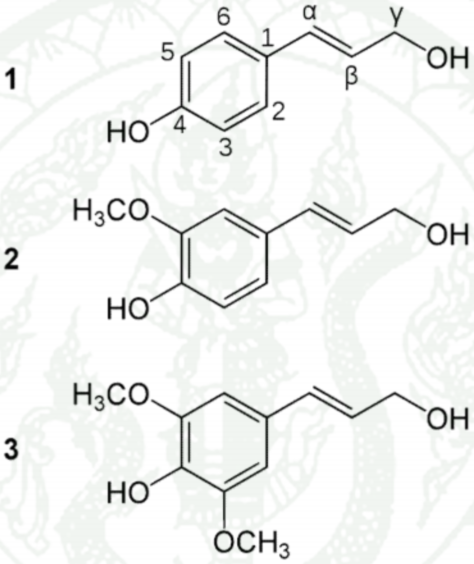


Figure 6 The three common monolignols monomers (1) *p*-coumaryl alcohol, (2) coniferyl alcohol and (3) sinapyl alcohol.

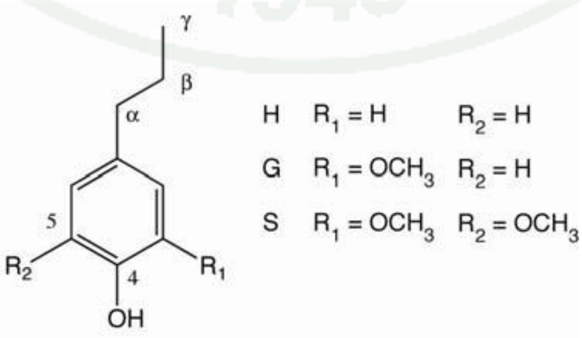


Figure 7 Lignin phenylpropanoid units.

Hence, natural fibers themselves are cellulose fiber reinforced materials as they consist of microfibrils in an amorphous matrix of lignin and hemicelluloses. These fibers consist of several fibrils that run all along the length of the fiber. The hydrogen bonds and other linkages provided the necessary strength and stiffness to the fibers. The chemical composition of natural fibers varies depending upon the types of the fiber. The properties of each constituent contribute to the overall properties of the fiber. Hemicelluloses is responsible for the biodegradation, moisture absorption, and thermal degradation of the fiber as it shows least resistance whereas lignin is thermally stable but is responsible for UV degradation. The percentage composition of each of these components varies for different fibers. Generally, the fibers contain 60-80% cellulose, 5-20% lignin, and up to 20% moisture.

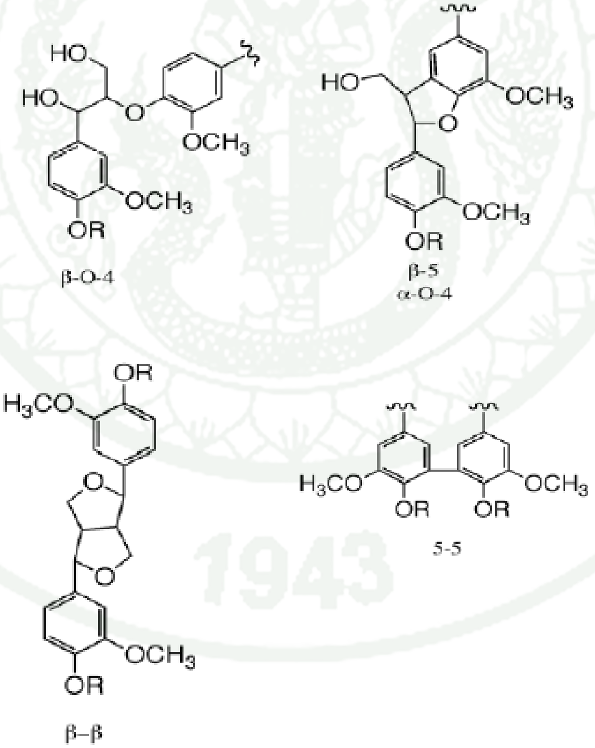


Figure 8 Illustrations of typical softwood lignin structure: β-O-4, β-5, α-O-4, β- β, and 5-5.

Properties of the fibers, the aspect ratio of the fibers (the ratio of length to diameter of a fiber), and the fiber-matrix interface govern the properties of the composites. The surface adhesion between the fiber and the polymer plays an important role in the transmission of the stress from the matrix to the fiber and thus contributes toward the performance of the composite. Another important aspect is the thermal stability of these fibers. These fibers are lignocellulosic and consist of mainly lignin, hemicelluloses, and cellulose. The cell walls of the fibers undergo pyrolysis with increasing processing temperature and contribute to char formation. These charred layers help to insulate the lignocellulosic from further thermal degradation. Since most thermoplastics are processed at high temperature, the thermal stability of the fibers at processing temperatures is important. Thus the key issues in development of natural reinforced composites are (i) thermal stability of the fibers, (ii) surface adhesion characteristics of the fibers, and (iii) dispersion of the fibers in the case of thermoplastic composites.

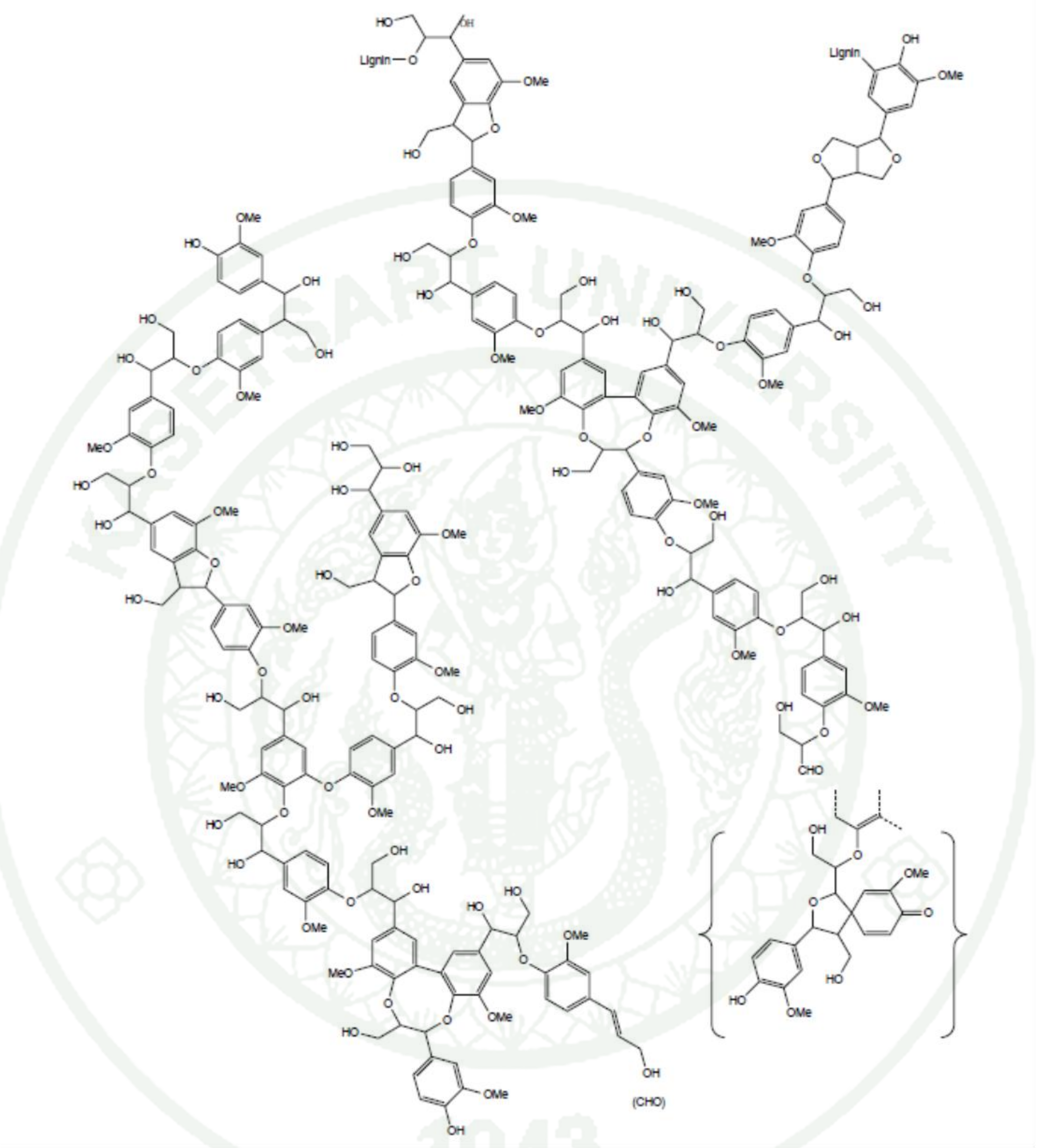
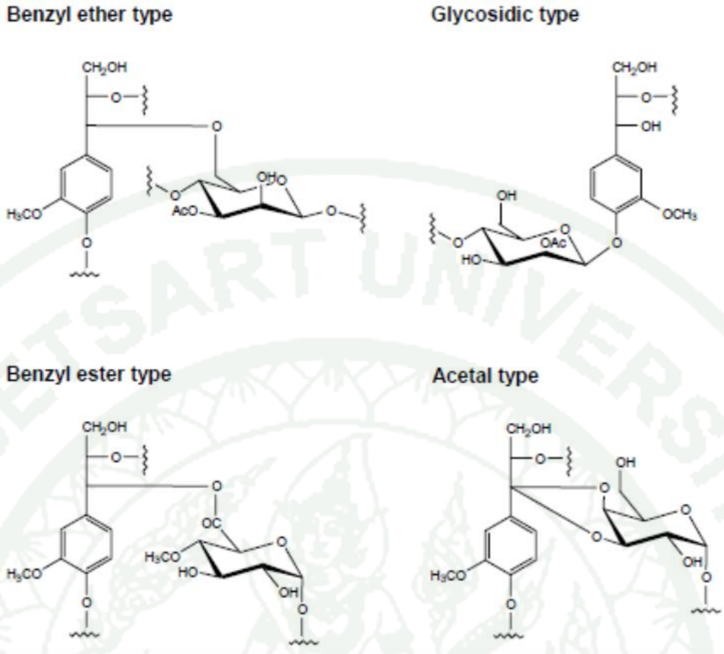


Figure 9 Schematic structure of softwood lignin.



Benzyl ether type

Glycosidic type

Benzyl ester type

Acetal type

Figure 10 Proposed structures of the different bonds between lignin and hemicelluloses.

As already mentioned, natural fibers are complex mixtures of organic materials (cellulose, hemicelluloses, pectin and lignin) and as a result, thermal treatment leads to a variety of physical and chemical changes. The thermal stability of natural fibers can be studied by thermogravimetric analysis (TGA). A typical TGA for jute fibers is shown in Figure 11. As can be seen from the figure, the natural fibers start degrading at about 240^{o}C. The thermal degradation of lignocellulosic materials has been reviewed (Nguyen *et al.*, 1981a and 1981b). Thermal degradation of natural fibers is a two-stage process, one in the temperature range 220-280^{o}C and another in the range 280-300^{o}C. The low temperature degradation process is associated with degradation of hemicelluloses whereas the high temperature process is due to lignin. The apparent activation energies for the two processes are about 28 and 35 kcal/mol, which correspond to the degradation of hemicelluloses and lignin, respectively. The degradation of natural fibers is a crucial aspect in the development of natural fiber composites and thus has bearing on the curing temperature in the case of thermosets and extrusion temperature in thermoplastic composites.

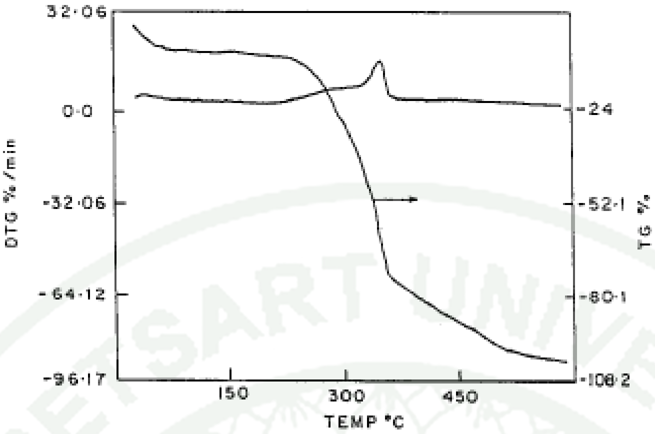


Figure 11 Typical TGA thermogram of cellulose fiber (jute powder).

The degradation of natural fibers leads to poor organoleptic properties such as odor and color and also deterioration of their mechanical properties. The thermal stability of jute fibers at temperature ranging from 150-300°C both in air and under vacuum was studied (Sridhar *et al.*, 1982). The degradation was monitored by measuring the weight loss, change in chemical structure, and mechanical properties. It was observed that heating under vacuum at 300°C for 2h resulted in 60% decrease in the tensile strength, which was ascribed to the depolymerization and oxidation of fibers. In actual practice, processing is carried out under atmospheric conditions and the possibility of thermal degradation leading to inferior mechanical properties cannot be ruled out.

The effect of thermal degradation on the mechanical properties of wood/polymer composites was studied by Myers *et al.* (1991) and Gonzalez and Myers (1993). The temperature range of study was form 220 to 260°C and the exposure time was varied from 4 to 4096 min. It was observed that although, in general, the mechanical properties deteriorate, as a result of thermal degradation of wood flour, toughness and bending strength were more affected. It was also pointed out that the changes in the surface chemistry might cause changes in the wood/polymer bonding that is responsible for the inferior properties of the composites. In another study of polypropylene/wood flour composites, similar loss in properties has been reported after extrusion at 250°C. The thermal degradation of fibers also results in production of volatiles at processing temperatures >200^{o}C. This can lead to porous polymer products with lower densities and inferior mechanical properties.

The matrix phase also plays a crucial role in the performance of polymer composites. Both thermosets and thermoplastics are attractive as matrix materials for composites. In thermoset composites, formulation is complex because a large number of components are involved such as base resin, curing agents, catalysts, flowing agents, and hardeners. These composites materials are chemically cured to a highly cross-linked, three-dimensional network structure. These cross-linked structures are highly solvent resistant, tough, and creep resistant. The fiber loading can be as high as 80% and because of the alignment of fibers, the enhancement in the properties is remarkable.

Thermoplastics offer many advantages over thermoset polymers. One of the advantages of thermoplastic matrix composites is their low processing costs. Another is design flexibility and ease of molding complex parts. Simple methods such as extrusion and injection molding are used for processing of these composites. In thermoplastics most of the work reported so far deals with polymers such as polyethylene, polypropylene, polystyrene and poly(vinyl chloride). This is mainly because the processing temperature is restricted to temperature between 200^{o}C to avoid thermal degradation of the natural fibers. For thermoplastic composites, the dispersion of the fibers in the composites is also an important parameter to achieve consistency in the product.Thermoplastic composites are flexible and tough and exhibit good mechanical properties. However, the percent loading is limited by the process ability of the composites. The fiber orientation in the composites is random and accordingly the property modification is not as high as is observed in the thermoset composites. Many times, it is observed that these fibers do not function as an effective reinforcement system due to poor adhesion at the fiber-matrix interface. Cellulose fibers also tend to aggregate and therefore the fibers do not disperse well in a hydrophobic polymer matrix and thus pose difficulties in achieving an uniform distribution of fiber in the matrix due to strong interfiber hydrogen bonding, which hold the fibers together. The surface characteristics of the reinforcing fiber are important in the transferring of stress from the matrix to the fiber. The pretreatment of the fiber with suitable additives prior to processing leads to good dispersion and significantly improved mechanical properties of the composites.

The properties of the composites are also influenced by the processing parameters in the case of thermoplastic composites. Takase and Shiraishi (1989) had reported the effect of processing parameters such as mixing time, rpm, and temperature in compounding polypropylene/wood composites. It was observed that tensile strength varied nonlinearly with rpm, mixing temperature, and time, indicating that fiber length and dispersion need to be optimum to obtain enhanced properties.

The mechanical properties of these thermoplastic composites depend on a number of parameters such as volume fraction of the fibers, fiber aspect ratio, fiber-matrix adhesion, stress transfer at the interface, and orientation. Most of the studies on the natural fiber composites involve study of mechanical properties as a function of fiber content, effect of various treatments of fibers, and the use of external coupling agents. Other aspects include the prediction of modulus and strength using some well-established models for two-phase systems and comparison with experimental data. Both the matrix and fiber properties are important in improving mechanical properties of the composites. The tensile strength is more sensitive to the matrix properties, whereas the modulus is dependent on the fiber properties. To improve the tensile strength, a strong interface, low stress concentration, fiber orientation is required whereas fiber concentration, fiber wetting in the matrix phase, and high fiber aspect ratio determine tensile modulus. The aspect ratio is very important for determining the fracture properties. In short-fiber reinforced composites, there exists a critical fiber length that is required to develop its full stressed condition in the polymer matrix. Fiber lengths shorter than this critical length lead to failure due to debonding at the interface a lower load. On the other hand, for fiber lengths greater than the critical length, the fiber is stressed under applied load and thus results in a higher strength of the composites. For good impact strength, an optimum bonding level is necessary. The degree of adhesion, fiber pullout, and a mechanism to absorb energy are some of the parameters that can influence the impact strength of a short fiber filled composites. The properties mostly vary with composites as per the rule of mixtures and increase linearly with composites. However, it has been observed that this linear dependence on percentage of the fiber content does not hold at high percentage (>80%) of the fiber, probably due to lack of wetting of the fiber surface by the polymer.

Plenty of examples can be found of the use of plant natural fibers for reinforcing non-biodegradable petroleum based thermoplastic polymers (Eichhorn *et al*., 2001) such as polypropylene (PP) (Table 7); high, medium, and low density polyethylene (HDPE, MDPE, LDPE); nylon; polyvinylchloride (PVC); and polyesters.

Table 7 Tensile strength and Young's modulus of sisal, flax, and glass-fiber reinforced polypropylene (PP) composites with a fiber content of 40 wt%.

Materials	**Tensile strength (MPa)**	**Young's modulus (MPa)**
PP-wood flour	19	2500
PP-sisal non-woven	38	3600
PP-sisal non-woven with surface treatment	55	4800
PP-flax non-woven	47	5100
PP-flax non-woven with surface treatment	67	6700
PP-glass non-woven	100	6000

Kuruvilla *et al*. (1993) studied the tensile properties of short sisal fibers (Agave-Veracruz) as reinforcements in low-density polyethylene (LDPE). The influence of the processing method and the effect of the fiber content, fiber length, and orientation on tensile properties of the composites were evaluated. The fiber damage that normally occurs during blending of fiber and LDPE by the meltmixing method is avoided by adopting a solution-mixing procedure. The tensile properties of the composites thus prepared showed a gradual increase with fiber content. The properties also increased with fiber length, to a maximum at the fiber of about 6 mm. Unidirectional alignment of the short fibers achieved by an extrusion process enhanced the tensile strength and modulus of the composites along the axis of fiber alignment by more than twofold compared to randomly oriented fiber composites.

Hornsby *et al*. (1997) reported the preparation and properties of polypropylene composites reinforced with wheat and flax straw fibers. Analysis of composite microstructures to determine the nature and consequences of fiber damage induced during melt-processing operations, fiber orientation occurring in moldings, and possible interfacial adhesion between the matrix and fibers and mechanical properties were discussed. Compared to unfilled polypropylene, addition of flax and wheat straw caused a significant increase in tensile modulus, particularly, in the case of flax fibers, which also gave higher tensile yield strength and Charpy toughness, despite a lack of interfacial bonding. Tensile strength was increased further through inclusion of 5% by weight of maleic anhydride-modified polypropylene, which was shown to promote adhesion between fibers and matrix.

Composites made of cellulose whiskers embedded into a latex matrix were presented by Favier *et al*. (1997). Results showed quite surprising elastic properties due to the fact that a continuous skeleton of hard whiskers was formed with some tight interactions. It also showed that the classical homogenization techniques could not applicable here, in particular because those techniques do not make any difference whether or not tight interactions are considered. The percolation problem was investigated by means of numerical simulations to quantify the percolation threshold and the mechanical properties are obtained by means of the Percolation Theory and a simple Voigt model.

Composites reinforced with cellulose based fibers were reviewed by Bledzki and Gassan in 1999. This review article introduces possible applications of material groups concerning natural and man-made cellulose fiber reinforced plastics. The physical properties of natural fibers were mainly determined by the chemical and physical composition, such as the structure of fibers, cellulose content, angle of fibrils, cross-section, and by the degree of polymerization. Only a few characteristic values, but especially the specific mechanical properties, can reach comparable values of traditional reinforcing fibers. The application of natural fibers as reinforcements in composite materials requires, just as for glass-fiber reinforced composites, a strong adhesion between the fiber and the matrix, regardless of whether a traditional polymer (thermoplastics or thermosets) matrix was used. The mechanical and other physical properties of the composite are generally dependent on the fiber content. The processing conditions play, next to the mechanical properties of natural fibers, an important role for the industrial use of these materials. The results showed that natural fibers can be processed with the already commonly applied methods: glass mat thermoplastic matrix (GMT), sheet molding compound (SMC) or bulk molding compound (BMC). For the processing of thermoplastics reinforced with natural fibers, new methods so called extrusion press processing (express processing) are of increasing importance. Natural fibers seem to have little resistance towards environmental influences. This can be recognized in the composite and can be advantageously utilized for the development of biological degradable composites with good physical properties.

