Songklanakarin J. Sci. Technol.
36 (2), 149-161, Mar. - Apr. 2014

SJST SONGKLANAKARIN JOURNAL OF SCIENCE AND TECHNOLOGY
http://www.sjst.psu.ac.th

Review Article

Sustainable green composites of thermoplastic starch and cellulose fibers

Amnuay Wattanakornsiri[1]* and Sampan Tongnunui[2]

[1] *Department of Agriculture and Environment, Faculty of Science and Technology, Surindra Rajabhat University, Mueang, Surin, 32000 Thailand.*

[2] *Division of Biological and Natural Resource Science (Conservation Biology Program), Mahidol University, Kanchanaburi Campus, Sai Yok, Kanchanaburi, 71150 Thailand.*

Received 30 August 2012; Accepted 28 November 2013

Abstract

Green composites have gained renewed interest as environmental friendly materials and as biodegradable renewable resources for a sustainable development. This review provides an overview of recent advances in green composites based on thermoplastic starch (TPS) and cellulose fibers. It includes information about compositions, preparations, and properties of starch, cellulose fibers, TPS, and green composites based on TPS and cellulose fibers. Introduction and production of these recyclable composites into the material market would be important for environmental sustainability as their use can decrease the volume of petroleum derived plastic waste dumps. Green composites are comparable cheap and abundant, but further research and development is needed for a broader utilization.

Keywords: green composites, thermoplastic starch, cellulose fibers

1. Introduction

Worldwide environmental problems and the approaching depletion of hydrocarbon resources, which are also used to make petroleum-derived plastics, are urging a more sustainable development of green composites, so-called environmental friendly materials (Wattanakornsiri *et al.*, 2011). Green composites comprise biodegradable crop-derived polymers as matrixes and biodegradable plant-derived fibers as fillers. When these integral parts are biodegradable, the composites are anticipated to be biodegradable (Averous and Boquillon, 2004). For a variety of reasons they are considered as very promising materials for environmental sustainability, mainly 1) substitution for depleting petrochemical feedstocks by renewable resources, 2) possibility of lower greenhouse gas (GHG) emissions by sequestering carbon dioxide (CO_2) from the atmosphere in polymers and other organic chemicals (Mohanty *et al.*, 2005), and 3) loop closure for organic carbon and nutrients as green composites can be returned to the soil by composting (Patel and Narayan, 2005). By this they would be novel materials of the twenty-first century and would be important for the environmental materials world (Mohanty *et al.*, 2002).

Starch is an attractive source and a promising raw material for the development of green composites because it is naturally renewable, cheap, and abundant (Teixeira *et al.*, 2009). Nevertheless, before thermally processable as for thermoplastic polymers, starch must be converted to thermoplastic starch (TPS) by the addition of plasticizers in the presence of high temperature and shear force (Angellier *et al.*, 2006). As traditional plasticizers, water (Kalichevsky and Blanshard, 1993; Teixeira *et al.*, 2009) and/or polyol plasticizers such as glycerol and sorbitol (Teixeira *et al.*, 2009) have been used. However, the main plasticizer used in TPS was glycerol owing to providing the best result in decreasing the friction between starch molecules (Janssen and Moscicki,

* Corresponding author.
Email address: amnuaywattanakornsiri@hotmail.co.th

2006). Furthermore, glycerol is a by-product generated in large amounts in the biofuel industry, and is becoming nowadays a waste product (Yazdani and Gonzalez, 2007).

Despite the above clear advantages of the use of starch-based plastics for a sustainable development, the applications of TPS are still restricted because of low mechanical properties and high moisture absorption that are considered as the main drawbacks when compared to conventional plastics (Averous and Boquillon, 2004). An alternative method to improve the properties of TPS is the reinforcement of cellulose fibers. Green composites of TPS and cellulose fibers were prepared using various sources of starch, including corn starch (Ma *et al.*, 2005), tapioca starch (Teixeira *et al.*, 2009), rice starch (Prachayawarakorn *et al.*, 2010), potato starch (Thuwall *et al.*, 2006), and wheat starch (Rodriguex-Gonzalez *et al.*, 2004), and different types of cellulose fibers, including flax and ramie fibers (Wollerdorfer and Bader, 1998), potato pulp fibers (Dufresne *et al.*, 2000), bleached leafwood fibers (Averous *et al.*, 2001), bleached eucalyptus pulp fibers (Curvelo *et al.*, 2001), wood pulp fibers (Carvalho *et al.*, 2002), cassava bagasse fibers (Teixeira *et al.*, 2009), and recycled paper cellulose fibers (Wattanakornsiri *et al.*, 2012).