Jiang *et al*. (2003) studied the mechanical properties of poly(vinyl chloride)(PVC)/wood flour/glass fiber hybrid composites. Short glass fibers were added to PVC/wood flour composites as reinforced agents. Unnotched and notched impact strength of PVC/wood flour/glass fiber hybrid composites could be increased significantly without losing flexural properties by adding type L glass fibers and over 40% of PVC. There was no such improvement when using type S glass fiber. The impact strength of hybrid composites increased along with the increment of the type L glass fiber content at a 50% PVC content. At high PVC contents, impact fracture surfaces were characterized by wood particle, glass fiber breakage and pullout, whereas interfacial debonding was the dominant fracture mode at higher filler concentrations. The significant in impact strength of hybrid composites was attributed to the formation of the three–dimensional network glass fiber architecture between type L glass fibers and wood flour.

Okubo *et al*. (2004) presented the development of composites for ecological purposes (Eco-composites) using bamboo fibers for fabrication of Bamboo Fiber Eco-Composites (BFEC). The steam explosion technique was applied to extract bamboo fibers from raw bamboo trees. The experiment results showed that bamboo fibers (bundles) had a sufficient specific strength, which is equivalent to that of conventional glass fibers. The tensile strength and modulus of PP based composites using steam-exploded fibers increased about 15 to 30%, respectively, due to well impregnation and the reduction of the number of voids, compared to the composite using fibers that are mechanically extracted. The steam explosion technique is an effective method to extract bamboo fibers for reinforcing thermoplastics.

Yao *et al*. (2008) prepared composite panels using virgin and recycled high-density polyethylene (VHDPE and RHDPE) and five types of natural fibers including four rice straw components (i.e., rice husk, rice straw leaf, rice straw stem, and whole rice straw) and wood fiber as control by melt compounding and compression molding. Fiber characteristics and the influences of fiber type and loading rate on HDPE crystallization behavior and composite mechanical properties were investigated. Fiber length and aspect ratio distributions for all fibers followed a lognormal distribution after milling with two parameters defining the curve location (i.e., mean fiber length/aspect ratio) and shape (i.e., mean fiber length/aspect ratio distribution). For both VHDPE and RHDPE, rice straw fiber systems had comparable mechanical properties with those of wood composites. Increase in fiber loading led to increase moduli and decreased tensile and impact strength. Composite panels with rice husk had the smallest storage moduli, but their impact strength was comparable or better than that of other straw fibers. Very little difference in mechanical properties existed among leaf, stem, and whole straw fibers. The particular recycled HDPE resin and its composites had significantly better moduli and strength properties compared to the virgin HDPE systems due to additives used during initial processing. X-ray diffraction experiments showed that introducing fiber to HDPE matrix did not change characteristic peak position, but the fiber increased crystalline thickness of HDPE system. Differential scanning calorimetry experiments showed that VHDPE had significantly larger peak heat flow during cooling run than the RHDPE, indicating higher crystallization rates for VHDPE. The use of fiber in both resin systems led to the reduced peak heat flow rate. The study showed that rice straw fibers can work well with both VHDPE and RHDPE as reinforcing filler.

Since these plant natural fibers reinforcing non-biodegradable petroleum based thermoplastic composites combine nondegradable resins with degraded fibers, at the end of life they can neither return to an industrial metabolism nor to a natural metabolism. Unfortunately, they cannot be food stock for neither system. They can only be downcycled because of property degradation in reprocessing or incinerated to recover to energy value.

As the result, significant research efforts are being spent in developing a new class of fully biodegradable composites or biocomposites (Figure 12). A variety of natural and synthetic biodegradable resins are available for use in such biocomposites (Netravali and Chabba, 2003) (Table 8). For examples, agro-polymers obtained from biomass by fractionation (e.g., polysaccharides), polyesters obtained by fermentation from biomass or from genetically modified plants (e.g., polyhydoxyalkanoate: PHA), polymers synthesized from monomers obtained from biomass (e.g., poly(lactic acid): PLA), and polyesters totally synthesized by petrochemical process or from fossil resources (e.g., poly(caprolactone): PCL, polyesteramide: PEA, aliphatic or aromatic copolyesters). A large number of these biodegradable polymers are commercially available. They show a large range of properties and at present, they can compete with non-biodegradable polymers in different industrial fields (e.g., packaing, agriculture, hygiene and cutlery). Most of these resins degrade through enzymatic reactions when exposed to compost environment. Many will also degrade in moist/wet outdoor environments through similar microbial/bacterial attack.

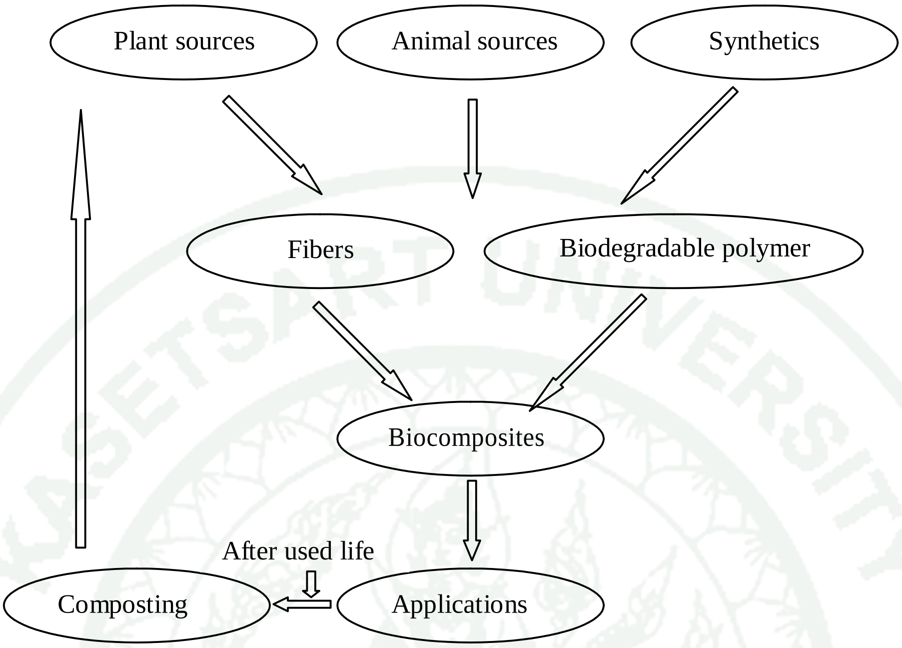


Figure 12 Typical life cycle of biocomposites.

A large number of papers in biocomposites have been published. A few publications are based on agropolymer matrices, such as plasticized starch or proteins, and on chemically modified agropolymers (e.g., cellulose acetate). (Avérous *et al.*, 2001; Mohanty *et al.*, 2002; Avérous, 2004; Avérous and Boquillon, 2004). Avérous *et al.* focused on the interactions between leafwood cellulose fibers and a plasticized wheat starch matrix. Different plasticized starch (TPS)-based composites have been elaborated. LDPE-based composites are used as reference materials (no fiber-matrix interactions). After extrusion and injection molding, the properties of different composites are analyzed. Mechanical properties (tensile tests), thermo mechanical properties (DMTA) and morphology (SEM) are evaluated. DMTA analysis shows for TPS composites a strong evolution of the main relaxation temperature, which can be linked to the existence of cellulose-starch interactions resulting in a decrease of starch chain mobility. This phenomenon is consistent with the evolution of mechanical behavior. SEM observations correlate this hypothesis. After cryogenic fracture, TPS composites present fibers, which are embedded in the matrix. On the composites, reinforcing effects have been observed according to the evolution of fiber length and fiber content.

Table 8 Biodegradable polymers.

Natural	**Synthetic**
1. Polysaccharides	1. Poly(amides)
- Starch	2. Poly(anhydrides)
- Cellulose	3. Poly(amide-enamines)
- Chitin	4. Poly(vinyl alcohol)
- Pullulan	5. Poly(ethylene-co-vinyl alcohol)
- Levan	6. Poly(vinyl acetate)
- Konjac	7. Polyesters
- Elsinan	- Poly(glycolic acid)
2. Proteins	- Poly(lactic acid)
- Collagen/Gelatin	- Poly(caprolactone)
- Casein, albumin, fibrogen, silk elastins	- Poly(ortho esters)
- Protein from grains	8. Poly(ethylene oxide)
3. Polyesters	9. Some poly(urethane)
- Polyhydroxyalkonates	10. Poly(phosphazines)
4. Other polymers	11. Poly(imino carbomates)
- Lignin	12. Some poly(acrylates)
- Lipids	
- Shellac	
- Natural rubber	

A great number of biocomposites are focused on biopolyesters such as polyhydroxyalkanoate (PHA) and polycaprolactone (PCL), which are numerous and largely available, in association with diverse lignocellulose fibers, from various origins. For instance, Bourban *et al*. (1997) developed biodegradable composite consisting of a degradable continuous cellulosic fiber and a degradable polymer matrix of poly (3-hydroxybutyrate)-*co*-poly(3-hydroxyvalerate). The composite was processed by impregnating the cellulosic fibers on-line with PHB/V powder in a fluidization chamber. The impregnated roving was then filament wound on a plate and hot-pressed. The resulting unidirectional composite plates were mechanically tested and optically characterized by SEM. The fiber content was 9.9±0.9 vol% by volumetric determination. The fiber content predicted by the rule of mixture for unidirectional composites was 13.8±1.4 vol%. Optical characterization showed that the fiber distribution was homogeneous and a satisfactory wetting of the fibers by the matrix was achieved. Using a blower to remove excess matrix powder during processing increased the fiber content to 26.5±3.3 vol% (volumetric) or 30.0±0.4 vol% (rule of mixture). The tensile strength of the composite parallel to the fiber direction was 128±12 MPa (10 vol% fiber) up to 278±48 MPa (26.5 vol% fiber), compared to 20 MPa for the PHB/V matrix. The Young's modulus was 5.8±0.5 GPa (10 vol% fiber) and reached 11.4±0.14 GPa (26.5 vol% fiber), versus 1 GPa for the matrix.

Wollerdorfer and Bader (1998) studied the influence of plant fibers such as flax, jute, ramie, oil palm fibers and fibers made from regenerated cellulose on the mechanical properties of biodegradable polymers using thermoplasts like polyesters, polysaccharides and blends of thermoplastic starch. The composites were produced by extrusion compounding with a co-rotating twin screw extruder. The pellets obtained were further processed into tensile test bars by injection molding. Depending on the kind of polymer, a fiber content of 20–35% could be achieved. Generally a considerable tensile strength improvement of polyesters could not be observed. However the chemical similarity of polysaccharides and plant fibers, which consist mainly of cellulose, resulted in an increased tensile strength of the reinforced polymers. For reinforced thermoplastic wheat starch, it was four times better (37 N:mm^2) than without fibers. The reinforcement of cellulose diacetate and starch blends caused a stress increase of 52% (55 N:mm^2) and 64% (25 N:mm^2), respectively.

Luo and Netravali (1999) characterized the physical and tensile properties of environment-friendly "green" composites made from pineapple fibers and poly(hydroxybutyrate-*co*-valerate) resin. Tensile properties of pineapple fibers, like most natural fibers, showed a large variation. The average interfacial shear strength between the pineapple fiber and poly(hydroxybutyrate-*co*-valerate) (PHBV) was 8.23 MPa as measured by the microbond technique. Scanning electron microscopy (SEM) photomicrographs of the microbond specimens revealed an adhesive failure of the interface. Fully degradable and environment-friendly "green" composites were prepared by combining pineapple fibers and PHBV with 20 and 30% weight content of fibers placed in a 0±/90±/0± fiber arrangement. Tensile and flexural properties of these "green" composites were compared with different types of wood specimens. Even though tensile and flexural strength and moduli of these "green" composites were lower than those of some wood specimens tested in grain direction, they were significantly higher than those of wood specimens tested in perpendicular to grain direction. Compared to PHBV virgin resin, both tensile and flexural strength and moduli of these "green" composites were significantly higher. SEM photomicrographs of the fracture surface of the "green" composites, in tensile mode, showed partial fiber pull-out indicating weak bonding between the fiber and the matrix.

The thermal and mechanical behaviour of a biotechnological polyester poly(3-hydroxybutyrate-*co*-hydroxyvalerate) (PHBV) reinforced with wheat straw fibers has been investigated by Avella *et al*. (2000). In order to improve chemical-physical interactions between the components, the reinforcing agent has been previously submitted to a treatment with high temperature steam leading to fibers richer in cellulose and more reactive. The addition of straw fibers has been found to increase the rate of PHBV crystallization, while it does not affect the crystallinity content. Furthermore, the comparison of the mechanical properties has shown that the composites exhibit higher Young moduli and lower values of both the stress and strain to break than the neat matrix of PHBV. The biodegradability in different environments by means of short and long term tests has been studied. It has been observed that the presence of straw does not affect biodegradation rate evaluated in liquid environment and in long term soil burial tests. In the composting simulation test the rate of biodegradation is reduced for composites with more than 10% of straw content. The morphology of the composites has also been investigated and correlated to the biodegradation process.

Lequart *et al*. (2000) investigated the action of an abiotic lignin oxidant and a diffusible xylanase degradation on wheat straw and characterized at the levels of the molecular structures by chemical analysis and of the cell wall ultrastructure by transmission electron microscopy. While distinct chemical changes in the target polymers were observed when each system was used separately, a combination of the two types of catalysts did not significantly increase either lignin oxidation or hemicellulose hydrolysis. Microscopic observations however revealed that the supramolecular organization of the cell wall polymers was significantly altered. This suggested that the abiotic Mn-oxalate complex and the xylanase cooperate in modifying the cell wall architecture, without noticeably enhancing the degradation of the constitutive polymers.

Mohanty *et al.* (2000a) investigated the chemical surface modifications of two variety of jute fabrics, i.e. hessian cloth(HC) and carpet backing cloth (CBC), involving bleaching, dewaxing, alkali treatment, cyanoethylation and vinyl grafting in view of their use as reinforcing agents in composites based on a biodegradable polyester amide matrix, Biopol™, a poly(3-hydroxybutyrate-*co*-8%-3-hydroxyvalerate). The effect of different fiber surface treatments and fabric amounts on the performance of resulting composites were investigated. The mechanical properties of composites such as tensile, bending strengths and impact strength increase in comparison to pure Biopol as a result of reinforcement with jute fabrics. More than 50% enhancement in tensile strength, 30% in bending strength and 90% in impact strength of the composites relative to pure Biopol sheets were observed under the present experimental conditions. SEM investigations showed that the surface modifications improve the fiber–matrix adhesion. From degradation studies it was found that after 150 days of compost burial more than 50% weight loss of the jute/Biopol composite occurred.

Mohanty *et al.* (2000b) also investigated the influence of chemical surface modifications of jute fabrics, involving bleaching, dewaxing, alkali treatment, cyanoethylation and vinyl grafting in view to their use as reinforcing agents in composites based on a biodegradable polyester amide matrix, BAK 1095. The effect of different fiber surface treatment and fabric amount on the performance of resulting composites were investigated. The mechanical properties of composites like tensile and bending strengths increase as a result of surface modification. Among all modifications, alkali treatment and cyanoethylation resulted in improved properties of the composites. The tensile strength of BAK was increased by more than 40% as a result of reinforcement with alkali treatment jute fabrics. SEM investigated showed that the surface modification improved the fiber-matrix interaction. From degradation studies it was found that after 15 days of compost burial about 6% weight loss was observed for BAK whereas cyanoethylted and alkali treated jute-BAK composites showed about 10% weight loss. The loss of weight as well as the decrease of bending strength of degraded composites was more or less directly related.

Van de Velde and Kiekens (2002) overviewed several properties of biodegradable polymers using of natural fibers as reinforcement because of their environmental benefits and consequences on their applications. The use of a biodegradable matrix is worth considering since this would result in a completely biodegradable composite. In order to assess the most suitable matrix polymer, one must know the properties of the available polymers. Since data tend to be widely scattered over many sources and are very scarce compared to the conventional polymers, an overview of the most relevant properties of a range of biodegradable polymers was presented to provide a useful guide in establishing the best compromise between conflicting property demands. Data are presented mostly as ranges (in tables) as well as in graphs for quick comparison reasons. One specific application on thermoplastic pultrusion with flax as reinforcement was also studied.

Södergård and Stolt (2002) focused on the properties of lactic acid based polymers and the correlation to the structure of the polymers. Lactic acid based polymers prepared by polycondensation (PC), ring-opening polymerization (ROP), and other methods (chain extension, grafting) were discussed as well as modifications where structural changes had occurred due to post-polymerization reactions (peroxide melt-modification, radiation processing). The different types of polymers included copolymers prepared by ROP form L,L-lactide and D,D-lactide, glycolide (GA), ε-caprolactone (CL), trimethylene carbonate (TMC), 1,5-dioxepan-2-one (DXO), and other cyclic analogues. The thermophysical properties, the solubility, the miscibility, and the mechanical properties were reviewed. In addition the hydrolytic stability, the thermal stability, the radiation degradation, and the biodegradation of the polymers were covered.

Avérous and Boquillon (2004) focused on the study of the thermal and mechanical behavior of reinforced agro-materials. Various formulations based on plasticized starch matrix had been carried out, varying matrix formulation, filler content, fibers length and nature. Cellulose and lignocellulose fibers, which showed unequal surface tensions, had been tested. After extrusion and injection molding, the properties of these wheat starch-based biocomposites were analyzed. Mechanical properties (tensile tests), thermo-mechanical properties (DMTA) and thermal degradation (TGA) were analzsed. DMTA analysis showed important variations of main relaxation temperature, which can be linked both, to interactions resulting in a decrease of starch chain mobility and to a regular reinforcing effect. These results were consistent with the static mechanical behavior, which varied according to the filler content (up to 30 wt%), firre nature (cellulose vs. lignocellulose) and fiber length (from 60 mm to 1 mm). Besides, it was shown that the addition of cellulose fillers improved the thermal resistance of these biocomposites. Finally, impact of the addition of biodegradable polyesters into these composites without significant effect on the postprocessing stability.

Ruseckaite and Jiménez (2003) investigated a series of mixtures based on polycaprolactone (PCL) with microcrystalline cellulose (MC) and sisal fiber (SF) powder by thermogravimetric analysis (TGA) in order to predict the thermal behavior of biodegradable matrixes reinforced with cellulose derivatives. The maximum degradation temperature of each component in the mixture was higher than those of the individual components; thus an increase in thermal stability was expected. Apparent activation energies were obtained from Friedman isoconversional plots. Mixtures were considered as multistage processes. Predicted apparent activation energies agreed well with the increment in thermal stability due to the presence of the co-components. This effect was associated with either, solid–solid or solid–gas interactions between cellulose derivatives and PCL during thermal degradation.

Fernandes *et al*. (2004) involved in assessing the potentiality of some agro-industrial overproduction and byproducts in the formulation of eco-compatible bio-based polymeric materials displaying, among others, the propensity to biodegrade under controlled environment conditions. Beech wood flour (Bwf) composites were prepared from plasticized poly(3-hydroxybutyrate) (PHB). The type of plasticizer [tri(ethyleneglycol)-bis(2-ethylhexanoate) (TEGB) and poly(ethyleneglycol) (PEG200)] and the amount (5 and 20 wt%) were selected as independent variables in a factorial design. Thermal and mechanical properties of 90 wt% PHB composites were investigated. Incorporation of PEG200 was found to compromise thermal stability of PHB as demonstrated by the higher decrease on the onset decomposition temperature (*T*d) and the drop in its average molecular weight ($\overline{M}_w$). The present study underlines the fact that TEGB/PHB/beech wood flour composites can be optimized to obtain new materials for disposable items.

Le Digabel *et al*. (2004) investigated the mechanical properties of lignocellulosic fractions from wheat straw as natural fillers in composites of a polyolefin (a copolymer of polyethylene and polypropylene) and a biodegradable polyester , poly(butyleneadipate-*co*-terephthalate. A reinforcing effect of wheat-straw residues was found for both types of composites. Compared with the polyester based composites, the polyolefin composites were more brittle. The addition of compatibilizing agents (γ-methacryloxypropyltrimethoxysilane, maleic anhydride modified polypropylene, and stearic acid) did not improve the properties of the polyolefin composites. The surface properties were studied with contact-angle measurements, and poor interfacial adhesion was found between the hydrophilic lignocellulosic filler and the hydrophobic polyolefin matrix. Thermal characterization revealed the formation of low intermolecular bonds between the polyester matrix and the lignocellulosic filler, in agreement with the surface tensions results and scanning electron microscopy observations.

Avérous and Digabel (2006) analyzed thermal and mechanical behavior of processed biocomposites (biodegradable composites) based on lignocellulosic fillers. These materials have been created by extrusion and injection molding. The matrix of biodegradable and aromatic copolyester of (polybutyleneadipate-*co*-terephthalate) was been fully characterized (NMR, SEC). The lignocellulosic materials used as fillers were a by-product of an industrial fractionation process of wheat straw. Different filler fractions have been selected by successive sieving, and then carefully analyzed (granulometry, chemical structure). Cellulose, lignin, and hemicellulose contents were determined through different techniques. The biocomposites thermal behavior were investigated by TGA (thermal degradation) and DSC (transition temperatures, crystallinity). These materials present good mechanical behavior due to high filler-matrix compatibility. The impacts of filler content, filler size and the nature of each fraction were also analyzed. To predict the mechanical behavior, Takayanagi's equation was used to provide an accurate answer to evaluate the modulus in a range, 0–30 wt% of fillers.

Yu *et al*. (2006) reviewed recent advances in polymer blends and composites from renewable resources, and introduced a number of potential applications for this material class. In order to overcome disadvantages such as poor mechanical properties of polymers from renewable resources, or to offset the high price of synthetic biodegradable polymers, various blends and composites have been developed over the last decade. The progress of blends from three kinds of polymers from renewable resources (1) natural polymers, such as starch, protein and cellulose; (2) synthetic polymers from natural monomers, such as polylactic acid; and (3) polymers from microbial fermentation, such as polyhydroxybutyrate–were described with an emphasis on potential applications. The hydrophilic character of natural polymers has contributed to the successful development of environmentally friendly composites, as most natural fibers and nanoclays are also hydrophilic in nature. Compatibilizers and the technology of reactive extrusion were used to improve the interfacial adhesion between natural and synthetic polymers.

Alemdar and Sain (2008) investigated the reinforcing potential of cellulose nanofibers obtained from agro-residues in a starch-based thermoplastic polymer. Cellulose nanofibers were isolated from wheat straw by a chemi-mechanical technique and determined to have diameters in the range of 10–80 nm and lengths of several thousand nanometers. Thermal stability of the fibers was investigated using thermogravimetric analysis and found that the degradation temperature of the fibers is increased after each step of the treatment. The nanocomposites from the wheat straw nanofibers and the thermoplastic starch were prepared by the solution casting method. Their thermal and mechanical performance were also evaluated and compared with the pure thermoplastic starch using thermogravimetric and dynamic mechanical analysis, and tensile testing. The scanning electron microscopy images of the nanocomposites showed a uniform dispersion of the nanofibers in the polymer matrix. The tensile strength and modulus of the nanocomposite films revealed significantly enhanced properties compared to the pure thermoplastic starch. The glass transition of the nanocomposites was shifted to higher temperatures with respect to the pure thermoplastic starch.

Avérous (2007) presented various biocomposites that were composed with cellulose or lignocelluloses fibers from diverse sources, with different lignin contents by analysis of fiber-matrix interactions of two types of biocomposites based on agropolymer (plasticized wheat starch) and biopolyester (polybutylene adipate-*co*-terephthalate), named APB and BPB, respectively. Processing and main properties of both biocomposites are shown and compared. Polyolefin-based composites (PPC), which is known to present very poor fiber-matrix interaction, was used as reference. Through the Young’s modulus, mechanical properties shown that the reinforcement, by increasing fiber content, was much more significant for APB compared to BPB. The evolution of chains mobility, evidenced through shift of T_g values, according to the increase in fiber content and thence in interfacial area, shown that the fiber-matrix interactions were higher for APB. BPB presented intermediate values, higher than PPC. These results were in agreement with the analysis of the composite morphologies performed by SEM on cryogenic fractures. Finally, by determining the theoretical works of adhesion and the interfacial tensions from contact angle measurement, it was shown that these parameters were partially able to predict the level of interaction between the fibers and the matrix.

Among biodegradable polymers, poly (lactic acid), PLA (Figure 13), has regarded as one of the most promising biodegradable polymers and is expected to substitute some of the petroleum-based plastics because of its high stiffness and strength. Poly(lactic acid) (PLA) is a typical biodegradable polyester obtained by synthesis of lactic acid (or lactide), which can be produced from renewable resources such as corn or sugarcane.

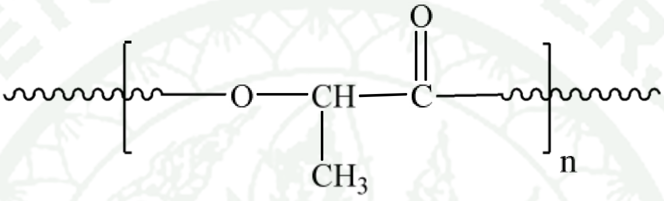


Figure 13 Structure of poly(lactic acid), PLA.

Nishino *et al.* (2003) investigated the mechanical properties of environmentally friendly composite made of kenaf fiber and poly-l-lactic acid (PLLA) resin. Young’s modulus (6.3 GPa) and the tensile strength (62 MPa) of the kenaf/PLLA composite (fiber content = 70 vol%) were comparable to those of traditional composites. These properties were higher than those of the kenaf sheet and the PLLA film themselves. This can be considered to attribute to the strong interaction between the kenaf fiber and PLLA. In addition, the storage modulus of the composite remained unchanged up to the melting point of PLLA. The effects of the molecular weight of PLLA, the orientation of the kenaf fibers in the sheet on the mechanical properties of the composite were also investigated. It was found that kenaf fiber can be a good candidate for the reinforcement fiber of high performance biodegradable polymer composites.

Plackett *et al.* (2003) converted commercial L-polylactide to film and then used in combination with jute fiber mats to generate composites by a film stacking technique. Composite tensile properties were determined and tensile specimen fracture surfaces were examined using environmental scanning electron microscopy. Degradation of the polylactide during the process was investigated using size exclusion chromatography. The tensile properties of composites produced at temperatures in the 180–220ºC range were significantly higher than those of polylactide alone. Composite samples failed in a brittle fashion under tensile load and showed little sign of fiber pull-out. Examination of composite fracture surfaces using electron microscopy showed voids occurring between the jute fiber bundles and the polylactide matrix in some cases. Size exclusion chromatography revealed that only minor changes in the molecular weight distribution of the polylactide occurred during the process.

Oksman *et al*. (2003) focused on the development of flax fibers as reinforcement in polylactic acid (PLA) composites. PLA is a thermoplastic polymer made from lactic acid and has mainly been used for biodegradable products, such as plastic bags and planting cups, but in principle PLA can also be used as a matrix material in composites. Because of the brittle nature of PLA triacetin was tested as plasticizer for PLA and PLA/flax composites in order to improve the impact properties. The studied composite materials were manufactured with a twin-screw extruder having a flax fiber content of 30 and 40 wt%. The extruded compound was compression molded to test samples. The processing and material properties have been studied and compared to the more commonly used polypropylene flax fiber composites (PP/flax). Preliminary results showed that the composite strength is about 50% better compared to similar PP/flax fiber composites, which can be used in many automotive panels. The addition of plasticizer did not show any positive effect on the impact strength of the composites. The study of interfacial adhesion showed that adhesion needs to be improved to optimize the mechanical properties of the PLA/flax composites. The PLA/flax composites did not show any difficulties in the extrusion and compression molding processes and they can be processed in a similar way as PP based composites.

Serizawa *et al*. (2006) developed high performance biomass-based plastics that consist of poly (lactic acid) (PLA) and kenaf fiber, which fixates CO_2 efficienctly. Adding this fiber to PLA greatly increased the heat resistance (distortion temperature under load) and modulus and also enhances its crystallization, so the ease of molding these materials was improved. Eliminating the short particles from the kenaf fiber improved its effect on the impact strength. Kenaf fiber without the particles exhibited effects on these characteristics of PLA practically comparable to the effects of glass fiber. Furthermore, adding a flexibilizer (a copolymer of lactic acid and aliphatic polyester) to the composites improved their strength. These composites (PLA/kenaf fiber and PLA/kenaf fiber/flexibilizer) showed good practical characteristics for housing materials of electronic products in comparison with petroleum-based plastics used in housing such as glass-fiber-reinforced acrylonitrile-butadiene-styrene (ABS) resin.

PLLA-based eco-composites reinforced with kenaf fiber and rice straw and containing red or yellow pigments have been studied by Dobreva *et al*. in 2009. The mechanical behavior of the composites was tested by DMTA at two different annealing temperatures (65ºC and 85ºC) and times (15 min and 120 min) as well as at two preparation conditions: vacuum drying and long time at room temperature. A decrease of microhardness was observed during the water absorption tests. Moreover, the rice straw-based composites absorbed more water than the kenaf-ones. Generally, the dyed NFs composites presented better water resistance than undyed ones. The pigments improved the adhesion and led to better mechanical performance. The natural fibers favored the cold crystallization process of PLLA and shifted the cold crystallization peak temperature to lower values, as it was confirmed by DSC measurements. The values of tensile storage modulus obtained after different preparation condition were strongly affected by the process of physical ageing. According to, tan d parameter, the samples stored at room temperature for a long time showed the highest amorphous content. The PLLA eco-composite reinforced with kenaf fibers, dyed with the red pigment, and annealed at 85ºC for 2 hours displays the best mechanical properties.

In 2009, Suryanegara *et al*. studied the thermal and mechanical properties of nanocomposites based on polylactic acid (PLA) and microfibrillated cellulose (MFC). MFC and PLA were mixed in an organic solvent with various fiber contents up to 20 wt%, followed by drying, kneading and hot pressing into sheets. It was found that the tensile modulus and strength of neat PLA were improved with an increase of MFC content in both amorphous and crystallized states. The addition of 20 wt% of MFC in PLA improved the storage modulus of crystallized PLA at a high temperature (120^{o}C) from 293 MPa to 1034 MPa.

A new manufacturing process similar to papermaking which enabled the production of thin sheets made of uniformly dispersed microfibrillated cellulose (MFC) with polylactic acid (PLA) fibers was devised by Nakagaito *et al*. in 2009. The composites were obtained by compression molding of the stacked sheets. The process is suitable for adoption at an industrial scale owing to the high yields and fast dewatering times. The measurement of tensile properties revealed that the modulus strength, and strain at fracture increased linearly with the MFC content. The improvement in toughness was considered one of the key benefits brought by MFC reinforcement.

Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion was studied by Jonoobi *et al*. in 2010. Nanocomposites were prepared by premixing a master batch with high concentration of CNFs in PLA and diluting to final concentration (1, 3, 5 wt%) during the extrusion. Morphology, mechanical and dynamic mechanical properties (DMA) were studied theoretically and experimentally to see how different CNF concentrations affected the composites's properties. The tensile modulus and strength increased from 2.9 GPa to 3.6 GPa and from 58 MPa to 71 MPa, respectively, for nanocomposites with 5 wt% CNF. The DMA results were also positive; the storage modulus increased for all nanocomposites compared to PLA; being more significant in the high temperature region (70^{o}C). The addition of nanofibers shifted the tan delta peak towards higher temperatures. The tan delta peak of the PLA shifted from 70^{o}C to 76^{o}C for composites with 5 wt% CNF.

Several composites of poly (L-lactic acid) (PLLA) with natural fibers (kenaf and rice straw) and pigments were prepared and analyzed by Dobreva *et al*. (2010). The study of the thermal behavior showed a rather important nucleation ability of these fillers for the crystallization of the PLLA component in the composites. Thus, the cooling from the melt of pure PLLA at 10ºC/min led to an almost completely amorphous sample, while a high crystallinity (around 60%) was exhibited by the sample PLLA and rice straw (PLLA-RS)-yellow under those conditions. The analysis of the isothermal crystallization from the melt indicated that a maximum rate of crystallization was obtained for all the samples at around 105ºC, although the rate was three times faster for samples PLLA and kenaf fiber (PLLA-KF), PLLA-KF-red, and PLLA-RS, in comparison with pure PLLA. The rate was increased by another factor of three for sample PLLA-RS-yellow. The analysis of the melting temperatures and crystallinities as a function of the crystallization temperature showed that there was a break at around 115ºC, which seemed to be related to the formation of ordered crystals at higher temperatures and disordered ones at lower temperatures. Besides, the natural fibers were environmentally friendly and nonexpensive materials, and the higher crystallization rates of the composites resulted in shorter production cycles of end-use articles.

Qin *et al*. (2011) prepared composites of poly(lactic acid) with modified rice straw fibers (RSF). The modified rice straw fibers were prepared by suspension polymerization technique of butyl acrylate (BA) monomer and rice straw fibers (RSF) in water solution. The results of Fourier transform infrared (FTIR) spectroscopy and scanning electron microscopy (SEM) indicated that poly(butyl acrylate) (PBA) was adsorbed and coated on RSF. The biodegradable composites were prepared with the modified rice straw fiber (MRSF) and poly(lactic acid) (PLA) by HAAKE rheometer. Mechanical properties showed that the tensile strength of PLA/MRSF composites (wt%) 7.98) increased by 6 MPa compared with blank sample. The water absorption of the PLA/MRSF composites was lower than PLA/RSF composites. The thermal properties of these composites were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The TGA results confirmed that thermal stability of PLA/RSF composites increased with increasing PBA. The DSC data showed that RSF played a role as a nucleating agent and PBA made crystallization of PLA more difficult and incomplete.

Therefore, many developments of natural fiber reinforced biodegradable polymeric biocomposites as an alternative to fiber reinforced nonbiodegradable polymeric composites have been reported in the last two decaded. Thailand has the fifth-largest amount of land under rice cultivation in the world and is the world's largest exporter of rice. It is estimated that 21.86 Mt of rice straw residue are produced and about 48% of this residue produced is subjected to open-field burning, about 30% is unused, 15% is being used as animal feed, 5% is used as organic fertilizer, 1.5% is being traded (sold), 0.18% as fuel and 0.27% for other activities in Thailand (Gadde *et al*., 2009) (Table 9). It could be concluded that there is an enormous potential from rice straw for other applications including as reinforcement of bioocomposites.

Table 9 Current uses of rice straw in Thailand.

Current practice	**Percentage**	**Quantity in kt**
Animal feeds	15.02	3,283.00
Burnt in the field	47.81	10,451.00
Fuel	0.18	39.00
Organic fertilizer	5.39	1,178.00
Sold	1.42	310.00
Others	0.27	59.00
Residue available	29.91	6,538.00
Total	100.00	21,858.00

Purac (Thailand) Limited is the worldwide market leader in lactic acid and derivatives manufacture and has officially opened its new lactic acid plant in Thailand at Map Ta Phut, Rayong, on April 4, 2008 to produce 100,000 tonnes of undiluted lactic acid that uses sugar as raw material. In addition, Purac decided to build another Bt2-billion lactic acid plant which will start to operate on the second half of 2011. The lactic acid plant with an annual production capacity of 100,000 tonnes of lactic acid and 15,000 tonnes of derivatives will supply raw materials to the lactide plant, whose annual production capacity will be 75,000 tonnes. Together the two plants will turn Thailand into the world’s biggest production base for upstream manufacturing of lactic acid, lactide and other derivatives and downstream manufacturing of poly (lactic acid). Technological knowledge advancements in the production of cellulose-based fiber from rice straw reinforcement of poly(lactic acid) biocomposites must be developed to be able for Thailand to benefits from these two readily available resources: rice straw and poly(lactic acid), as a whole.

MATERIALS AND METHODS

Materials

1. Rice straw

Rice straw was obtained from Chainart rice variety, Nakornsawan province, Thailand. The straw was washed under running tap water and the wet straw was dried at 60±5°C in hot air oven (ED53/E2, Binder, Germany) for 24 hours and was kept in polyethylene bag for further use (Figure 14).

Figure 14 Rice straw from Chainart rice variety, Nakornsawan province, Thailand after washing and drying.

2. Chemicals

The following chemicals were obtained from commercial sources and used directly without further purification unless noted:

2.1 Polylactic acid (PLA) $–[O\text{-}CH(CH_3)\text{-}CO\text{-}]_n\text{-}$, (NatureWorks PLA polymer 2002D) was purchased from Fresh Bag Company Limited, Bangkok, Thailand. This

PLA has a density of 1.24 g/cm^3 and the melt flow index (MFI) of 5-7 g/10 min at 210^{o}C/2.16 kg (Figure 15).

Figure 15 Polylactic acid pellets (NatureWorks 2002D).

2.2 Chloroform ($CHCl_3$) (Analytical reagent grade, Lab-Scan)

2.3 Hydrochloric acid (HCl) (Analytical reagent grade, Merck, Germany)

2.4 Hydrogen peroxide (30% H_2O_2, Analytical reagent grade, Carlo Erba, Italy)

2.5 Sodium hydroxide (NaOH) pellets (Analytical reagent grade, Merck, Germany)

2.6 Sodium hypochlorite (NaOCl) (Analytical reagent grade, Merck, Germany)

3. Equipments

3.1 Chemical composition determination

The chemical compositions of lignocellulosic rice straw fibers (cellulose, holocellulose and lignin) were determined at the Center of Excellence Oil Palm, Kasetsart University. Cellulose and lignin were obtained by the methods of Technical Association of the Pulp and Paper Industry (TAPPI) T 203 om-88 and T 222 om-88 respectively. Holocellulose was analyzed according to the procedure described by Browning (Browning, 1967).

3.2 Mechanical properties

3.2.1 Tensile testing

Tensile properties of PLA/rice straw biocomposites were performed using a Tensile Universal Testing Machine (INSTRON 5566) according to ASTM D638 at Research and Development Centre for Thai Rubber Industry, Faculty of Science, Mahidol University, Salaya, Nakorn Pathom. An average value was taken from a minimum of five measurements under the same conditions for each biocomposites. The elastic modulus (Young's modulus) was calculated from the initial part of the slope from the stress-strain curves.

3.2.2 Hardness Testing

Shore D hardness of PLA/rice straw biocomposites was measured using hardness tester (Zwick Model 3102, Germany) according to ASTM D2240 at Research and Development Centre for Thai Rubber Industry, Faculty of Science, Mahidol University, Salaya, Nakorn Pathom. The tested specimens were compression molded at 10 MPa into 1.25 mm thickness at 190^{o}C by pre-heating for 15 min, compression for 10 min and cooling for 15 min.

3.3 Thermal properties

3.3.1 Differential Scanning Calorimetry (DSC)

The glass transition temperature (T_g), melting temperature (T_m) and crystallization temperature (T_c) were measured with a DSC7 series (Perkin Elmer) from 0-200°C using heating rate of 10°C/min and cooling rate of 5°C/min at the Department of Chemistry, Kasetsart University. Indium was used as standard for temperature calibration and the measurements were made under constant stream of nitrogen.

3.3.2 Thermogravimetric Analysis (TGA)

The thermal stability is determined by thermogravimetric analysis (TGA) with TGA7 series (Perkin Elmer) from the compression molded PLA/rice straw biocomposites sheet from 30-550°C with heating rate of 10°C/min in nitrogen atmosphere at the Department of Chemistry, Kasetsart University.

3.3 Morphology analysis

The phase structures of PLA/rice straw biocomposites were determined with a Scanning Electron Microscopy (SEM XL30, Philips) at Department of Materials Engineering, Faculty of Engineering, Kasetsart University. The compression molded PLA/rice straw biocomposites sheet were first fractured in liquid nitrogen and then coated the surface with a thin gold layer. Their fractural cross-sectional SEM morphologies were determined.

Methods

1. Lignocellulosic rice straw fibers

Cleaned and dried rice straw was then cut into 2 centimeter strips and the strips were ground using hammer mill (PX-MFC, Polymix, Switzerland) (Figure 16) at 4500 rpm. The ground rice straw were sieved with a 40 screen mesh size (ASTM E11, Retsch, Germany) to obtain lignocellulosic rice straw fiber (LCF) having particle size ≥425 µm (STL, rice straw long fiber). The rice straw, that passed through the 40 screen mesh size, was further sieved with a 60 screen mesh size (ASTM E11, Retsch, Germany) to obtain rice straw having particle size ≤250 µm (STP, rice straw powder). Both lignocellulosic rice straw fibers having particle size ≥425 µm (STL) and ≤250 µm (STP), were packed in polyethylene bag and kept in refrigerator (10 ±2^{o}C) for further use (Figure 17).

Figure 16 PX-MFC, Polymix, Switzerland.

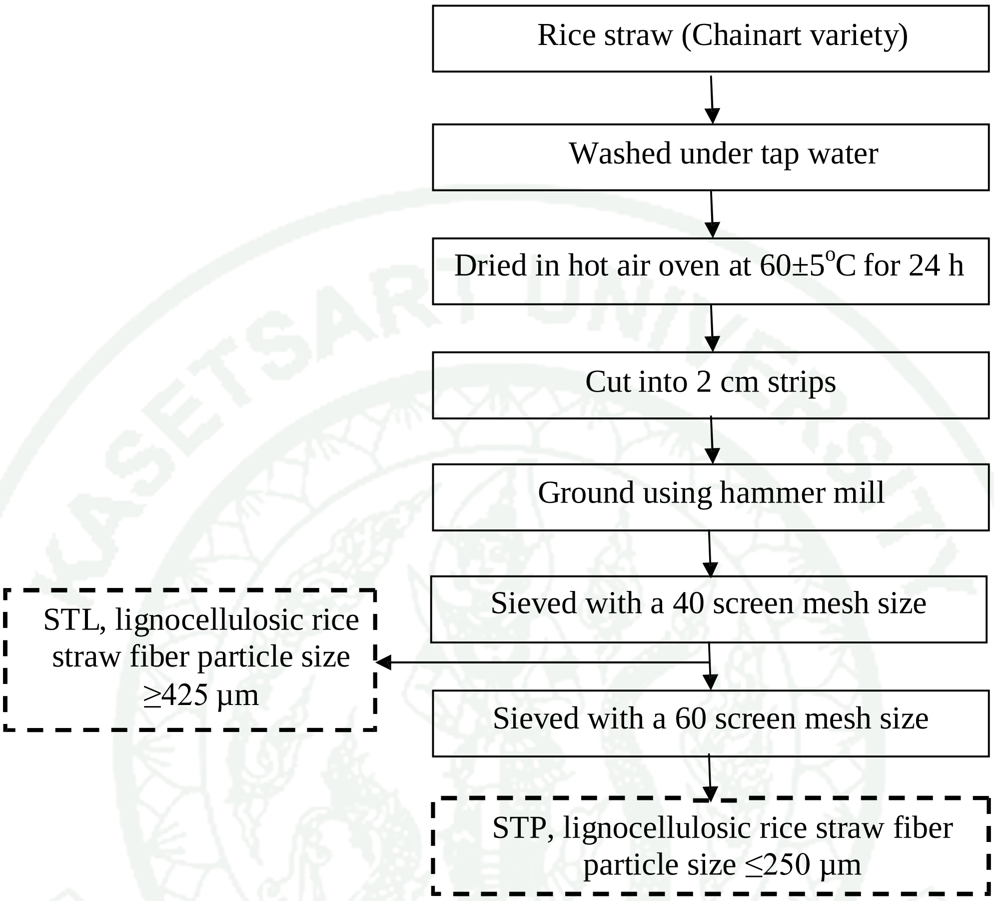


Figure 17 Flow chart for preparation of lignocellulosic rice straw fibers.