These studies have shown that tensile strength and elastic modulus of the composites increased since cellulose fibers were mixed with TPS due to a good compatibility between both polysaccharides, i.e. starch and cellulose fibers (Averous and Boquillon, 2004). Besides, water resistance of the composites apparently increased (Ma *et al.*, 2008) as a consequence of the addition of the less hydrophilic fibrous fillers (Ma *et al.*, 2005). The constraint exerted by the cellulose fibers at the interface on the matrix could perhaps also work in order to reduce the swelling (Wattanakornsiri *et al.*, 2011). In the present review, the compositions, preparations and properties of starch, cellulose fibers, TPS, and green composites of TPS and cellulose fibers, is addressed as the use of green composites is attaining increased importance and the world's material manufacturers seek to replace dwindling petroleum-based feedstock with green composites including their advantages, i.e. biodegradability, low cost, abundance, and renewability (Espigule *et al.*, 2013).

2. Starch

Starch is a polysaccharide polymer of D-anhydroglucose ($C_6H_{10}O_5$) repeating units comprising two main constituents, i.e. amylose and amylopectin. Amylose is an essential linear polymer consisting of mainly α-1,4-D-glucosidic bond and slightly branched α-1,6-D-glucosidic bond as shown in Figure 1, and is soluble in water and forms a helical structure (Lu *et al.*, 2009). Besides, amylopectin is composed of α-1,4-D-glucosidic bond units interlinked by α-1,6-D-glucosidic bond units to form a multiply branched structure as shown in Figure 2 (Souza and Andrade, 2001), and is able to form helical structures which crystallize. Generally, the amylose and amylopectin contents are about 10 to 20% and 80 to 90%, respectively, depending on the type of starches (Lu *et al.*, 2009). Starch is totally biodegradable in a wide variety of environments. It can be hydrolyzed into glucose by microorganisms or enzymes, and then metabolized into CO_2 and water (Wattanakornsiri *et al.*, 2012).

2.1 Starch gelatinization

Starch is partially in crystalline form. When dry starch granules are heated, thermal degradation occurs before the crystalline granule melting point is reached. As a result, starch cannot be processed in its native form (Prachayawarakorn *et al.*, 2013). In order to melt native starch, the hydrogen bonds holding the starch molecules together have to be destructed and accordingly reduced. The reduction of starch hydrogen bonds can be achieved in the presence of plasticizers, e.g. water, glycerol and sorbitol (Kim *et al.*, 1997). Consequently, the plasticizer interacts with the starch hydroxyl groups; thus, reduces the hydrogen bonds among the starch molecules. This allows individual chains to move freely relative to each other (Willett and Doane, 2002).

When starch granules are heated in a plasticizer, their native crystalline structure is disrupted and they swell irreversibly many times of their original size. This process is called "gelatinization" (Kim *et al.*, 1997). Gelatinization gives rises not only to swelling but also to loss of original crystals and solubility in the plasticizer (Park *et al.*, 2000). During the swelling amylose leaches out the plasticizer, but amylopectin forms gel (Ke and Sun, 2001). The temperature at which starch begins to undergo this process is called "gelatinization temperature". Due to the fact that not all granules of a given starch begin to gelatinize at exactly the same temperature, the gelatinization temperature therefore is suitably defined as a narrow temperature range instead of one specific temperature. The temperature ranges also vary according the source of starch (Szegda, 2009).

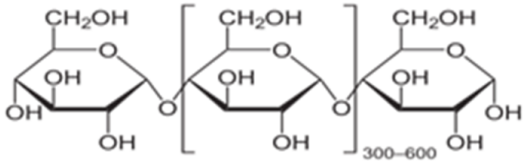

Figure 1. Chemical structure of amylose (Chiou *et al.*, 2005).