Cellulose content in the lignocellulosic rice straw fibers (STL, particle size ≥425 µm or STP, particle size ≤250 µm) was isolated from modified method (Triakarabenjakul, 2006) according to Anouk *et al.* (2005) and Sang *et al.* (2003) as followed (Figure 18).

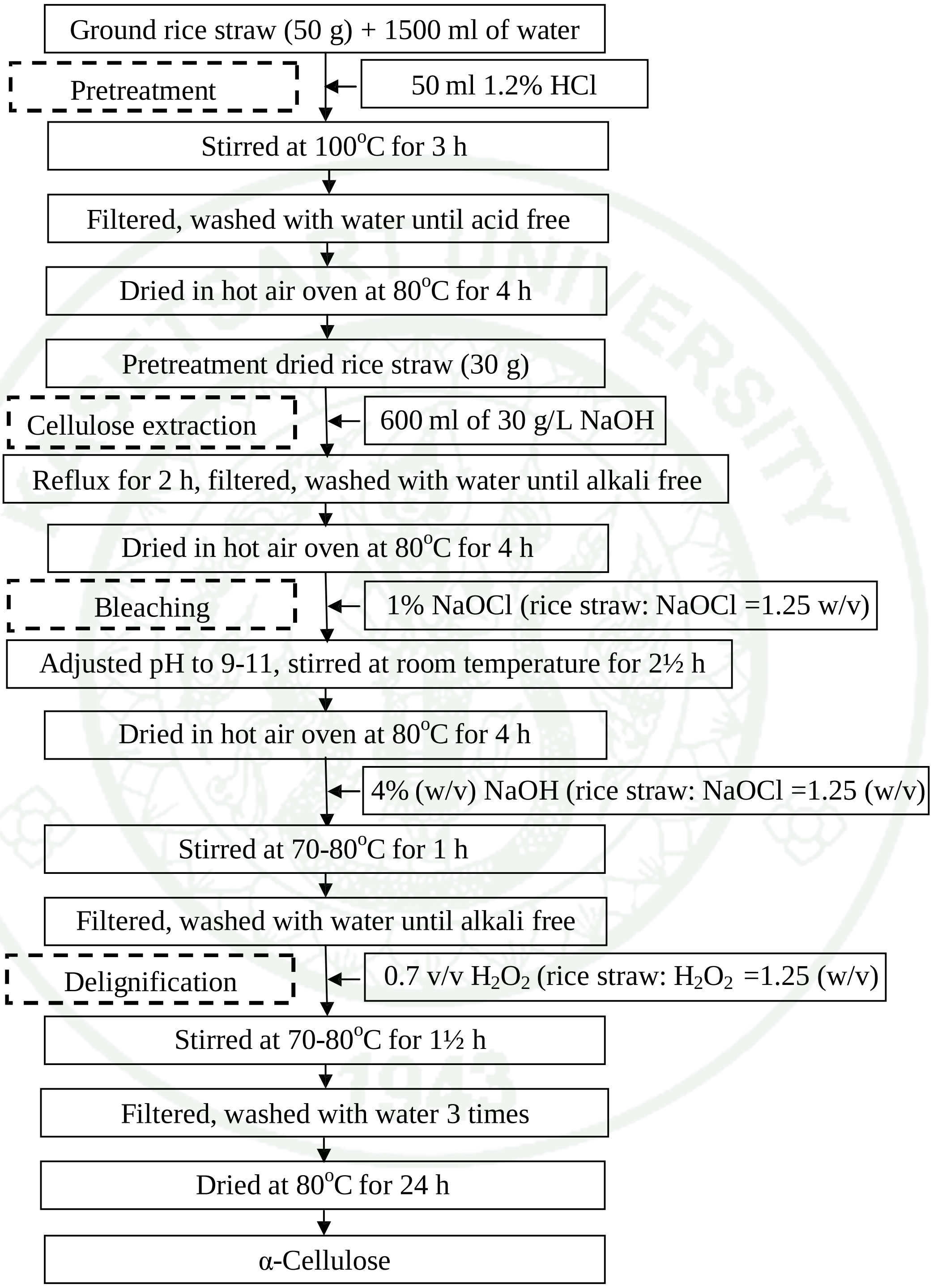


Figure 18 Cellulose isolation from rice straw according to Anouk, *et al*. and Sang *et al*. modified method (Triakarabenjakul, 2006).

1.1 Pretreatment

Ground lignocellulosic rice straw fibers (STL, particle size ≥425 µm or STP, particle size ≤250 µm) 30g together with 1500 ml of distilled water was put into a 2000 ml beaker, and then 50 ml of 1.2 % HCl (v/v) was added. The mixture was stirred at 100°C for 3 h (Figure 19), filtered, washed with 3000 ml of distilled water, and then dried in hot air oven at 80°C for 4 h.

Figure 19 Pretreatment of lignocellulosic rice straw fibers.

1.2 Alkali treatment

Residues from pretreatment after drying (30 g) were put into a 2000 ml beaker and 600 ml of 30 g/L NaOH solution (residues: NaOH solution = 1:20 w/v) was added. The mixture was reflux at 100°C for 2 h (Figure 20), filtered, washed with distilled water until neutral and then dried in hot air oven at 85°C overnight.

Figure 20 Alkali treatment of pretreatment rice straw residues.

1.3 Bleaching

Residues from alkali treatment and 1% sodium hypochlorite solution (residues: 1% NaOCl = 1:25 w/v) were added into an Erlenmeyer flask, and then adjusted the solution to pH 9-11 with acetic acid. The Erlenmeyer flask was closed with a glass stopper and stirred at room temperature for 2½ h (Figure 21), filtered and washed the residues with distilled water.

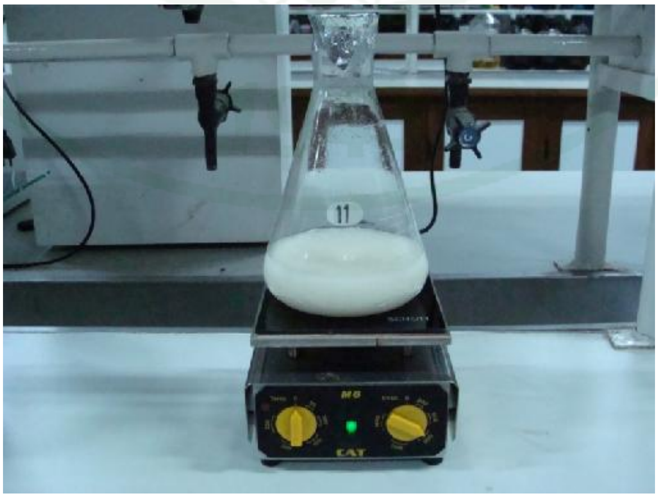


Figure 21 Bleaching of rice straw residues from alkali treatment with 1%NaOCl.

1.4 Alkali extraction

Residues from bleaching step were put into a 600 ml beaker and 4% NaOH solution (residues: 4% NaOH = 1:25 w/v) was added. The mixture was stirred at 70-80°C for 1 h (Figure 22), filtered and then washed with distilled water 2 times.

Figure 22 Alkali extraction of rice straw.

1.5 Delignification

Residues from alkali extraction together with 0.7 v/v of hydrogen peroxide solution (residues: H_2O_2 = 1:25 w/v) were put into a 600 ml beaker. The mixture was stirred at 80-90°C for 1½ h (Figure 23), filtered, washed with distilled water (3 times), and then dried in hot air oven at 80°C for 24 h.

Figure 23 Delignification of rice straw with H_2O_2.

2. Preparation of lignocellulosic rice straw fibers polylactic acid biocomposites (PLA/rice straw biocomposites)

A series of PLA and rice straw lignocellulosic fibers particle size ≥ 425 µm (STL) or particle size ≤250 µm (STP), PLA/rice straw, varying from 95:5, 90:10, 85:15 and 80:20 wt% were prepared as shown in Table 10. Prior to process, rice straw lignicellulosic fibers are dried in a hot air oven at 80°C for up to 10 h and polylactic acid pellets are dried in a vacuum oven for overnight. PLA was first dissolved in 400 ml of chloroform and stirred on magnetic stirrer at room temperature (25°C) and about 72% relative humidity for 24 h. Rice straw was then added and the mixtures were further stirred at room temperature until the mixtures became homogeneous. The mixtures were casting uniformly on a glass plate (0.10m x 0.10m) with the help of glass rod to maintain the sheet and the required thickness (approximately <1 mm) was controlled with the aid of an appropriate spacers provided on both ends of the glass plate (Figure 24). The solvent was evaporated at room temperature for 24 h followed by vacuum drying for another 24 h. The dried PLA/rice straw biocomposites was kneaded by a two roll mill (Model YFCR 6, Chor. Sri-Anan Co.Ltd.,Thailand) (Figure 25) at 120°C by varying the roll gap from 1.6-0.2 mm which the roll gap would decrease by 0.2 mm at every 4 rounds. The PLA/rice straw biocomposites were cut into small pieces and compression molded at 10 MPa into 1.25 mm thickness sheet at 190°C by pre-heating for 15 min, compression for 10 min and cooling for 15 min for further characterization (Figure 26).

Table 10 Formulation of PLA/rice straw biocomposites.

Samples	PLA(g)	STL(g)	STP(g)
Pure PLA	70	-	-
PLA/5% STL	66.5	3.5	-
PLA/10% STL	63	7	-
PLA/15% STL	59.5	10.5	-
PLA/20% STL	56	14	-
PLA/5% STP	66.5	-	3.5
PLA/10% STP	63	-	7
PLA/15% STP	59.5	-	10.5
PLA/20% STP	56	-	14

Figure 24 Casting of PLA/rice straw biocomposites on a glass plate.

Figure 25 Two roll mill (YFCR 6, Chor. Sri-Anan Co.,Ltd., Thailand).

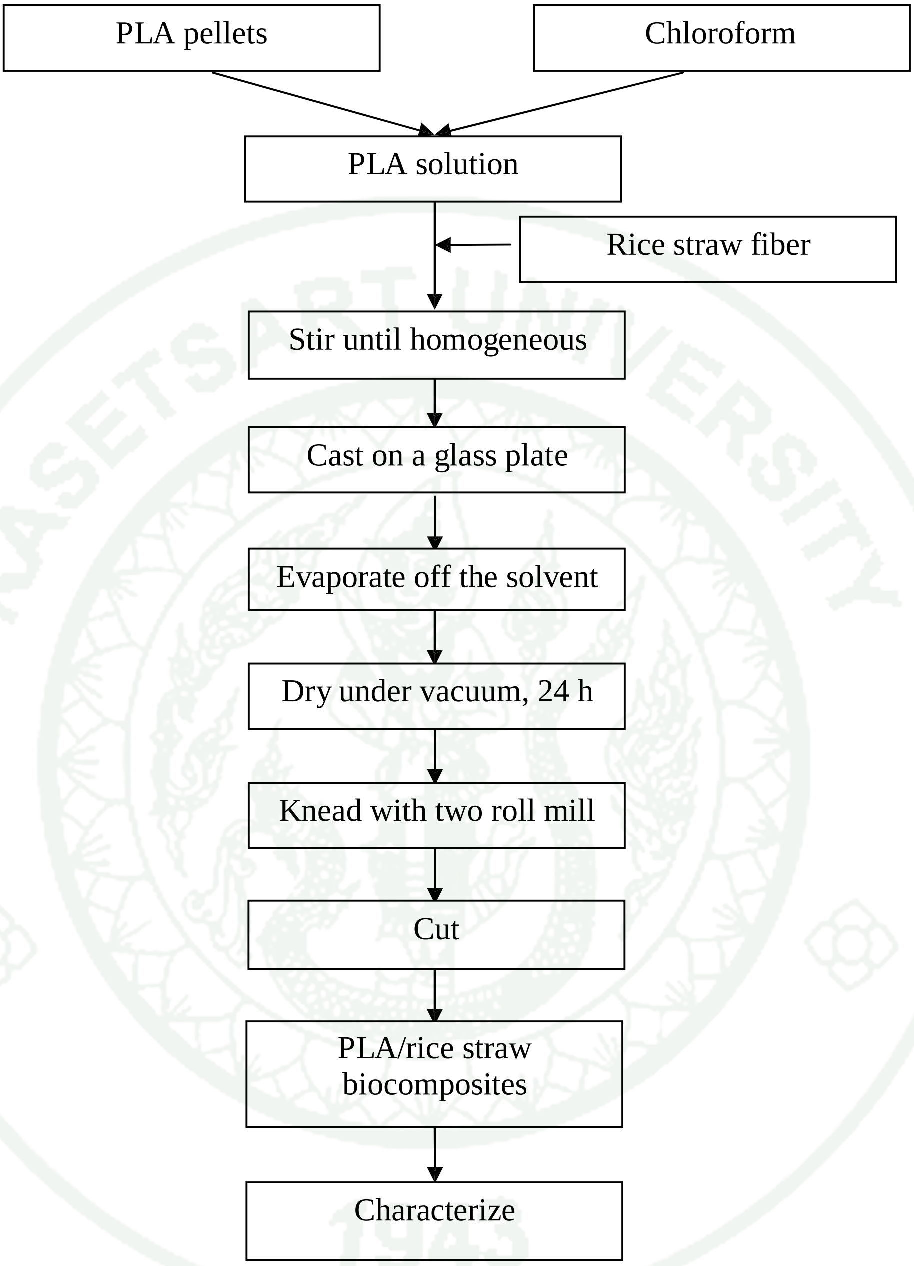


Figure 26 Flow chart for preparation of PLA/rice straw biocomposites.

RESULTS AND DISCUSSION

1. Chemical composition of rice straw

Performance of rice straw biocomposites is uncertain without information on the chemical composition of rice straw. In general, chemical composition of lignocellulosic rice straw fibers is similar to that of softwoods. Many chemical compositions of rice straw have been reported, for example, values with the percentages of cellulose, hemicelluloses and lignin within the ranges of 40-45%, 20-25% and 26-35% were reported by Summers (2000) and 43-49%, 23-28% and 12-16% were reported in Fiber Futures in 2007 respectively.

Results of chemical composition of rice straw fibers of both STL (particle size ≥425 µm) and STP (particle size ≤250 µm) obtained in this study were shown in Table 11. Cellulose, holocellulose (hemicelluloses + cellulose) and lignin composition in STL (particle size ≥425 µm) and STP (particle size ≤250 µm) are in the ranges of 54.5%, 75.9% and 25%, and 52.8%, 72.9% and 25.9% respectively. Results showed that chemical composition obtained from both STL (particle size ≥425 µm) and STP (particle size ≤250 µm) is within the usual ranges although cellulose content is slightly higher when compared with the values reported in the literatures. This is common since chemical composition of cellulose, hemicelluloses and lignin content varied greatly among different rice straw varieties, the various tissue parts, age and the different producing area, and the testing process. The higher the cellulose content, the better performance as reinforcement since cellulose is the main component responsible for the structure and rigidity properties. Thus, rice straw fibers are good sources of cellulose as a base for obtaining resistant and biodegradable fibers that can replace wood fiber or plastic derived from petroleum.

Table 11 Comparison of chemical composition of rice straw fibers (Chainart rice variety) with values reported in literature.

Sample	Lignin (%)	Holocellulose (%)	α-Cellulose (%)
Rice straw (Xiao *et al*., 2001)	24.4	67.7	32.0
Rice residues (Garay *et al*., 2009)	23.4	84.0	45.1
STL, particle size ≥425 µm	25.0	75.9	54.5
STP, particle size ≤250 µm	25.9	72.9	52.8

Furthermore, cellulose content of lignocellulosic rice straw fiber was isolated by pretreatment, bleaching, alkali extraction and delignification. The overall purpose of pretreatment is to break down the shield formed by lignin and hemicellulose, disrupt the crystalline structure and reduce the degree of polymerization of cellulose as shown in Figure 27 (Mosier *et al*., 2005 and Zheng *et al*., 2009). Residues obtained from pretreatment were shown in Figure 28.

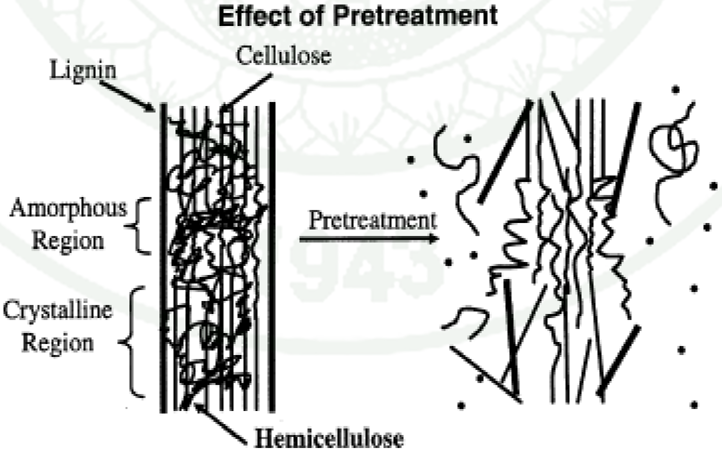


Figure 27 Schematic of pretreatment on lignocellulosic material.

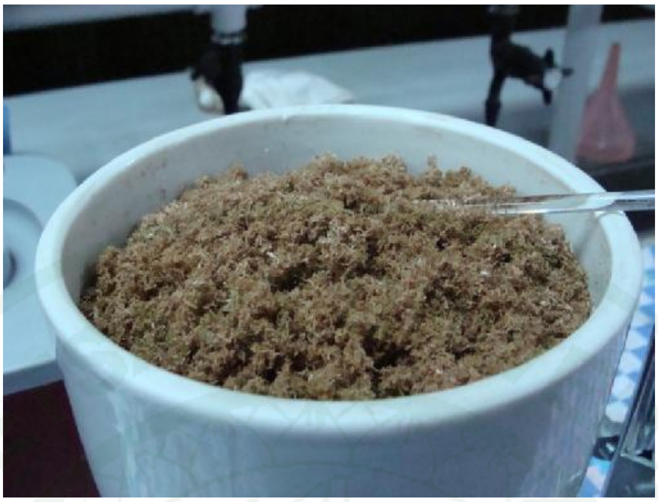


Figure 28 Rice straw residues obtained from pretreatment.

Alkali treatment of pretreatment lignocellulosic rice straw (30 g) is to disrupt the cell wall by dissolving hemicelluloses, lignin and silica by hydrolyzing uronic and acetic esters and by swelling cellulose, decreasing the crystallinity of cellulose. In addition, the alkali treatment also cleaves the α-ether linkages between lignin and hemicelluloses and the ester bonds between lignin and/or hemicelluloses and hydroxycinnamic acids, such as *p*-coumaric and ferulic acids (Xiao *et al*., 2001). About 11.83 g or 39.4 % of residues rice straw after alkali treatment or α-cellulose was obtained as shown in Figure 29. Results from bleaching of residues rice straw after alkali treatment and from further treating with alkali to remove the less crystallized fractions of polysaccharides were shown in Figures 30-31 respectively. After delignification, about 6.6 g or 22 % of dried pure α-cellulose was obtained (Figures 32-33). Percent cellulose obtained before and after bleaching and delignification are both lower than the values obtained by analysis from TAPPI method.

Figure 29 Rice straw residues obtained from alkali treatment.

Figure 30 Rice straw residues obtained from bleaching with 1% NaOCl.

Figure 31 Rice straw residues obtained from alkali extraction.

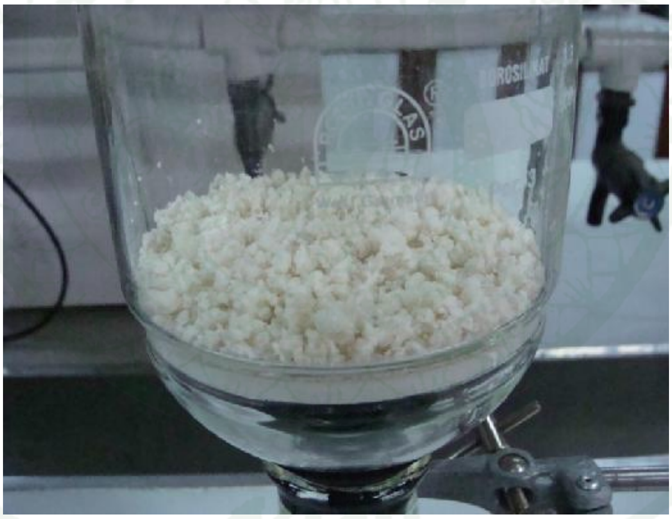


Figure 32 Rice straw residues obtained from delignification with H_2O_2.

Figure 33 Dried pure α-cellulose obtained from rice straw.

2. Morphology of the PLA/rice straw lignocellulosic fiber biocomposites

Morphology of prepared PLA/rice straw (STL, particle size ≥425 µm) and PLA/rice straw (STP, particle size ≤250 µm) was investigated by scanning electron microscopy (SEM) and their cross sectional SEM morphologies are shown in Figure 34 and Figure 35 respectively. It can be seen that the cross sectional morphologies of PLA/rice straw (STL, particle size ≥ 425 µm) had a rougher surface than PLA/rice straw (STP, particle size ≤250 µm), and the biocomposites with 20 wt% lignocellulosic rice straw fiber had a rougher surface compared to those with lower lignocellulosic rice straw fiber contents.

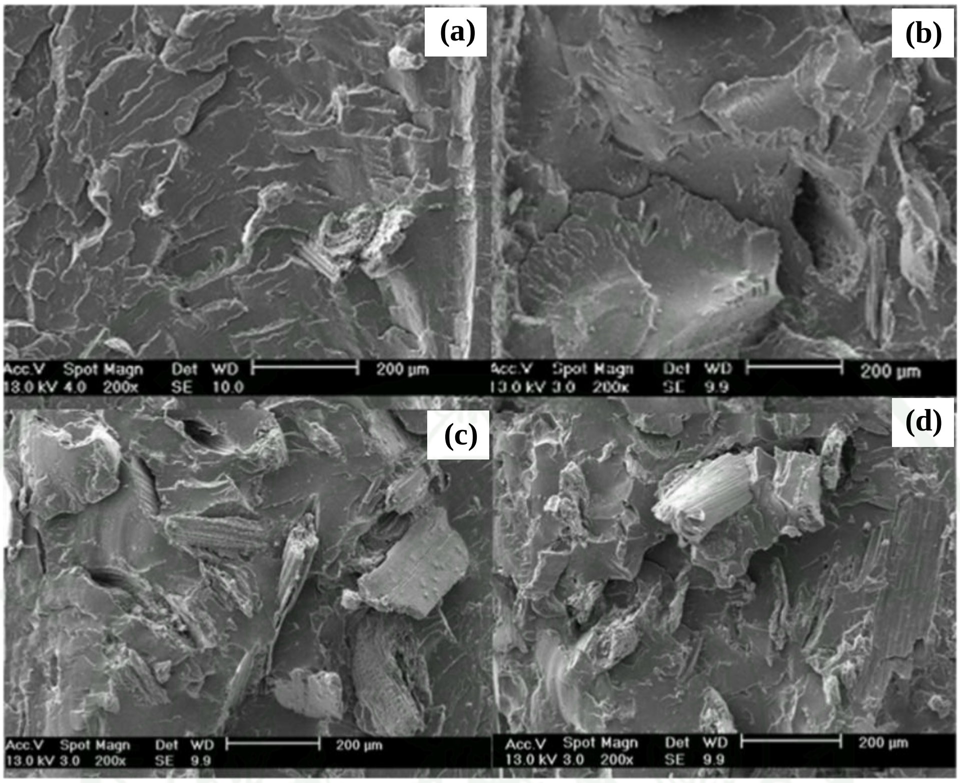


Figure 34 SEM cross section morphology (200X) of PLA/STL (particle size ≥425 µm) biocomposites: (a) 5%STL, (b) 10%STL, (c) 15%STL and (d) 20%STL.

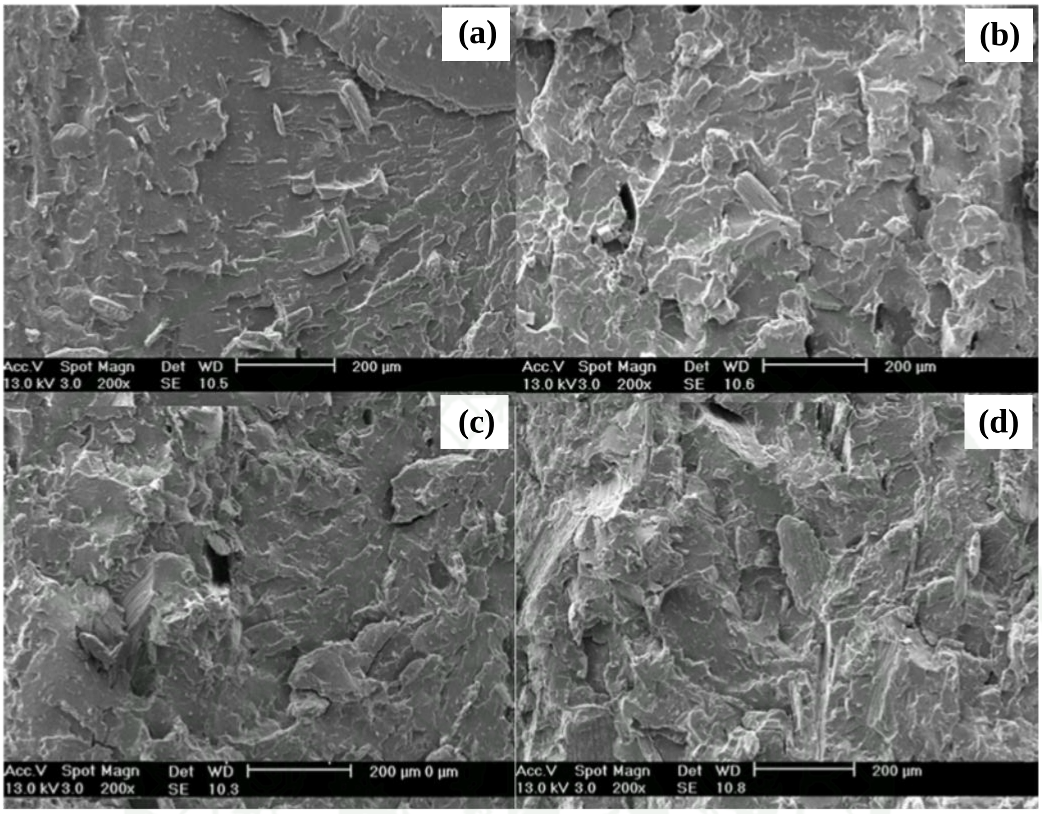


Figure 35 SEM cross section morphology (200X) of PLA/STP (particle size ≤250 µm) biocomposites: (a) 5%STP, (b) 10%STP, (c) 15%STP and (d) 20%STP.

A more detailed micrograph of both PLA/rice straw (STL, particle size ≥425 µm) and PLA/rice straw (STP, particle size ≤250 µm) biocomposites is shown in Figure 36 and Figure 37. It can be seen that both rice straw fibers still remain as single fiber and there are no voids around PLA matrix and both STL and STP rice straw fibers interfaces. In addition, rice straw fiber pullouts are observed only in PLA/STL rice straw biocomposites. This indicated that there is an adhesion between the PLA matrix and rice straw fibers in PLA/STP rice straw biocomposites, but there is no adhesion between the PLA matrix and rice straw fiber in PLA/STL rice straw biocomposites. Furthermore, it is also possible to see the dispersion of both STL and STP rice straw fibers in the PLA matrix. This could be due to a specific interaction between the carbonyl group (–COO-) of ester linkage in PLA matrix and the hydroxyl group (–OH) in cellulose of rice straw fibers, and interaction of PLA/STP rice straw fibers (particle size ≤250 µm) is better when compared to PLA/STL rice straw fibers (particle size ≥425 µm). This could be due to a better dispersion of smaller particle size (STP) in the PLA matrix, and a relatively good dispersion was achieved with low rice straw fiber contents in all PLA/rice straw biocomposites (Mathew *et al.*, 2005).

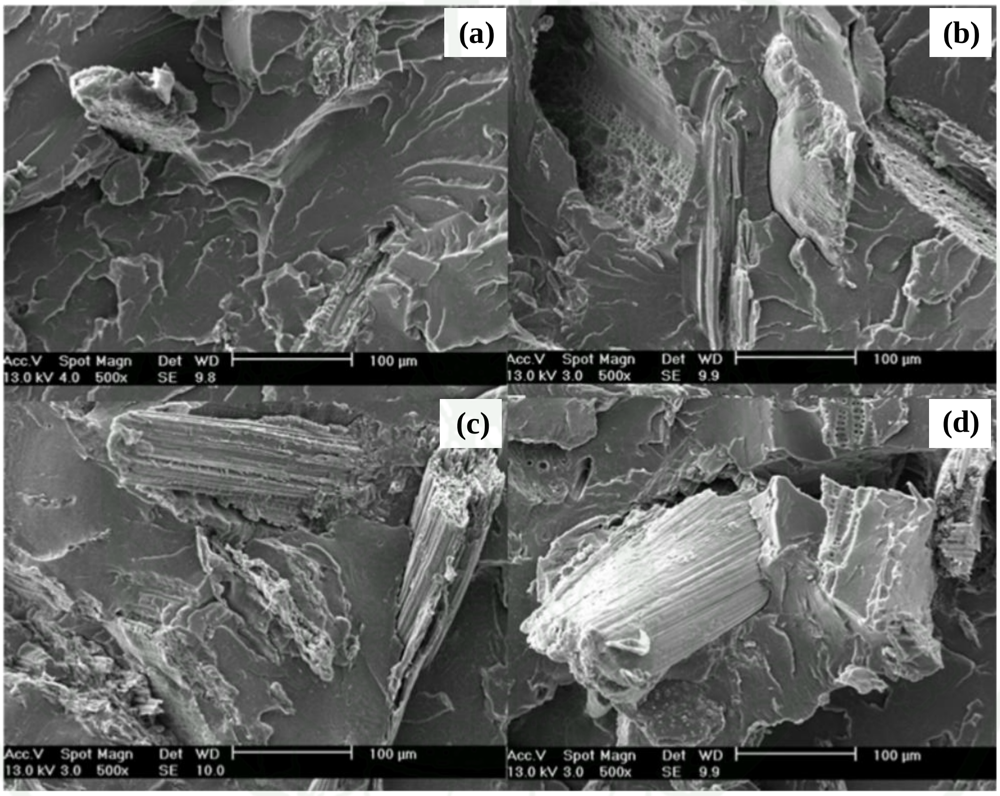


Figure 36 SEM cross section morphology (500X) of PLA/STL (particle size ≥425 µm) biocomposites: (a) 5%STL, (b) 10%STL, (c) 15%STL and (d) 20%STL.

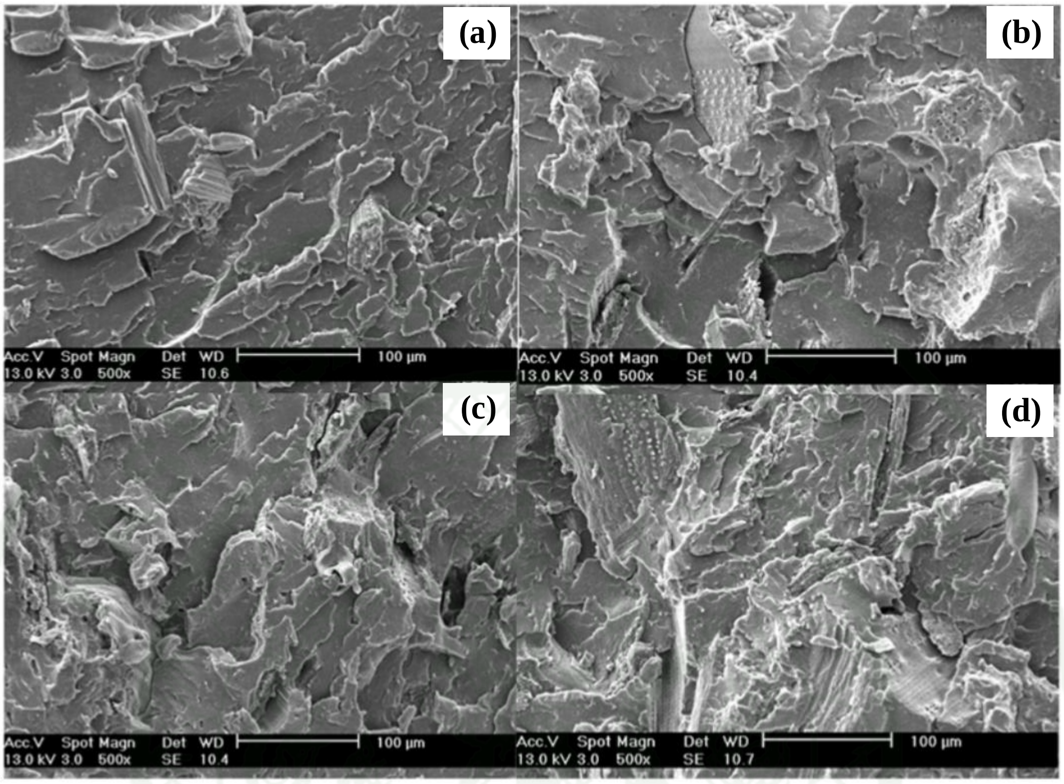


Figure 37 SEM cross section morphology (500X) of PLA/STP (particle size ≤250 µm) biocomposites: (a) 5%STP, (b) 10%STP, (c) 15%STP and (d) 20%STP.

3. Mechanical properties

A series of polylactic acid and lignocellulosic rice straw fibers (PLA/rice straw) biocomposites was prepared from rice straw lignocellulosic fiber particle size ≥ 425 µm (STL) or particle size ≤250 µm (STP) with various rice straw fiber contents up to 20 wt% varying from 95:5, 90:10, 85:15 and 80:20 wt%. Table 12 summarizes the mean and standard deviation of the mechanical properties of pure PLA, PLA/rice straw (STL) and PLA/rice straw (STP) biocomposites. Figure 38 and Figure 39 show the tensile stress and strain deformation curves of the obtained PLA/rice straw (STL) and PLA/rice straw (STP) biocomposites with different rice starw content respectively. The results are also presented in more detail in separate figures.

Table 12 Results of the mechanical properties of PLA/rice straw (STL, particle size ≥425 µm) and PLA/rice straw (STP, particle size ≤250 µm) biocomposites.

Sample	**Hardness** (Shore D)	**Tensile trength at break** (MPa)	**Elongation at max load** (%)	**Elongation at break** (%)	**Young's Modulus** (GPa)
Pure PLA	82.0 ± 0.7	47.5 ± 2.8	2.1 ± 1.2	5.2 ± 1.2	3.9 ± 0.2
5%STL	83.6 ± 0.5	46.8 ± 4.7	0.9 ± 0.2	0.9 ± 0.2	5.1 ± 0.2
10%STL	85.0 ± 1.6	46.2 ± 2.1	1.2 ± 0.5	1.2 ± 0.5	3.9 ± 0.5
15%STL	85.2 ± 1.1	40.4 ± 3.8	0.9 ± 0.3	0.9 ± 0.3	4.5 ± 1.0
20%STL	85.4 ± 0.5	41.6 ± 3.4	0.8 ± 0.2	0.8 ± 0.2	5.5 ± 1.1
5%STP	85.6 ± 1.3	50.4 ± 6.7	1.7 ± 0.4	1.7 ± 0.4	3.4 ± 0.4
10% STP	84.0 ± 0.7	45.9 ± 0.5	1.0 ± 0.4	1.0 ± 0.4	4.4 ± 0.7
15%STP	83.8 ± 1.1	52.5 ± 5.2	1.5 ± 0.7	1.5 ± 0.7	5.3 ± 1.5
20% STP	85.8 ± 1.8	48.5 ± 9.4	1.0 ± 0.4	1.0 ± 0.4	5.6 ± 0.7

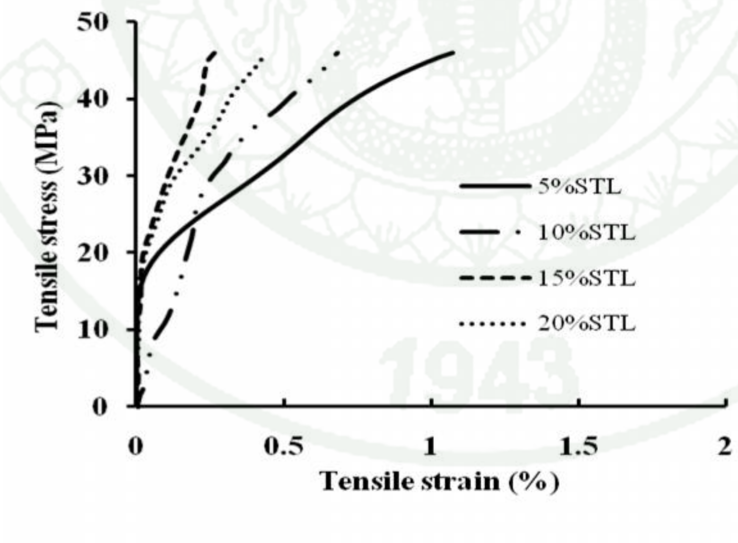


Figure 38 Tensile stress-strain curves of PLA/rice straw (STL, particle size ≥425µm) biocomposites with different rice starw content.

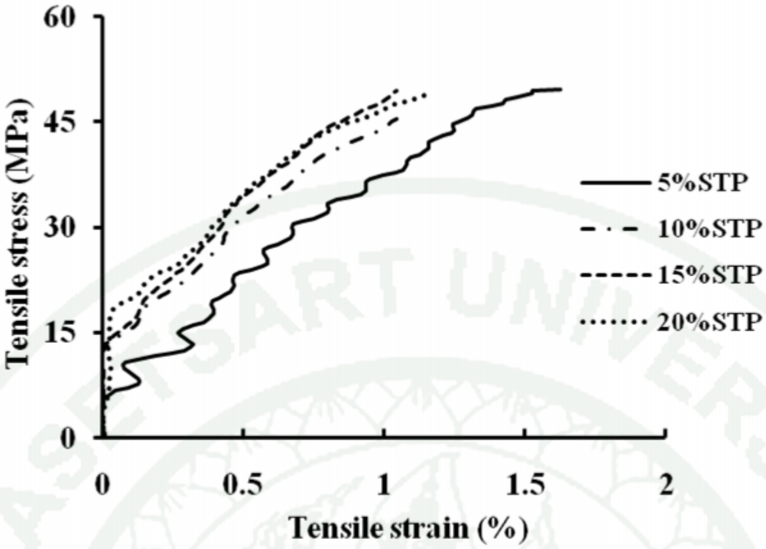


Figure 39 Tensile stress-strain curves of PLA/rice straw (STP, particle size ≤250 μm) biocomposites with different rice starw content.

Figure 40 and Figure 41 show the tensile strength at break, percentage of elongation at maximum load and Young's modulus of PLA/rice straw (STL, particle size ≥425 μm) and PLA/rice straw (STP, particle size ≤250 μm) biocomposites with different rice starw content respectively. Results show that percentage of elongation at maximum load are lower but the Young's modulus is slightly better for both PLA/rice straw (STL, particle size ≥425 μm) biocomposites and PLA/rice straw (STP, particle size ≤250 μm) biocomposites compared to pure PLA. While the tensile strength at break is lower for PLA/rice straw (STL, particle size ≥425 μm) biocomposites, but is better for PLA/rice straw (STP, particle size ≤250 μm) biocomposites compared to pure PLA. It is indicated that rice straw content with particle size ≥425 μm has a negative effect on PLA/rice straw (STL, particle size ≥425 μm) biocomposites strength compared to pure PLA.

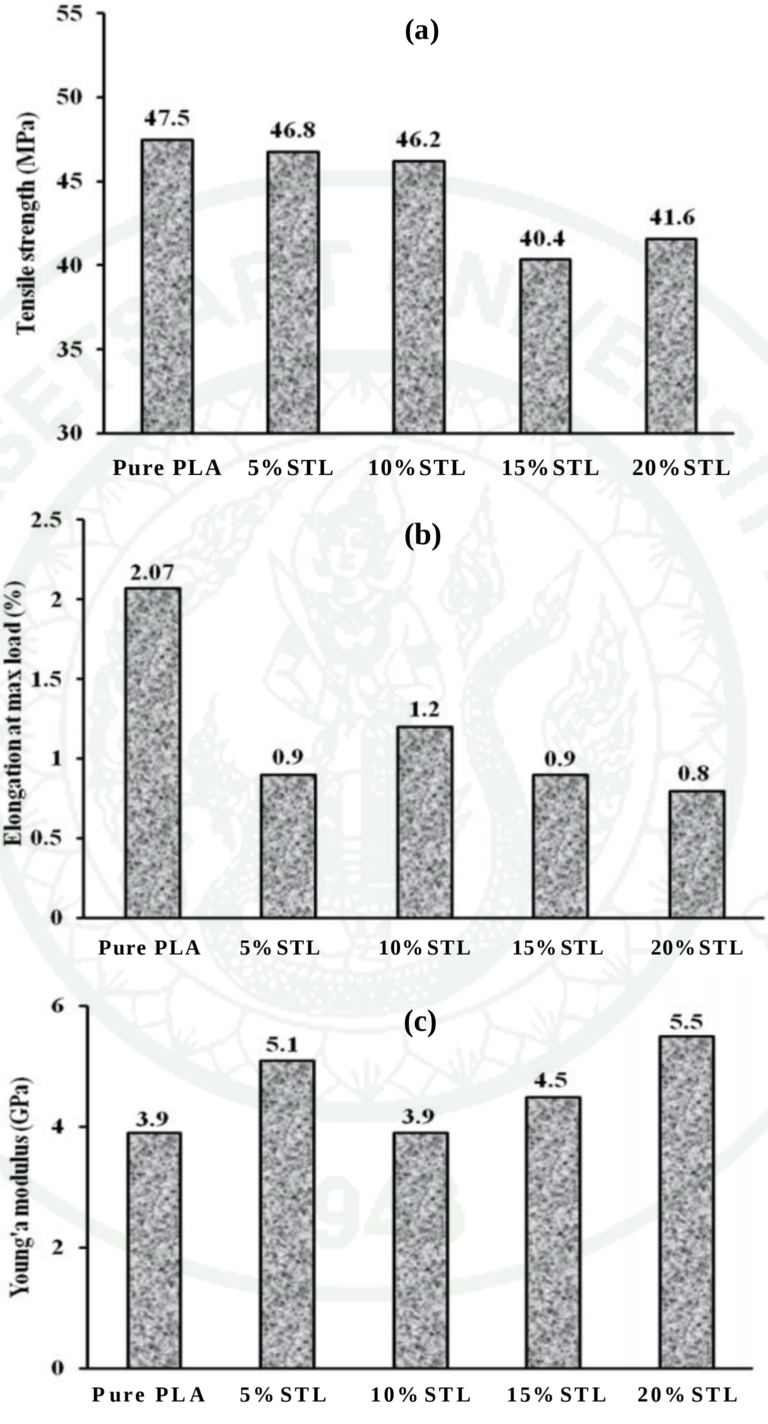


Figure 40 (a) Tensile strength at break (b) elongation at max load (c) Young’s modulus of PLA/rice straw (STL, particle size ≥425 µm) biocomposites.