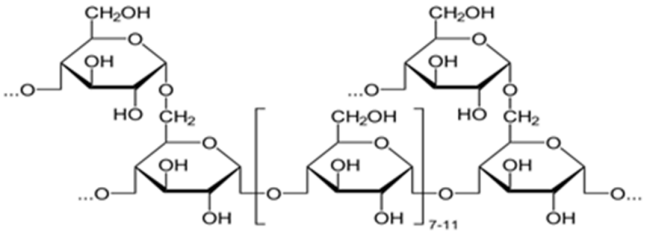

Figure 2. Chemical structure of amylopectin (Chiou *et al.*, 2005).

2.2 Starch as a material

The use of starch as a plastic material has been recorded since 1950s (Chadehumbe, 2006). Since then there have been a lot of researches done on different starches, but starch has gained limited applications as general material, e.g. packaging material. The main advantages of starch as a material are that it is naturally renewable, cheap, abundant, and biodegradable (Teixeira *et al.*, 2009). Nevertheless, when compared with synthetic polymeric material starch has two main disadvantages. First, starch contains hydroxyl groups, which indicate hydrophilic properties to starch. Amylose dissolves in water and amylopectin swells in the presence of water (Lu *et al.*, 2009). This means that starch disintegrates in water and loses its properties when exposed to moisture (Carvalho *et al.*, 2002). Second, starch in its native form is not thermoplastic. When it is heated, pyrolysis occurs before the crystalline melting point of starch is reached; then, it cannot be melt-processed by using conventional plastic equipment (Chadehumbe, 2006).

There are various techniques given for supporting starch using as a suitable material such as destructuring starch as TPS, filling synthetic polymers with starch, blending starch with other thermoplastic polymers, and making starch based composites. This review provides the technique of destructuring starch as TPS.

3. Thermoplastic Starch

TPS is processed through the destructuring of native starch granules by heating at relatively high temperature, under high shear conditions (Ma *et al.*, 2005) and with limited amounts of liquid so-called plasticizer (Prachayawarakorn *et al.*, 2010). The plasticizer swells starch granules and reduces hydrogen bonding and crystal in the granules. This causes an increment of molecular mobility and renders it possible to melt-process native starch below its degradation temperature. The TPS with different properties can be made by altering plasticizer contents and electric mixing, followed by hot-press molding, extrusion or injection molding parameters (Bikiaris *et al.*, 1998).

The amount of plasticizer used in combination with the chosen temperature has a significant effect on starch conversion that can be achieved in two ways. First, all crystals in starch are pulled apart by swelling, leaving none of them to be melted at higher temperatures, under an excess plasticizer condition. Second, the conversion can be achieved under a limited plasticizer condition, which is the usual condition during electric mixing, extrusion, or injection. For the latter process, swelling forces are less significant and crystals melt at temperatures much higher than the gelatinization temperature in the excess plasticizer condition (Yu and Christie, 2001).

For example, during extrusion starch is affected by relatively high pressure up to 10^3 psi, heat during 90 to 180°C (Yu *et al.*, 2005) and mechanical shear forces, resulting in gelatinization, melting, and fragmentation. Starch extrusion is carried out at lower moisture contents from about 12 to 16%, which is below the amount of plasticizer necessary for gelatinization (Chadehumbe, 2006). The starch granules are physically torn apart by mechanical shear forces that have an influence on a faster transfer of plasticizer into the starch molecules. This results in the interruption of molecular bonds and loss of crystals, which lead to higher molecular mobility, causing the starch to be processed below its degradation temperature (Averous *et al.*, 2001). This clarifies that a mixture of small amounts of gelatinized and melted states of starch as well as fragments exists simultaneously during extrusion. Gelatinization is influenced by various variables such as moisture content, screw speed, temperature, feed composition (ratio of amylose to amylopectin), and residence time (Yu and Christie, 2001).

3.1 Plasticizer

Plasticizer is a material used to incorporate into a plastic material in order to increase flexibility and workability. Plasticizer molecules penetrate the starch granules and destruct the inner hydrogen bonds of the starch under high temperature, high shear force (Ma *et al.*, 2005), and high pressure (Chadehumbe, 2006). This eliminates starch-starch interactions; hence, they are replaced by starch-plasticizer interactions. Due to the plasticizer molecules are smaller and more mobile than the starch molecules, the starch network can be easily deformed without rupture (Yu *et al.*, 1998).