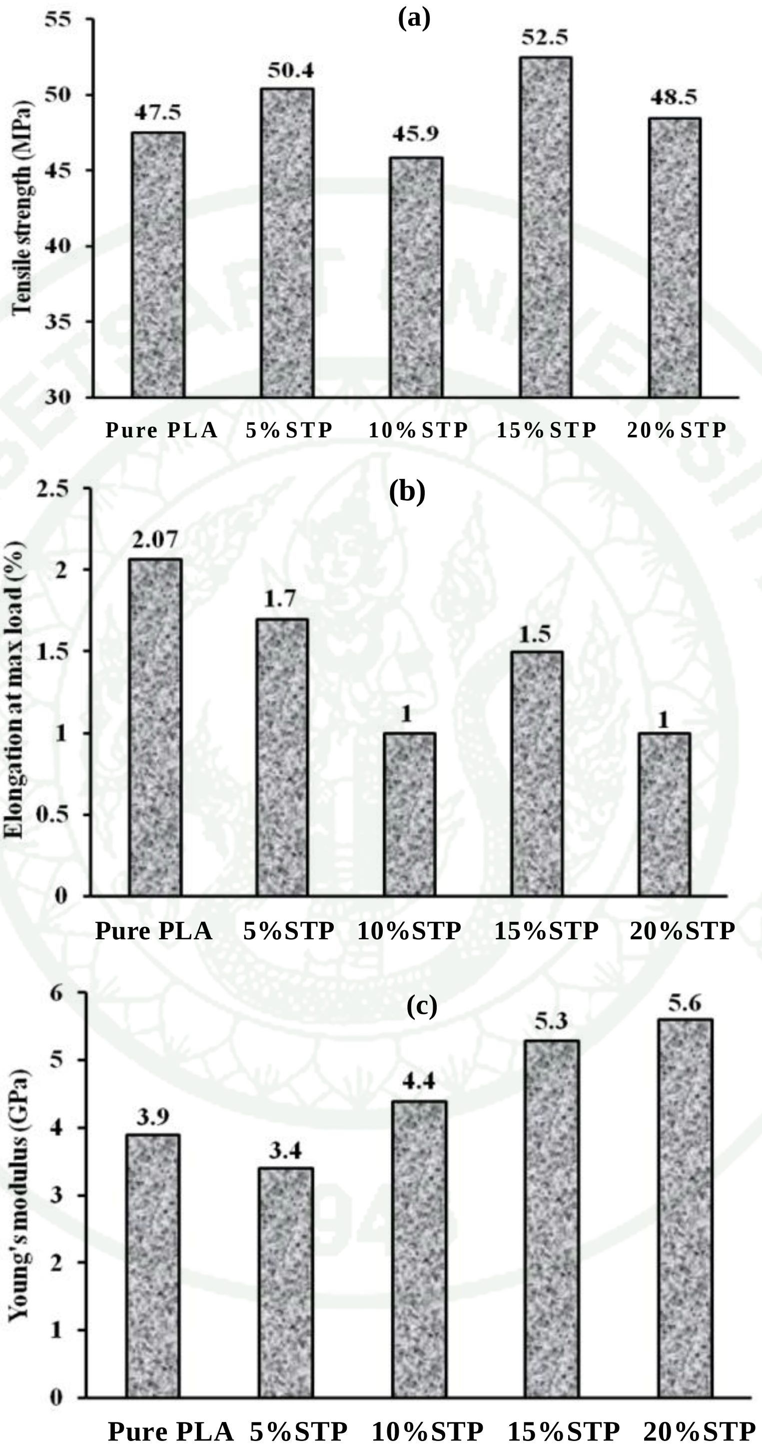


Figure 41 (a) Tensile strength at break (b) elongation at max load (c) Young's modulus of PLA/rice straw (STP, particle size ≤250 μm) biocomposites.

As already mentioned previously, the mechanical properties of PLA/ cellulosic fibers composites depend on a number of parameters such as volume fraction of the fibers, fiber aspect ratio, fiber-matrix adhesion, stress transfer at the interface, and orientation. The tensile strength is more sensitive to the matrix properties, whereas the modulus is dependent on the fiber properties. To improve the tensile strength, a strong interface, low stress concentration, fiber orientation is required whereas fiber concentration, fiber wetting in the matrix phase, and high fiber aspect ratio determine tensile modulus. The aspect ratio is very important for determining the fracture properties. In short-fiber reinforced composites, there exists a critical fiber length that is required to develop its full stressed condition in the polymer matrix. Fiber lengths shorter than this critical length lead to failure due to debonding at the interface a lower load. On the other hand, for fiber lengths greater than the critical length, the fiber is stressed under applied load and thus results in a higher strength of the composites.

PLA is a brittle polymer, and it seems that the brittleness even increases with the addition of rice straw fibers. The tensile strength at break of PLA/rice straw (STL, particle size ≥425 µm) biocomposites is decreasing from 47.5 MPa of pure PLA to 46.8MPa, 46.2 MPa, 40.4MPa and 41.6 MPa of PLA/rice straw (STL) = 95:5, 90:10, 85:15 and 80:20 wt% respectively. Thus, the decrease in tensile strength of PLA/rice straw (STL, particle size ≥425 µm) biocomposites is an indication of poor stress transfer across the interface, which means that there is practically no interfacial adhesion between the rice straw fiber and PLA matrix in PLA/STL rice straw biocomposites which is in agreement with the SEM results. The poor adhesion between the PLA matrix and STL rice straw fibers initiates the stress transfer to the fibers, which are the load bearing entities, becomes inefficient leading to low tensile strength values in PLA/STL rice straw fiber biocomposites. On the contrary, the tensile strength of PLA/rice straw (STP, particle size ≤250 µm) biocomposites is increases from 47.5 MPa for pure PLA to 50.4 MPa, 45.9 MPa, 52.5 MPa and 48.5 MPa for PLA/rice straw (STP) = 95:5, 90:10, 85:15 and 80:20 wt% respectively. The increasing of tensile strength at break of PLA/ STP rice straw fiber biocomposites could be due to the good interfacial adhesion between the PLA matrix and STP rice straw fibers, and is in agreement with the SEM results showing better adhesion between PLA matrix and the rice straw fiber in the PLA/ STP rice straw than PLA/ STL rice straw biocomposites. Although, both STL and STP rice straw fibers still remain as single fiber and there are no voids around PLA matrix and both STL and STP rice straw fibers interfaces.

The Results also show that tensile strength at break of PLA/rice straw (STL, particle size ≥425 µm) biocomposites decreases but PLA/rice straw (STP, particle size ≤250 µm) biocomposites increases with increasing the rice straw content. This could be due to a relatively good dispersion was achieved with low rice straw fiber contents in all PLA/rice straw biocomposites (Mathew *et al*., 2005).

The elongation at maximum load, for all PLA/rice straw biocomposites in this study is lower than that of pure PLA. The lower of elongation at max load with the addition of rice straws to PLA is common trend observed in thermoplastic composites. Comparison between PLA/rice straw (STL, particle size ≥425 µm) biocomposites and PLA/rice straw (STP, particle size ≤250 µm) biocomposites, the percentage of elongation at max load of PLA/rice straw (STP, particle size ≤250 µm) biocomposites is slightly higher than PLA/rice straw (STL, particle size ≥425 µm) biocomposites. The elongation at max load of PLA/rice straw (STL, particle size ≥425 µm) biocomposites decreases from 2.07% of pure PLA to 0.9%, 1.2%, 0.9% and 0.8% for PLA/rice straw (STL) = 95:5, 90:10, 85:15 and 80:20 wt% respectively. While elongation at max load of PLA/rice straw (STP, particle size ≤250 µm) biocompositesis decreasing from 2.07 MPa of pure PLA to 1.7%, 1.0%, 1.5% and 1.0% of PLA/rice straw (STP) = 95:5, 90:10, 85:15 and 80:20 wt% respectively. This may due to the embrittlement of longer rice straw (STL, particle size ≥425 µm) fibers in the PLA matrix.

As the standard deviation of elongation at max load values are within the limits of difference, therefore, it can be concluded that the elongation remains almost constant between 5% to 20% rice straw content.

The Young’s modulus of both PLA/rice straw biocomposites is increased by adding STL and STP rice straw fibers. These effects of lignocellulosic rice straw fiber reinforcement are in accordance with the results obtained in the previously study (Suryanegara *et al*., 2009). The Young’s modulus of PLA/rice straw (STL, particle size ≥425 µm) and PLA/rice straw (STP, particle size ≤250 µm) biocomposites are increasing from 3.9 GPa of pure PLA to 5.1 GPa, 3.9 GPa, 4.5 GPa and 5.5 GPa and to 3.4 GPa, 4.4 GPa, 5.3 GPa and 5.6 GPa of PLA/rice straw = 95:5, 90:10, 85:15 and 80:20 wt% respectively. It is found that the Young’s modulus of the both PLA/STL rice straw and PLA/STP rice straw biocomposites at 20 wt% content was improved from 3.9 GPa of pure PLA to 5.5-5.6 GPa. As already mentioned earlier, the Young's modulus is more dependent on the fiber properties. Thus, fiber content, and high fiber aspect ratio (L/D, length/diameter) do determine tensile Young'modulus. In general, a critical fiber length is required to develop its full stressed condition in the polymer matrix, and fiber lengths shorter than a critical length lead to failure due to debonding at the interface a lower load. On the other hand, for fiber lengths greater than the critical length, the fiber is stressed under applied load and thus results in a higher modulus or stiffness of the composites. Thus, it clearly shows that the Young’s modulus of both PLA/STL and PLA/STP rice straw biocomposites improve with increase of rice straw fiber content and length of the rice straw fibers.

Figure 42 and Figure 43 show the hardness (Shore D) of PLA/rice straw (STL, particle size ≥425 µm) and PLA/rice straw (STP, particle size ≤250 µm) biocomposites. Results of hardness indicate that there is a slightly increase in mean hardness (Shore D) from 82.0 of pure PLA to 85.4 and 85.8 for both PLA/rice straw = 80/20 biocomposites with particle size ≥425 µm (STL) and particle size ≤250 µm (STP) repectively. This indicates that the hardness of PLA/rice straw is not depended on the particle size of rice straw fiber but depends on the rice straw content. The hardness of PLA/rice straw biocomposites increases linearly with increasing the rice straw content from 5 wt% to 20 wt%. This indicates that both STL and STP contribute the same dispersion in the PLA matrix.

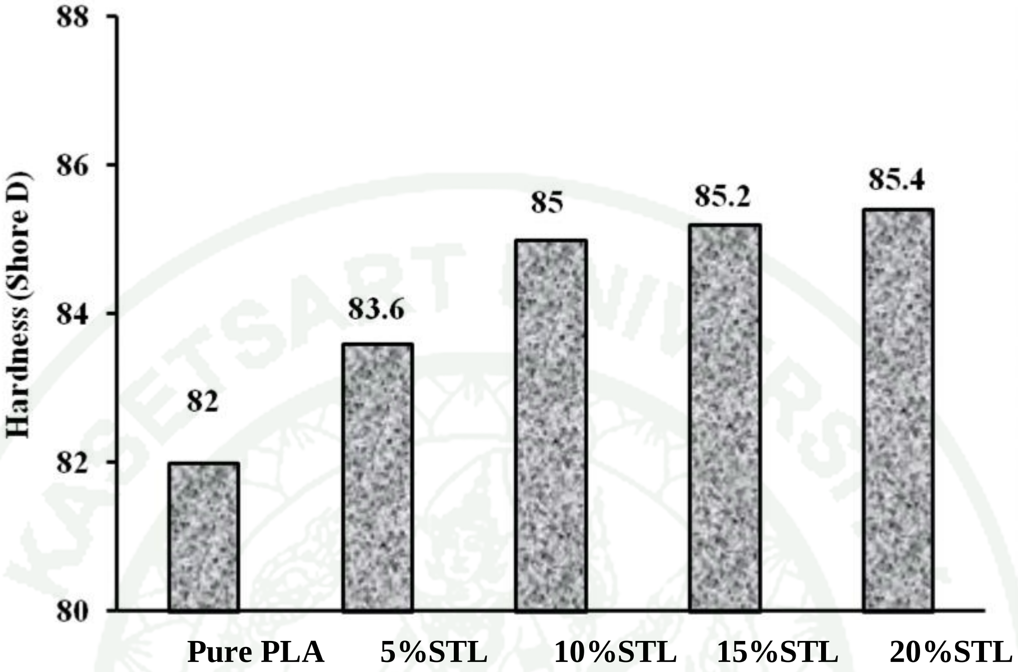


Figure 42 Hardness (Shore D) of PLA/rice straw (STL, particle size ≥425 µm) biocomposites.

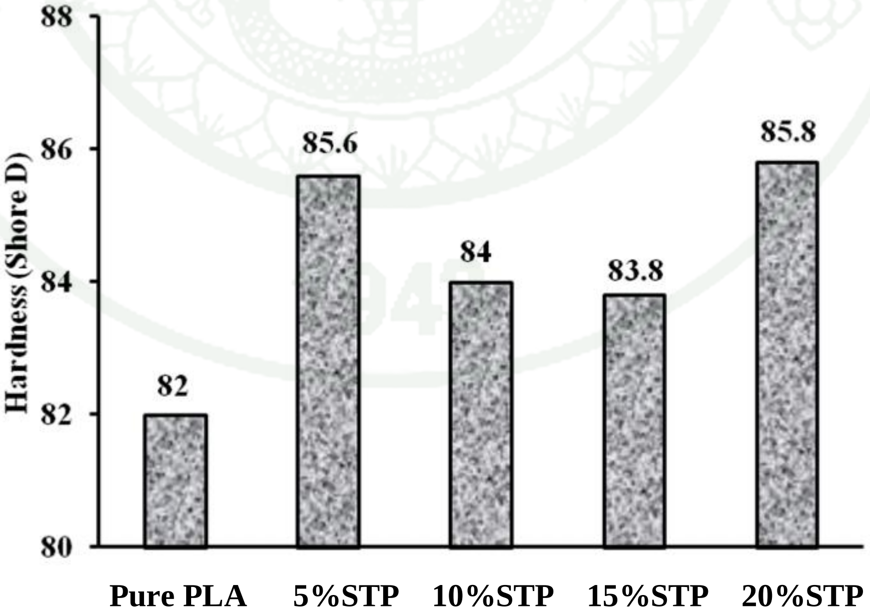


Figure 43 Hardness (Shore D) of PLA/rice straw (STP, particle size ≤250 µm) biocomposites.

4. Thermal properties

Table 13 summarizes the DSC measurements of PLA/rice straw (STL, particle size ≥425 µm) and PLA/rice straw (STP, particle size ≤250 µm) biocomposites. Figure 44 and Figure 45 show the results of the first heating scan DSC thermograms of PLA/rice straw (STL, particle size ≥425 µm) biocomposites and PLA/rice straw (STP, particle size ≤250 µm) biocomposites respectively showing the glass transition temperature (T_g), crystallization temperature (T_c) and melt temperature (T_m). Both PLA/rice straw (STL, particle size ≥425 µm) and PLA/rice straw (STP, particle size ≤250 µm) biocomposites show the same trend of glass transition temperature (T_g) and melt temperature (T_m) as pure PLA at around 60-62^{o}C and 150-152^{o}C respectively, but a slightly lower melt temperature (T_m) is observed from 173^{o}C and 166^{o}C of pure STL and STP rice straw fibers to 150^{o}C and 152^{o}C of PLA/STL and PLA/STP rice straw fibers biocomposites respectively. Additionally, an exothermic peak of crystallization temperature (T_c) is also observed at around 106-116^{o}C for both PLA/rice straw (STL, particle size ≥425 µm) and PLA/rice straw (STP, particle size ≤250 µm) biocomposites. This is an indication that the presence of rice straw fibers on both biocomposites can act as nucleating agent and attribute for the crystalline reorganization during heating on the PLA matrix, which is on agreement with the increasing of Young's modulus observed in both PLA/STL and PLA/STP rice straw fibers biocomposites.

Table 13 DSC measurements of PLA/rice straw (STL, particle size ≥425 µm) and PLA/rice straw (STP, particle size ≤250 µm) biocomposites.

Sample	T_g (^oC)	T_m (^oC)	T_c (^oC)
Pure PLA	61.9	151.5	-
Pure STL	-	173.5	-
Pure STP	-	165.9	-
5% STL	61.4	149.1	115.8
10% STL	60.2	150.6	108.3
15% STL	60.4	149.2	109.7
20% STL	61.5	149.4	110.2
5% STP	60.0	152.0	110.5
10% STP	59.8	150.5	110.4
15% STP	59.4	149.7	108.8
20% STP	60.1	149.2	106.2

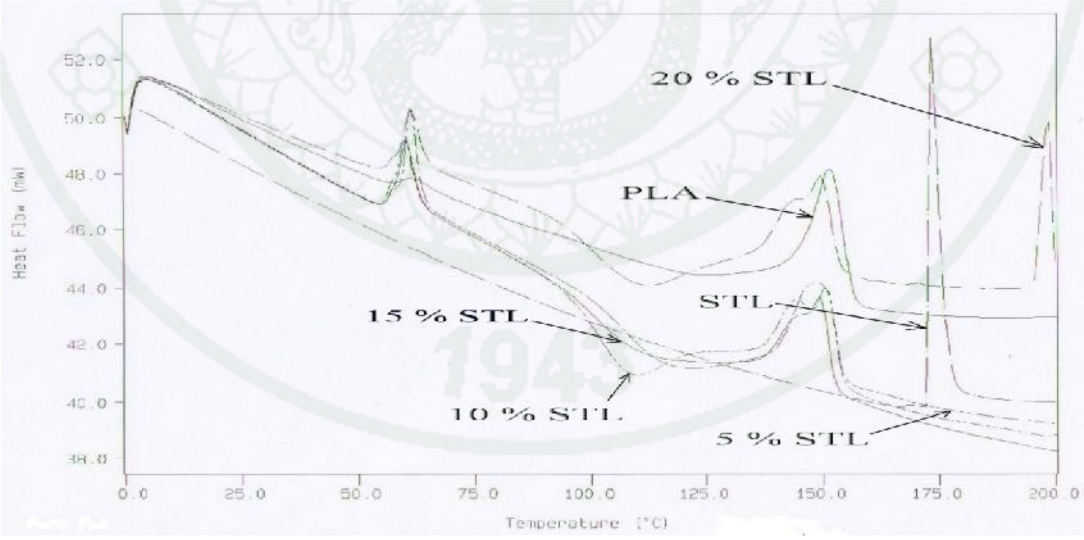


Figure 44 DSC thermogram of PLA/rice straw (STL, particle size ≥425 µm) biocomposites.

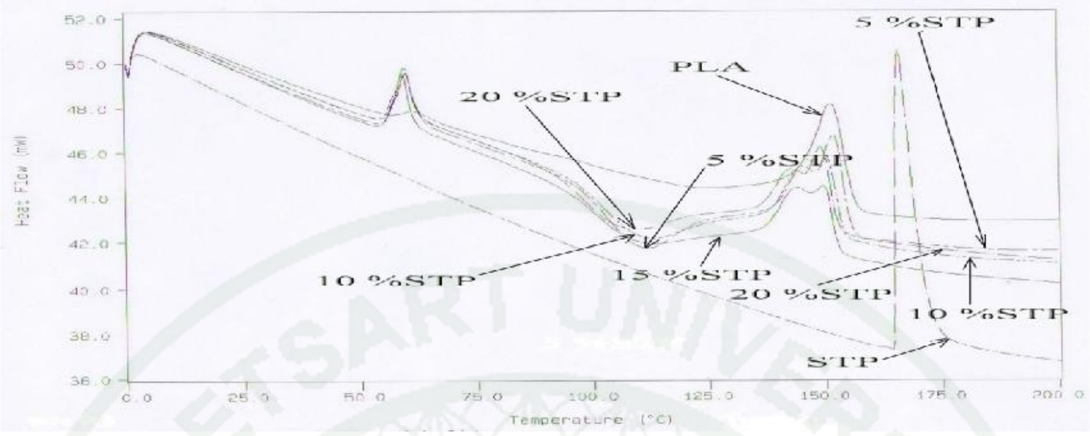


Figure 45 DSC thermogram of PLA/rice straw (STP, particle size ≤250 µm) biocomposites.

Thermogravimetric analysis (TGA) has been carried out to evaluate the thermal behavior of both PLA/rice straw (STL, particle size ≥425 µm) and PLA/rice straw (STP, particle size ≤250 µm) biocomposites with different rice straw content. Table 14 summarizes the TGA measurements of PLA/rice straw (STL, particle size ≥425 µm) and PLA/rice straw (STP, particle size ≤250 µm) biocomposites. Figure 46 and Figure 47 show the results of TGA thermograms of PLA/rice straw (STL, particle size ≥425 µm) biocomposites and PLA/rice straw (STP, particle size ≤250 µm) biocomposites respectively. The degradation temperature of rice straw fibers is crucial aspect to the PLA/rice straw biocomposites thermal properties. As can be seen from the figures, both rice straw (STL and STP) fibers start to degrade at about 250^{o}C. Hence, rice straw is suitable for using as reinforcement in PLA biocomposites since the rice straw are thermally stable up to 250^{o}C which is compatible with the PLA processing temperature. Results show that the onset temperature of both PLA/rice straw (STL, particle size ≥425 µm) and PLA/rice straw (STP, particle size ≤250 µm) biocomposites is closed to 300^{o}C and the weight loss decrease with an increase of both rice straw fibers content which is on agreement with most of results reported in the literature. Results also show that the PLA matrix degradation temperature and the corresponding onset temperature decrease with increasing the rice straw fibers content in both PLA/rice straw (STL, particle size ≥425 µm) and

PLA/rice straw (STP, particle size ≤250 µm) biocomposites, which are in contradiction with most degradable temperature of the PLA/cellulosic fiber composites reported in the literatures (Saheb and Jog, 1999; Avérous *et al*., 2006). Because of, degradation temperature of most reported of the natural fibers used in cellulosic composites are higher than the matrix, for example, degradation temperatures of 362°C and 332°C of natural fibers and matrix respectively were used by Avérous *et al*. (2006). In general, the degradation temperatures of composites are between the values of each component (fibers and matrix). Therefore, the maximum degradation temperatures at around 322-342°C of PLA/rice straw (STL, particle size ≥425 µm) and at around 313-337°C of PLA/rice straw (STP, particle size ≤250 µm) are observed which are in between the maximum degradation temperatures at 345°C of pure PLA matrix and at 286°C and 311°C of pure STL (particle size ≥425 µm) and STP (particle size ≤250 µm) rice straw respectively.