During the TPS process, plasticizers play an indispensable role (Hulleman *et al.*, 1998) because they can form hydrogen bonds with starch. This is because it is a multihydroxyl polymer with three hydroxyl groups per monomer and there are high numbers of intermolecular and intramolecular hydrogen bonds in the starch. When the plasticizers form hydrogen bonds with the starch, the original hydrogen bonds between hydroxyl groups of starch molecules are destroyed, thus enabling the starch to display the plasticization (Ma *et al.*, 2005).

Hydrophilic liquids used as plasticizers for TPS are water, glycerol, sorbitol, glycol, urea, and others (Prachayawarakorn *et al.*, 2010). Water is the most common solvent or plasticizer used with starch. The use of water as a plasticizer is not preferable because the resulting TPS products are brittle when equilibrated with ambient humidity (Forssell *et al.*, 1997). The use of plasticizers such as glycerol and sorbitol results in a rubbery material with better properties than the TPS plasticized by water in various applications (Sugih, 2008). For the two most promising plasticizers of polyols, glycerol and sorbitol, glycerol provides the better results in decreasing the friction between starch molecules (Janssen and Moscicki, 2006) and the brittleness of resulting materials, and by this making it easier to manipulate the material after TPS processing (Teixeira *et al.*, 2009).

Glycerol is a chemical compound being a sugar alcohol and its molecular structure is $C_3H_8O_3$. Generally,

glycerol has three hydrophilic hydroxyl groups that are responsible for its solubility in water and its hygroscopic nature (Yazdani and Gonzalez, 2007). Moreover, during the biodiesel production, glycerol is representing as a "co-product" and rapidly becoming a waste product with a disposal cost attributed to it. Therefore, glycerol should be considered as a valuable by-product using as a plasticizer for TPS.

Janssen and Moscicki (2006) prepared TPS by blending potato starch plasticized with varying glycerol contents of 20 to 30 wt% in two main processing steps. First, the starch was gelatinized and thoroughly mixed with glycerol in an extruder; after that, the blending materials were pelletized to form TPS pellets. Second, these pellets were fed to an injection molding machine to produce TPS specimens. The results showed that the tensile strength values of TPS were changed by varying starch to glycerol ratios and injection temperatures that were 100 to 180 °C. An increase of the glycerol content from 20 to 22 wt% led to a fivefold decrease of the tensile strength from 20 to 4 MPa. The appropriate temperature of molding was 140 °C, indicating the highest tensile strength being 20 MPa. This value is comparable to the tensile strength of commercial polystyrene.

According to the studies of Curvelo *et al.* (2001) and Wattanakornsiri *et al.* (2012), their preliminary experiments performed that the glycerol content should be in the ranges of 20 to 40% and 20 to 35% without added water, respectively. Lower and higher glycerol content led to samples that were too much brittle or to exudation phenomena of glycerol, respectively.

4. Cellulose Fibers

Cellulose fibers are derived from plants, e.g. bast, leaf, seed and wood. They are a class of hair-like materials being continuous filaments and their molecular chains are very long and strong (Kaushik *et al.*, 2010). They are aligned along the length of the fibers that provide maximum tensile and flexural strengths as well as support rigidity. Mechanical properties are mainly determined by the cellulose content, degree of polymerization (DP), and fibrillar angle. Typically, the reinforcing efficiency of cellulose fibers depends on the cellulose nature and their crystallinity. Importantly, a high cellulose content and low fibrillar angle are desired properties of fiber to be used as reinforcement for biological composites (John and Thomas, 2008).

Cellulose is a polysaccharide and natural linear crystalline polymer comprising D-anhydroglucose ($C_6H_{10}O_5$) repeating units linked together by α-1,4-D-glucosidic bond (Rowell *et al.*, 1997) as shown in Figure 3 and 4. Each repeating unit contains three hydroxyl groups. These hydroxyl groups and their ability of hydrogen bonding play an important role in directing the crystalline packing and control the physical properties of cellulose (Bismarck *et al.*, 2005). Solid cellulose forms a microcrystalline structure with regions of crystalline and amorphous material. Besides, cellulose is also formed of slender rod like crystalline microfibers (Mo *et al.*, 2010). Cellulose has received more attention for green composites since it is attacked by a wide variety of microorganisms and represented an appreciable fraction of waste products and composites that make up sewage and refuse (Lu *et al.*, 2009).

4.1 Chemically treated botanical cellulose fibers

There have been many studies about the utilization of botanical fibers as reinforcement of plastics; however, these botanical fibers are mainly composed of cellulose, hemicellulose, and lignin including lignocellulose. In order to use botanical cellulose fibers for green composites, they would be chemically treated. This review provides only the alkalization treatment of the botanical cellulose fibers because it is one of the most appropriate treatments, effectively changing the surface topologies of the fibers, i.e. hemp, sisal, jute and kapok, and their crystallographic structures (Mwaikambo and Ansell, 2002). In addition, cellulose fibers are resistant to strong alkali treatment up to 17.5 wt% but are easily hydrolyzed by acid treatment to water-soluble sugars (John and Thomas, 2008).

Alkalization treatment is one of the most used chemical treatments for cellulose fibers when used to reinforce thermoplastics. An important modification done by the alkalization treatment is the disruption of hydrogen bonding

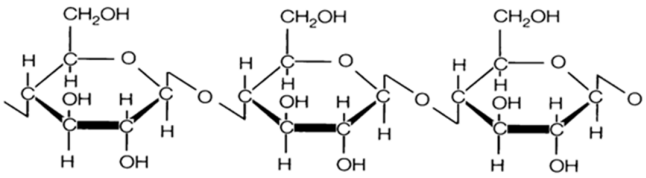

Figure 3. Chemical structure of cellulose (Bismarck *et al.*, 2005).

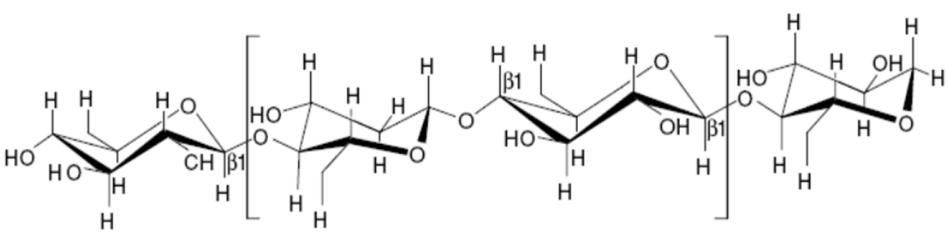

Figure 4. Configuration of cellulose (Bismarck *et al.*, 2005).

in the network structure, thereby increasing surface roughness (Li, 2008). Addition of sodium hydroxide (NaOH) to botanical cellulose fibers promotes the ionization of hydroxyl group to the alkoxide as shown in the following Equation 1. Therefore, the alkalization treatment directly influences the cellulose fibers, DP, and extraction of lignin and hemicellulose compounds (Jahn, 2002).

$$\text{Fiber-OH} + \text{NaOH} \longrightarrow \text{Fiber-O-Na} + H_2O \qquad (1)$$

In the alkalization treatment, botanical fibers are immersed in NaOH solution for a given period of time. A solution of 5% NaOH had been used to treat jute and sisal fibers for 2-72 hrs at room temperature (Mishra *et al.*, 2001; Ray *et al.*, 2001). Jacob *et al.* (2004) examined the effect of NaOH concentrations ranging from 0.5 to 10% in treating sisal fiber-reinforced composites and concluded that the maximum tensile strength resulted from the 4% NaOH treatment at room temperature. Mishra *et al.* (2002) investigated that sisal fiber-reinforced composite treated with 5% NaOH had better tensile strength than treated with 10% NaOH. Moreover, the alkalization treatment also significantly improves the mechanical, impact fatigue, and dynamic mechanical behaviors of fiber-reinforced composites (Sarkar and Ray, 2004).

Bisanda (2000) investigated the effect of alkali treatment on the wetting ability and coherence of sisal-epoxy composites. Treatment of sisal fiber in NaOH solution resulted in more rigid composites with lower porosity and hence higher density. Additionally, the treatment showed to improve the adhesion characteristics due to an increase in surface tension and roughness. The composites showed the improvements in the compressive strength and water resistance. The suggestion was that the removal of intracrystalline and intercrystalline lignin and other surface waxy substances by alkalinization substantially increases a possibility for mechanical interlocking and chemical bonding.

Mwaikambo and Ansell (2002) recovered that alkalization of plant fibers, i.e. hemp, sisal, jute, and kapok, effectively changes the surface morphologies of the fibers and their crystallographic structures. However, the concentration of NaOH for alkalization has to be taken into consideration. Besides, removal of surface impurities on plant fibers may be an advantage for fiber to matrix adhesion. This may provide both mechanical interlocking and bonding reaction because of the exposure of fiber to chemicals, e.g. resins and dyes.