Table 14 TGA measurements of PLA/rice straw (STL, particle size ≥425 µm) and PLA/rice straw (STP, particle size ≤250 µm) biocomposites.

Sample	Onset Temperature (°C)	Maximum Temperature (°C)
Pure PLA	304.0	345.4
Pure STL	225.0	286.2
Pure STP	221.2	311.4
5% STL	287.7	341.7
10% STL	278.8	330.4
15% STL	272.7	324.9
20% STL	268.2	322.5
5% STP	287.9	336.6
10% STP	286.4	329.1
15% STP	272.7	326.0
20%STP	259.1	312.8

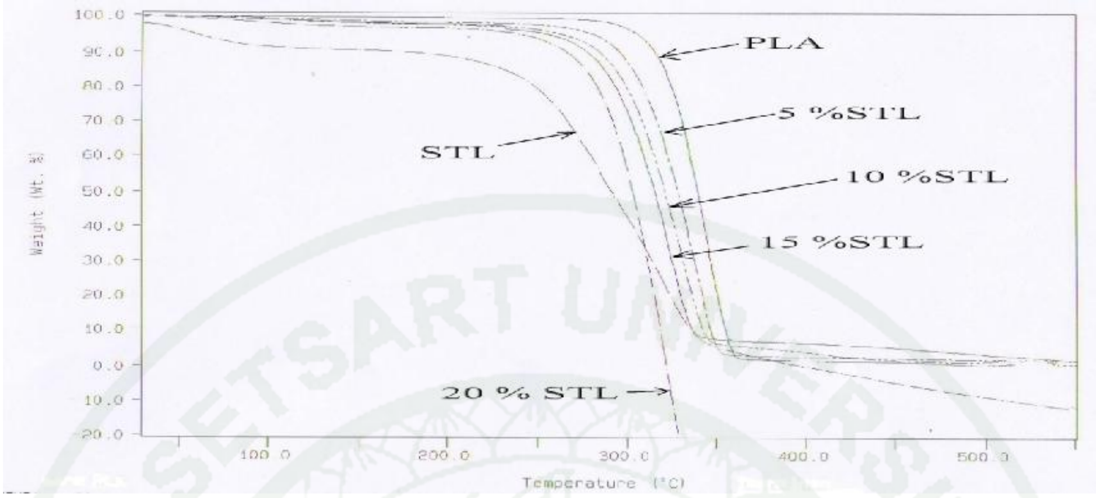


Figure 46 TGA thermogram of PLA/rice straw (STL, particle size ≥425 µm) biocomposites.

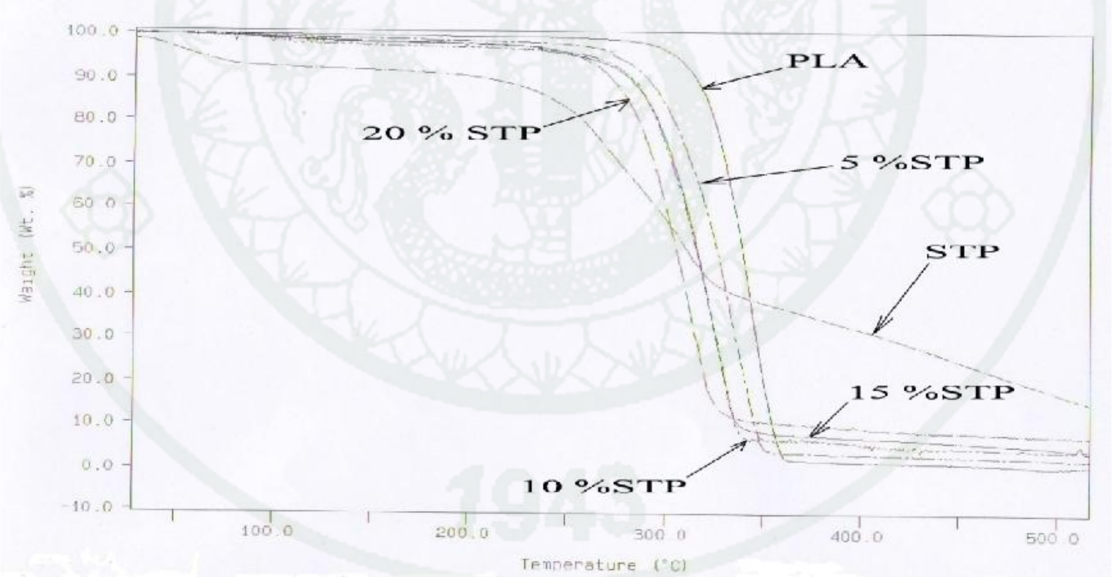


Figure 47 TGA thermogram of PLA/rice straw (STP, particle size ≤250 µm) biocomposites.

CONCLUSION

The chemical composition of rice straw fibers of both STL (particle size ≥425 µm) and STP (particle size ≤250 µm) was studied by TAPPI methods. Results showed that cellulose content was the ranges of 52.8-54.5% which is slightly higher when compared with the values reports in the literatures. Whereas, cellulose content (22%) of lignocellulosic rice straw isolated by method modified by Triakarabenjakul found was lower than the values obtained by analysis fron TAPPI method.

The morphology of PLA/rice straw biocomposites of both STL (particle size ≥425 µm) and STP (particle size ≤250 µm) found that PLA/rice straw(STL, particle size ≥425 µm) had a rougher surface than PLA/rice straw (STP, particle size ≤250 µm) and the biocomposites 20wt% rice straw content had a rougher surface when compared with lower rice straw contents. Both STL and STP still remain as single fiber and no voids around PLA matrix, but only STL rice straw pullout was oberved. These indicated that there is an adhesion between PLA matrix and STP rice straw but no adhesion between PLA matrix and STL rice straw.

The mechanical properties of PLA/rice staw biocomposites with different rice straw content showed that percentage of elongation at maximum load are lower than pure PLA but the Young's modulus is slightly better in both PLA/rice straw (STL and STP) biocomposites when compared with pure PLA. While the tensile strength at break is lower for PLA/rice straw (STL) but is better for PLA/rice atraw (STP) when compared with pure PLA. Whereas, the hardness of PLA/rice straw biocomposites is slightly increase with increasing the rice straw content from 5wt% to 20wt%.

The biocomposites of both PLA/rice straw (STL) (T_g = 60-62^{o}C and T_m = 149-150^{o}C) and PLA/rice straw (STP) (T_g = 60^{o}C and T_m = 150-152^{o}C) had the same trend of glass transition (T_g) and melt temperature (T_m) as pure PLA (T_g = 61.9^{o}C and T_m = 152^{o}C) but slightly lower than melt temperature of pure STL (T_m = 173.5^{o}C) and STP (T_m =165.9^{o}C) rice straw. In addition, an exothermic crystallization temperature

(T_c) peak at about 106-116°C for both PLA/rice straw (STL and STP) showed that rice straw fibers can act as nucleating agent and attribute for the crystalline reorganization during heating on the PLA matrix.

The thermogravimetric measurements of both PLA/rice straw (STL and STP) biocomposites showed that the PLA matrix degradation temperature and the corresponding onset temperature decrease when the rice straw content increase which was in contradiction with most degradable temperature of the PLA/cellulosic fiber composites reported in the literatures. Although the weight loss of both PLA/rice straw (STL and STP) biocomposites decreases with an increase of both rice straw fiber content. However, the degradation temperatures of both PLA/rice straw biocomposites (PLA/STL = 322-342°C, PLA/STP = 313-337°C) are in between the values of both PLA (345°C) and rice straw (STL= 286°C and STP = 311°C) components.

LITERATURE CITED

Alemdar, A. and M. Sain. 2008. Biocomposites from wheat straw nanofibers: morphology, thermal and mechanical properties. **Composites Science and Technology**. 68(2): 557-565.

Anouk, V., M. Roggeman, S. Bouillon, M. Elskens, H. Beeckman and N. Koedam. 2005. Comparison between δ^{13}C of α-cellulose and bulk wood in the mangrove tree Rhizophora mucronata: implications for dendrochemistry. **Chemical Geology**. 219: 275-282.

Avella, M., G. La Rota, E. Martuscelli, M. Raimo, P. Sadocco, G. Elegir and R. Riva. 2000. Poly(3-hydroxybutyrate-co-3-hydroxyvalerate) and wheat straw fibre composites: thermal, mechanical properties and biodegradation behaviour. **Journal of Materials Science**. 35(4): 829–836.

Avérous, L., C. Fringant and L. Moro. 2001. Plasticized starch-cellulose interactions in polysaccharide composites. **Polymer**. 42(15): 6571–6578.

Avérous, L. 2004. Biodegradable multiphase systems based on plasticized starch: a review. **Journal of Macromolecular Science – Part C:Polymer Reviews**, C4(3): 231–274.

Avérous, L. and N. Boquillon. 2004. Biocomposites based on plasticized starch: thermal and mechanical behaviours. **Carbohydrate Polymers**. 56(2): 111–122.

Avérous, L. and F. Le Digabel. 2006. Properties of biocomposites based on lignocellulosic filler. **Carbohydrate Polymers**. 66: 480-493.

Avérous, L. 2007. Cellulose-based biocomposites:comparison of different multiphasic systems. **Composites Interface**. 14(7-9): 787-805.

Bledzki, A. K. and J. Gassan. 1999. Composites reinforced with cellulose based fibres. **Progress in Polymer Science**. 24: 221–274.

Bledzki, A. K. and A. Jaszkiewicz. 2010. Mechanical performance of biocomposites based on PLA and PHBV reinforced with natural fibres – A comparative study to PP. **Composites Science and Technology**. 70: 1687-1696.

Bourban, Ch. E. Karamuk, M. J. De Fondaumiere, K. Ruffieux, J. Mayer and E. Wintermantel. 1997. Processing and characterization of a new biodegradable composite made of a PHB/V matrix andregenerated cellulosic fibers. **Journal of Environmental Polymer Degradation**. 5(3): 159–166.

Browning, B. L. 1967. **Methods of wood chemistry**. New York. Interscience Publisher.

DEDE. 2003. In: DEDE, Editor. Rice in Thailand. **Department of Alternative Energy Development and Efficiency** (DEDE). p. 43.

Dobreva, J. M., E. Perena, R. Perez, R. Benavente and M. Garcia. 2009. Effect of Different Thermal Treatments on the Mechanical Performance of Poly (L-lactic acid) Based Eco-composites. **Journal of Applied Polymer Science**. 116(2): 1088-1098.

Dobreva, J. M., E. Perena, R. Perez, R. Benavente and M. Garcia. 2010. Crystallization behavior of poly(L-lactic acid)-based ecocomposites prepared with kenaf fiber and rice straw. **Polymer Composites**. 31(6): 974-984.

Eichhorn, S. J., C.A. Baillie, N. Zafeiropoulos, L.Y. Mwaikambo, M.P. Ansell, A. Dufresne, K.M. Entwistle, P.J. Herrera-Franco, G.C. Escamilla, L. Groom, M. Hughes, C. Hill, T.G. Rials and P.M. Wild. 2001. Current international research into cellulose fibres and composites. **Journal of Materials Science**. 36: 2107-2131.

Favier, V., R. Dendievel, G. Canova, J. Y. Cavaille and P. Gilormini. 1997. Simulation and modeling of three-dimensional percolating structures: case of a latex matrix reinforced by a network of cellulose fibers. **Acta Materialia**. 45(4): 1557–1565.

Fernandes, E. G., M. Pietrini, and E. Chiellini. 2004. Bio-based polymeric composites comprising wood flour as filler. **Biomacromolecules.** 5(4): 1200–1205.

Gadde, B., C. Menke and R. Wassmann. 2009. Rice straw as a renewable energy source in India, Thailand, and the Philippines: Overall potential and limitations for energy contribution and greenhouse gas mitigation. **Biomass and Bioenergy**. 33(11): 1532-1546.

Garay, R.M.M., M. de la B Rallo, R. C. Carmona and J. C. Araya. 2009. Characterization of anatomical, chemical, and biodegradable properties of fibers from corn, wheat, and rice residues. **Chilean Journal of Agricultural Research**. 69(3): 406-415.

Gonzalez, C. and G. E. Myers. 1993. Thermal degradation of wood fillers at the melt-processing temperatures of wood-plastic composites: effects on wood mechanical properties and production of volatiles. **International Journal of Polymeric Materials.** 23(1& 2): 67-85.

Hornsby, P. R., E. Hinrichsen and K. Tarverdi. 1997. Preparation and properties of polypropylene composites reinforced with wheat and flax straw fibers. Part II: Analysis of composite microstructure and mechanical properties. **Journal of Materials Science**. 32: 1009–1015.

Jiang, H. H., D. P. Kamdem, B. Bezubic and P. Ruede. 2003. Mechanicl properties of poly(vinyl chloride)/wood flour/glass fiber hybrid composites. **Journal of Vinyl and Additive Technology**. 9(3): 138-145.

Jonoobi, M., J. Harun, A.P. Mathew and K. Oksman. 2010. Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. **Composites Science and technology**. 70: 1742-1747.

Kuruvilla, J., T. Sabu, C. Pavithran and M. Brahmakumar. 1993. Tensile properties of short fiber-reinforced polyethylene composites. **Journal of Applied Polymer Science**. 47(10): 1731-1739.

Le Digabel, F., N. Boquillon, P. Dole, B. Monties and L. Avérous. 2004. Properties of thermoplastic composites based on wheat straw lignocellulosic fillers. **Journal of Applied Polymer Science**. 93(1): 428–436.

Lequart, C., K. Ruel, C. Lapierre, B. Pollet and B. Kurek. 2000. Abiotic and enzymatic degradation of wheat straw cell wall: a biochemical and ultrastructural investigation. **Journal of Biotechnology**. 80: 249–259.

Luo, S. and A. N. Netravali. 1999. Interfacial and mechanical properties of environment-friendly ‘‘green’’ composites made from pineapple fibers and poly(hydroxybutyrate-co-valerate) resin. **Journal of Materials Science**. 34(15): 3709–3719.

Mathew, A. P., K. Ossman, M. Sain. 2005. Mechanical properties of biodegradable composites from polylactic acid (PLA) and microcrystalline cellulose (MCC). **Journal Applied Polymer Science**. 97(5): 2014-2025.

Mohanty, A. K., M. A. Khan and G. Hinrichsen. 2000a. Surface modification of jute and its influence on performance of biodegradable jute-fabric/Biopol composites. **Composites Science and Technology**. 60(7): 1115–1124.

Mohanty, A. K., M. A. Khan and G. inrichsen. 2000b. Influence of chemical surface modification on the properties of biodegradable jute fabrics – polyester amide composites. **Composites Part A: Applied Science and Manufacturing**. 31(2): 143–150.

Mohanty, A. K., M. Misra and T. Drzal. 2002. Sustainable bio-composites from renewable resources: opportunities and challenges in the green materials world. **Journal of Polymers and the Environment.** 10(1/2): 19-26.

Mosier, N., C. Wyman, B. Dale, R. Elander, Y. Y. Lee, M. Holtzapple and M. Ladisch. 2005. Features of promising technologies for preteatment of lignocellulosic biomass. **Bioresources Technology**. 96: 673-686.

Myers G. E., I. S. Chahyadi, C. Gonzalez, C. A. Coberly and D. S. Ermer. 1991. Wood flour and polypropylene or high density polyethylene composites: influence of maleated polypropylene concentration and extrusion temperature on properties. **International Journal of Polymeric Materials.** 15(3& 4): 171-186.

Nakagaito, A. N, A. Fujimura, T. Sakai, Y. Hama and H. Yano. 2009. Production of microfibrillated cellulose (MFC)-reinforced polylactic acid (PLA) nanocomposites from sheets obtained by a papermaking-like process. **Composites Science and Technoloy**. 2009: 1293-1297.

Netravali, A. N. and S. Chabba. 2003. Composites get greener. **Materials Today**. 6(4): 22–29.

Nguyen, T., E. Zavarin and E. M. Barrall II. 1981a. Thermal analysis of lignocellulosic materials. Part I. Unmodified materials. **Journal of Macromolecular Science, Part C: Polymer Reviews**. C20: 1-65.

Nguyen, T., E. Zavarin and E. M. Barrall II. 1981b. Thermal analysis of lignocellulosic materials. Part II. Modified materials. **Journal of Macromolecular Science, Part C: Polymer Reviews**. C21: 1-60.

Nishino, T., K. Hirao, M. Kotera, K. Nakamae and H. Inagaki. 2003. Kenaf reinforced biodegradable composite. **Composites Science and Technology**. 63(9): 1281–1286.

Oksman, K., M. Skrifvars and J.-F. Selin. 2003. Natural fibres as reinforcement in polylactic acid (PLA) composites. **Composites Science and Technology**. 63(9): 1317–1324.

Okubo, K., T. Fujii and Y. Yamamoto. 2004. Development of bamboo-based polymer composites and their mechanical properties**. Composites:Part A**. 35: 377-383.

Plackett, D., T. Logstrup Andersen, W. Batsberg Pedersen and L. Nielsen. (2003). Biodegradable composites based on L-polylactide and jute fibres. **Composites Science and Technology**. 63(9): 1287–1296.

Qin, L. J., J. H. Qiu, M. Z. Liu, S. L. Ding, L. Shao, G. H. Zhang and Y. Zhao. 2011. Composites of poly(lactic acid) with rice straw fibers modified by poly(butyl acrylate). **Materials Science Forum**. 675-677: 357-360.

Ruseckaite, C. R. and A. Jiménez. 2003. Thermal degradation of mixtures of polycaprolactone with cellulose derivatives. **Polymer Degradation and Stability**. 81(2): 353–358.

Saheb, D. N. and Jog, J. P. 1999. Natural fiber polymer composites: a review. **Advances in Polymer Technology**. 18: 351-363.

Sang O. Y., F. Twaiq, R. Zakaria, A. Mohamed and S. Bhatia. 2003. Biofuel production from catalytic cracking of palm oil. **Energy Sources**: **Part A**. 25: 859-869.

Serizawa, S., K. Inoue and I. Masatoshi. 2006. Kenaf-fiber reinforced poly(lactic acid) used for electronic products. **Journal of Applied Polkymer Science**. 100: 618-624.

Södergård A. and M. Stolt. 2002. Properties of lactic acid based polymers and their correlation with composition. **Progress in Polymer Science**. 27(6): 1123-1163.

Sridhar, M., G. Basavarajjappa, S. Kasturi and N. Balasubramanian. 1982. Evaluation of jute as reinforcement in composites. **Indian Journal of Textile Research**. 7: 87-92.

Summers, M. D. 2000. **Fundamental properties of rice Straw in comparison with softwoods**. Requirements of ESPM 286: Physiscal properties of Wood. Forest Products Laboratory, University of California.

Suryanegara, L., N., A. N. Nakagaito and H. Yano. 2009. The effect of crystallization of PLA on the thermal and mechanical properties of microfibrillated cellulose-reinforced PLA composites. **Composites Science and Technology**. 69: 1187-1192.

Takase, S. and N. Shiraishi. 1989. Studies on composites from wood and polypropylenes II. **Journal Applied Polymer Science**. 37: 645-659.

Triakarabenjakul, S. 2006. Production of carboxymethylcellulose from rice straw for food application. M.S. **Asian Institute of Technology**.

Van de Velde, K. and P. Kiekens. 2002. Biopolymers: overview of several properties and consequences on their applications. **Polymer Testing**. 21(4): 433–442.

Wollerdorfer, M. and H. Bader. 1998. Influence of natural fibres on the mechanical properties of biodegradable polymers. **Industrial Crops and Products**. 8: 105–112.