Kaushik *et al*. (2010) expressed that the alkaline steam explosion of wheat straw fibers with NaOH in an autoclave at pressure around 15 lb for 4 hrs resulted in a substantial breakdown of lignocellulosic strucuture, partial hydrolysis of hemicellulosic fraction, and depolymerization of lignin components. Additionally, Liu and Huang (2013) represented that the treatment of rice straw fibers by alkalization changed surface properties, improved wettability and improved mechanical properties of rice straw fibers.

Moreover, the effect of fiber treatment on the mechanical properties of unidirectional sisal reinforced epoxy composites was investigated by Rong *et al.* (2001). The treatments of alkalization and heating were carried out to modify the fiber surface and its internal structure. The results showed that chemical methods generally led to an active surface by introducing some reactive groups, and provided the fibers with higher extensibility through partial removal of lignin and hemicellulose. On the other hand, thermal treatment of the fibers resulted in higher fiber stiffness due to the increased crystallinity of hard cellulose. The treatments of sisal fiber, which increased the fiber strength and the adhesion between the fiber bundles and the matrix, would favor an overall improvement of mechanical properties, especially tensile property, of the laminated sisal fibers.

5. Green Composites of Thermoplastic Starch and Cellulose Fibers

TPS can be reinforced with cellulose fibers in order to improve its low resistance to mechanical stresses and moisture (Teixeira *et al.*, 2009). TPS is first introduced as matrix and cellulose fiber is then reinforced as biodegradable filler to preserve their biodegradability. There have been many studies on different starch types of TPS and varied types of cellulose fibers. Wollerdorfer and Bader (1998) first reported that the reinforced TPS prepared by wheat starch and flax and ramie cellulose fibers was four times better (37 N/mm^2) than the pure TPS. The reinforcement of cellulose fibers and starch blends caused a stress increase of 52% (55 N/mm^2) and 64% (25 N/mm^2), respectively.

Curvelo *et al.* (2001) applied cellulose fibers from *Eucalyptus urograndis* pulp as the reinforcement material for TPS in order to improve its mechanical properties. The green composites were prepared from regular corn starch plasticized with glycerol and reinforced with short cellulose fibers (16% wt/wt) from bleached pulp. The cellulose fibers were added directly to the TPS in an intensive batch mixer at 170°C. The mixture was hot-pressed in 2-3 mm-thick plates and then cut to prepare the specimens for mechanical tests. The composites showed an increase of 100% in tensile strength and more than 50% in modulus with respect to the pure TPS.

Averous and Boquillon (2004) prepared green composites from wheat starch with glycerol with and without water, and incorporated natural cellulose fibers with varying lengths of 60 to 900 μm from leafwood. Particularly, TPS_1 and TPS_2 matrixes were prepared from the ratios of dried wheat starch/glycerol/water as 70:18:12 and 65:35:0, respectively; besides, all fibers were supplied from companies. After extrusion and injection molding, mechanical, thermo-mechanical and thermal properties of the composites were analyzed. Dynamic thermal mechanical analysis (DMTA) showed important variations of main relaxation temperature, which can be linked both resulting interactions in a decrease of starch chain mobility and regular reinforcing effects. The

results were consistent with the static mechanical behavior, which varied according to the filler content as well as fibers' nature and length. In addition, the results showed that the addition of cellulose fibers improves the thermal resistance of these green composites.

Muller *et al.* (2009) investigated the effect of the addition of cellulose fibers on the mechanical and physical properties of TPS films plasticized with glycerol. The green composites were prepared from solutions with 3 wt% of cassava starch plasticized by glycerol (0.3 g/g of starch; 23 wt%) with the addition of 0.1 to 0.5 g of eucalyptus cellulose fibers (about 1.2 mm length) per gram of starch. The mechanical properties of green composites conditioned at differently relative humidity (RH) values were determined through tensile and stress relaxation tests. Scanning electron microscopy (SEM) micrographs of the TPS films showed a homogeneous and random distribution of the cellulose fibers, without pores or cracks. The TPS films with cellulose fibers were more crystalline and had higher tensile strength and rigidity, but lower elongation capacity. In contrast, the addition of cellulose fibers raised the stability of TPS films subjected to RH variations in relative air humidity.