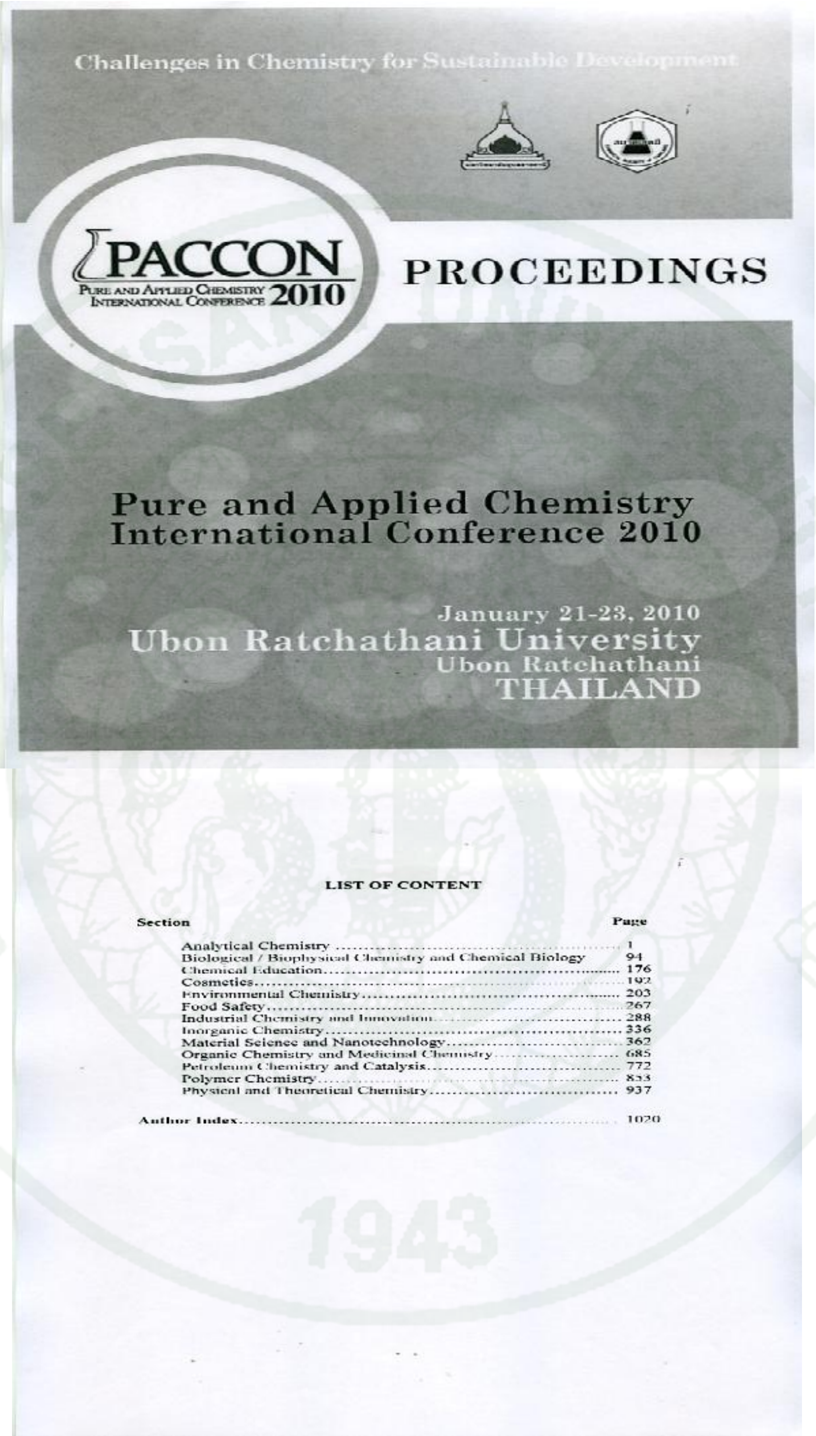
Xiao, B., X. F. Sun and R-C. Sun. 2001. Chemical, structural and thermal characterization of alkali soluble lignin and hemicelluloses, and cellulose from maize, stems, rye straw, and rice straw. **Polymer Degradation and Stability**. 74: 307-319.

Yao, F., Q. Wu, Y. Lei and Y. Xu. 2008. Rice straw fiber reinforced high density polyethylene composites: effect of fiber type and loading. **Journal of Industrial Crops and Products**. 28: 63-72.

Yu, L., K. Dean and L. Li. 2006. Polymer blends and composites from renewable resources. **Progress in Polymer Science**. 31: 576-602.

Zheng, Y., Z. L. Pan and R. H. Zhang. 2009. Overview of biomass pretreatment for cellulosic etanol production. **International Journal of Agricultural and Biological Engineering**. 2(3): 51-68.

APPENDIX



Challenges in Chemistry for Sustainable Development

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Poly(lactic acid)/lignocellulosic filler from rice straw biocomposites

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Abstract: Biocomposites were obtained by the combination of biodegradable poly(lactic acid) (PLA) matrix and biodegradable lignocellulosic filler (LCF). Among biodegradable polymers, PLA has a great potential to replace petroleum–based plastics, however, PLA has some limitations such as high cost, high glass transition temperature, brittleness and low crystallization rate. To improve these properties, composites with renewability, environmental friendly, low cost and low density lignocellulosic filler were investigated. The LCF used was from rice straw. The objective of this study was to process and to characterize thermal and mechanical behaviors of PLA/LCF biocomposites. The matrix PLA and the LCF were mixed in chloroform, followed by drying, kneading and hot pressing into sheet. The biocomposites thermal stability behavior has been investigated by TGA (thermal gravimetric analysis) and DSC (differential scanning calorimeter). PLA/LCF biocomposites showed an addition crystallization (T_c) peak at 106.2-115.8°C from the DSC measurements. The impacts of the cellulose fiber content (5%, 10%, 15% and 20 wt%), size (>40 mesh and <60 mesh) on the mechanical of the biocomposites have been investigated. It was found that tensile modulus of PLA/LCF biocomposites was increased by adding of LCF, whereas the tensile strength was decreased by adding the LCF.

Introduction

Over the last two decades, polymers from renewable resources or bio-based polymers have attracted an increasing amount of attention predominantly due to two major reasons: firstly environmental concerns, and secondly the realization those petroleum resources are finite. Generally, polymers from renewable resources can be classified into three groups: (1) natural polymers, such as starch, protein and cellulose; (2) synthetic polymers from natural monomers, such as poly(lactic acid) (PLA); and (3) polymers from microbial fermentation, such as polyhydroxyalkanoate (PHA). A large number of these biodegradable polymers are commercially available. They show a large range of properties and at present, they can compete with non-biodegradable polymers in different industrial fields (e.g., packaging, agriculture, hygiene, and cutlery).

Biodegradable polymers are rarely used by themselves. Generally, fibers, such as carbon fibers and glass fibers are widely used to improve their mechanical properties. However, these fiber-reinforced polymeric composites cause environmental problems upon disposal. Reinforcements of biodegradable polymers by utilizing renewability, environmentally friendly, low cost and low density natural lignocellulosic fibers are required to obtain fully biodegradable composites together with to improve mechanical properties. Since both components are biodegradable, the biocomposites (biodegradable composites) are also expected to be biodegradable. A large number of biocomposites have been investigated in association with diverse lignocellulosic fibers from various origins such as bleached cellulose fibers, bamboo fibers or flax, oil palm, jute or ramie fibers [1-5]

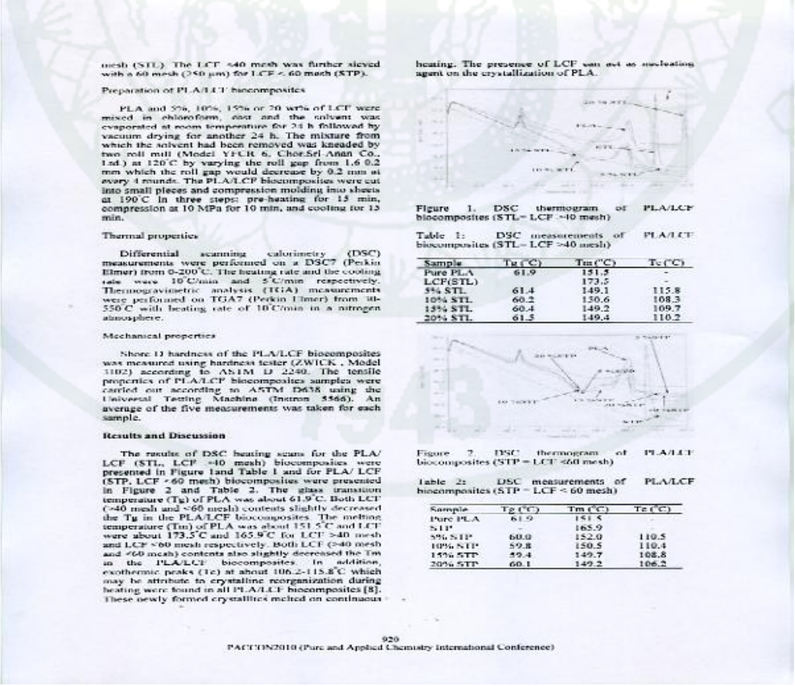
Rice straw is principally used as animal feed, and as raw material for fiber in paper industry. Burning is still the most common practice for rice straw disposal resulting in emissions to air that have a deleterious effect on air quality and human health [6-7]. Utilization of rice straw as an alternate for reinforcements of biocomposites is not only reducing greenhouse gas emission from open burning the rice straw but also gaining monetary value of these agricultural wastes.

Among biodegradable polymers, poly(lactic acid) (PLA) has a great potential to replace petroleum-based plastics because of its high stiffness and strength. Thailand is the world's top producer and exporter of tapioca, derived from cassava, and its second biggest sugar exporter, two crops in demand for the production of lactic acid, the precursor for production of poly(lactic acid). As Thailand is an agricultural country, it is a potential base to produce biomass plastic material and this would be a new business opportunity for the country. Development of new technologies, emergence of new end-use applications, and evolution of new markets are all expected to offer opportunities for future growth.

This paper described thermal and mechanical properties of biocomposites based on biodegradable poly(lactic acid) (PLA) and rice straw lignocellulosic filler (LCF) with the goal to obtain fully biodegradable composites together with to improve mechanical properties.

Materials and Methods

PLA used was Polymer 2002D from NatureWorks ($\overline{M}_w$ = 155741). LCF used was from rice straw. It was washed and dried in oven at 60±5°C for 2 days, milled, sieved with a 40 mesh (425 μm) for LCF >40 mesh (STL). The LCF <40 mesh was further sieved with a 60 mesh (250 μm) for LCF < 60 mesh (STP).



Preparation of PLA/LCF biocomposites

PLA and 5%, 10%, 15% or 20 wt% of LCF were mixed in chloroform, cast and the solvent was evaporated at room temperature for 24 h followed by vacuum drying for another 24 h. The mixture from which the solvent had been removed was kneaded by two roll mill (Model YFCR 6, Chor.Sri-Anan Co., Ltd.) at 120°C by varying the roll gap from 1.6-0.2 mm which the roll gap would decrease by 0.2 mm at every 4 rounds. The PLA/LCF biocomposites were cut into small pieces and compression molding into sheets at 190°C in three steps: pre-heating for 15 min, compression at 10 MPa for 10 min, and cooling for 15 min.

Thermal properties

Differential scanning calorimetry (DSC) measurements were performed on a DSC7 (Perkin Elmer) from 0-200°C. The heating rate and the cooling rate were 10°C/min and 5°C/min respectively. Thermogravimetric analysis (TGA) measurements were performed on TGA7 (Perkin Elmer) from 30-550°C with heating rate of 10°C/min in a nitrogen atmosphere.

Mechanical properties

Shore D hardness of the PLA/LCF biocomposites was measured using hardness tester (ZWICK , Model 3102) according to ASTM D 2240. The tensile properties of PLA/LCF biocomposites samples were carried out according to ASTM D638 using the Universal Testing Machine (Instron 5566). An average of the five measurements was taken for each sample.

Results and Discussion

The results of DSC heating scans for the PLA/LCF (STL, LCF >40 mesh) biocomposites were presented in Figure 1and Table 1 and for PLA/ LCF (STP, LCF <60 mesh) biocomposites were presented in Figure 2 and Table 2. The glass transition temperature (Tg) of PLA was about 61.9°C. Both LCF (>40 mesh and <60 mesh) contents slightly decreased the Tg in the PLA/LCF biocomposites. The melting temperature (Tm) of PLA was about 151.5°C and LCF were about 173.5°C and 165.9°C for LCF >40 mesh and LCF <60 mesh respectively. Both LCF (>40 mesh and <60 mesh) contents also slightly decreased the Tm in the PLA/LCF biocomposites. In addition, exothermic peaks (Tc) at about 106.2-115.8°C which may be attribute to crystalline reorganization during heating were found in all PLA/LCF biocomposites [8]. These newly formed crystallites melted on continuous heating. The presence of LCF can act as nucleating agent on the crystallization of PLA.

Figure 1. DSC thermogram of PLA/LCF biocomposites (STL= LCF >40 mesh)

Table 1: DSC measurements of PLA/LCF biocomposites (STL= LCF >40 mesh)

Sample	Tg (°C)	Tm (°C)	Tc (°C)
Pure PLA	61.9	151.5	-
LCF(STL)		173.5	-
5% STL	61.4	149.1	115.8
10% STL	60.2	150.6	108.3
15% STL	60.4	149.2	109.7
20% STL	61.5	149.4	110.2

Figure 2. DSC thermogram of PLA/LCF biocomposites (STP = LCF <60 mesh)

Table 2: DSC measurements of PLA/LCF biocomposites (STP = LCF < 60 mesh)

Sample	Tg (°C)	Tm (°C)	Tc (°C)
Pure PLA	61.9	151.5	-
STP	-	165.9	-
5% STP	60.0	152.0	110.5
10% STP	59.8	150.5	110.4
15% STP	59.4	149.7	108.8
20% STP	60.1	149.2	106.2

Appendix Figure 1 (Continued)

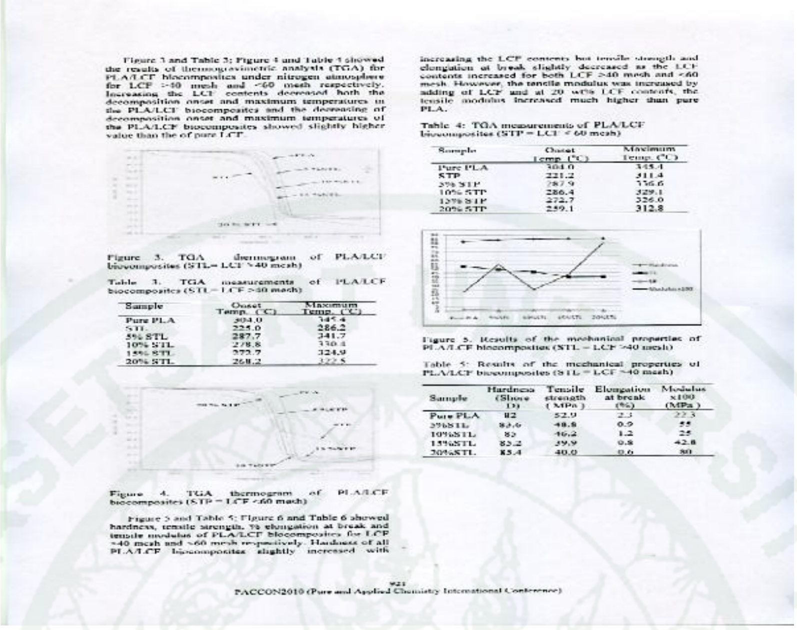


Figure 3 and Table 3; Figure 4 and Table 4 showed the results of thermogravimetric analysis (TGA) for PLA/LCF biocomposites under nitrogen atmosphere for LCF >40 mesh and <60 mesh respectively. Increasing the LCF contents decreased both the decomposition onset and maximum temperatures in the PLA/LCF biocomposites and the decreasing of decomposition onset and maximum temperatures of the PLA/LCF biocomposites showed slightly higher value than the of pure LCF.

Figure 3. TGA thermogram of PLA/LCF biocomposites (STL= LCF >40 mesh)

Table 3. TGA measurements of PLA/LCF biocomposites (STL = LCF >40 mesh)

Sample	Onset Temp. (°C)	Maximum Temp. (°C)
Pure PLA	304.0	345.4
STL	225.0	286.2
5% STL	287.7	341.7
10% STL	278.8	330.4
15% STL	272.7	324.9
20% STL	268.2	322.5

Figure 4. TGA thermogram of PLA/LCF biocomposites (STP = LCF <60 mesh)

Figure 5 and Table 5; Figure 6 and Table 6 showed hardness, tensile strength, % elongation at break and tensile modulus of PLA/LCF biocomposites for LCF >40 mesh and <60 mesh respectively. Hardness of all PLA/LCF biocomposites slightly increased with increasing the LCF contents but tensile strength and elongation at break slightly decreased as the LCF contents increased for both LCF >40 mesh and <60 mesh. However, the tensile modulus was increased by adding of LCF and at 20 wt% LCF contents, the tensile modulus increased much higher than pure PLA.

Table 4: TGA measurements of PLA/LCF biocomposites (STP = LCF < 60 mesh)

Sample	Onset Temp. (°C)	Maximum Temp. (°C)
Pure PLA	304.0	345.4
STP	221.2	311.4
5% STP	287.9	336.6
10% STP	286.4	329.1
15% STP	272.7	326.0
20% STP	259.1	312.8

Figure 5. Results of the mechanical properties of PLA/LCF biocomposites (STL = LCF >40 mesh)

Table 5: Results of the mechanical properties of PLA/LCF biocomposites (STL = LCF >40 mesh)

Sample	Hardness (Shore D)	Tensile strength (MPa)	Elongation at break (%)	Modulus x100 (MPa)
Pure PLA	82	52.9	2.3	22.3
5%STL	83.6	48.8	0.9	55
10%STL	83	46.2	1.2	25
15%STL	83.2	39.9	0.8	42.8
20%STL	85.4	40.0	0.6	80

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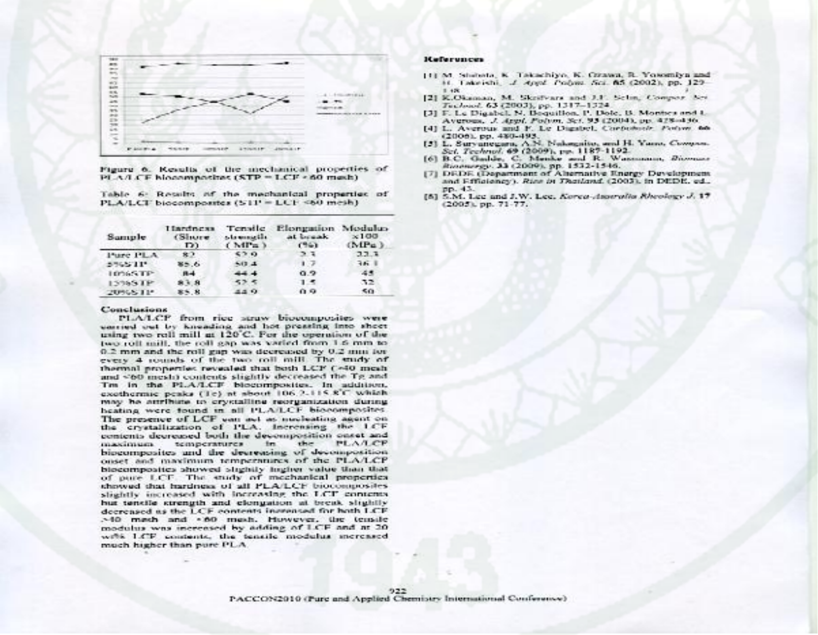

Figure 6. Results of the mechanical properties of PLA/LCF biocomposites (STP = LCF <60 mesh)

Table 6: Results of the mechanical properties of PLA/LCF biocomposites (STP = LCF <60 mesh)

Sample	Hardness (Shore D)	Tensile strength (MPa)	Elongation at break (%)	Modulus x100 (MPa)
Pure PLA	82	52.9	2.3	22.3
5%STP	85.6	50.4	1.7	36.1
10%STP	84	44.4	0.9	45
15%STP	83.8	52.5	1.5	32
20%STP	85.8	44.9	0.9	50

Conclusions

PLA/LCF from rice straw biocomposites were carried out by kneading and hot pressing into sheet using two roll mill at 120°C. For the operation of the two roll mill, the roll gap was varied from 1.6 mm to 0.2 mm and the roll gap was decreased by 0.2 mm for every 4 rounds of the two roll mill. The study of thermal properties revealed that both LCF (>40 mesh and <60 mesh) contents slightly decreased the Tg and Tm in the PLA/LCF biocomposites. In addition, exothermic peaks (Tc) at about 106.2-115.8°C which may be attribute to crystalline reorganization during heating were found in all PLA/LCF biocomposites. The presence of LCF can act as nucleating agent on the crystallization of PLA. Increasing the LCF contents decreased both the decomposition onset and maximum temperatures in the PLA/LCF biocomposites and the decreasing of decomposition onset and maximum temperatures of the PLA/LCF biocomposites showed slightly higher value than that of pure LCF. The study of mechanical properties showed that hardness of all PLA/LCF biocomposites slightly increased with increasing the LCF contents but tensile strength and elongation at break slightly decreased as the LCF contents increased for both LCF >40 mesh and <60 mesh. However, the tensile modulus was increased by adding of LCF and at 20 wt% LCF contents, the tensile modulus increased much higher than pure PLA.

References

[1] M. Shibata, K. Takachiyo, K. Ozawa, R. Yosomiya and H. Takeishi, *J. Appl. Polym. Sci.* 85 (2002), pp. 129–138.
[2] K.Oksman, M. Skrifvars and J.F. Selin, *Compos. Sci. Technol.* 63 (2003), pp. 1317–1324.
[3] F. Le Digabel, N. Boquillon, P. Dole, B. Monties and L. Averous, *J. Appl. Polym. Sci.* 93 (2004), pp. 428-436.
[4] L. Averous and F. Le Digabel, *Carbohydr. Polym.* 66 (2006), pp. 480-493.
[5] L. Suryanegara, A.N. Nakagaito, and H. Yano, *Compos. Sci. Technol.* 69 (2009), pp. 1187-1192.
[6] B.C. Gadde, C. Menke and R. Wassmann, *Biomass Bioenergy.* 33 (2009), pp. 1532-1546.
[7] DEDE (Department of Alternative Energy Development and Efficiency). *Rice in Thailand.* (2003). in DEDE. ed., pp. 43.
[8] S.M. Lee and J.W. Lee, *Korea-Australia Rheology J.* 17 (2005), pp. 71-77.

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Appendix Figure 1 (Continued)

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