In addition, Teixeira *et al.* (2009) prepared green composites based on tapioca starch with either glycerol or glycerol/sorbitol (1:1) as the plasticizers and tapioca bagasse cellulose nanofibers from a by-product of the tapioca starch industry. The cellulose nanofibers displayed a relatively low crystallinity and were found to be about 2-11 nm thick and 360 to 1,700 nm long. The reinforcing effect of the cellulose nanofibers evaluated by DMTA and tensile tests was found to depend on the nature of the employed plasticizer. Their results showed a decrease of the glass transition temperature of the starch after the incorporation of nanofibers and the increase of elongation at break in tensile test.

Wattanakornsiri *et al.* (2012) used different cellulose fibers from used office paper and newspaper as reinforcement for TPS in order to improve their poor mechanical, thermal, and water resistance properties. These green composites were prepared using tapioca starch plasticized by glycerol at 30% wt/wt of glycerol to starch as matrix reinforced by the extracted cellulose fibers with the contents ranging from 0 to 8% wt/wt of fibers to matrix. The results showed that the introduction of either office paper or newspaper cellulose fibers caused the improvement of tensile strength and elastic modulus, thermal stability, and water resistance for composites when compared to the pure TPS.

A summary of the previous studies on green composites prepared from TPS reinforced with cellulose fibers and with different types of starch, plasticizer, plasticizer ratio, fiber and fiber ratio are shown in Table 1.

5.1 Preparation of green composites

TPS reinforced with cellulose fibers processing is similar to most conventional synthetic thermoplastic processing (Janssen and Moscicki, 2006). Most thermoplastic operations involve heating and forming into desired shapes, and then cooling (Li, 2008). Processing techniques used on thermoplastics can also be used in the TPS reinforced with cellulose fibers. These include extrusion, injection molding, internal mixing, compression molding, and others.

Henson (1997) indicated that extrusion is basically a thermoplastic processing, continuously shaping a plastic or polymer through an orifice of an appropriate mold, and

Table 1. Previous studies of green composites prepared from TPS reinforced with cellulose fibers.

Study	Starch type	Plasticizer ratio (% wt/wt of plasticizer to starch)	Fiber type	Fiber ratio (% wt/wt of fibers to matrix*)
Curvelo *et al.* (2001)	Corn	30 wt% (glycerol)	*Eucalyptus urograndis*	0 and 16
Averous and Boquillon (2004)	Wheat	TPS_1: 18 wt% (glycerol), and 12 wt% (water) TPS_2: 35 wt% (glycerol)	Leafwood, and paper pulpfibers from broad-leaved species	TPS_1: 0, 15, and 30TPS_2: 0, 4, 8, 10, 12, 16, and 20
Ma *et al.* (2005)	Corn	15.4 wt% (urea), and 7.7 wt% (formamide)	Winceyette	0, 5, 10, 15, and 20
Muller *et al.* (2009)	Cassava	23 wt% (glycerol)	Eucalyptus	0, 7, 19, and 28
Teixeira *et al.* (2009)	Cassava (tapioca)	TPS_1: 30 wt% (glycerol) TPS_2: 15 wt% (glycerol), and 15 wt% (sorbitol)	Cassava bagasse	TPS_1 and TPS_2: 0, 5, 10, and 20
Wattanakornsiri *et al.* (2012)	Tapioca	30 wt% (glycerol)	Used office paper and newspaper	0, 2, 4, 6, and 8

Remark: * Starch plus plasticizer

subsequently solidifying it into a product. Temperature in an extruder should be high enough to ensure the plastic fully melted and low enough to avoid burning fibers. Typically, the extrusion is necessary for injection molded composite products before injection molding because injection molding machines and screws are much shorter than extruders. Therefore, the ratio of length to diameter for injection molding screws is lower than for extruders. The lower length to diameter ratio of the screw in injection machine makes it less efficient in mixing and non-homogenous melt comparison with extruders. The reason is that if the composite is processed by injection molding, prior extrusion compounding is necessary for materials (Li, 2008).

Advani and Sozer (2002) suggested that an injection molding is an important plastic processing method with the characteristics of rapid production rates and high volume production. It can manufacture geometrically complex components with accurate dimensions and its process is automated. In contrast, there is limitation on fiber fraction and fiber length when using the injection molding to process fiber-reinforced biological composites because higher natural fiber fraction and longer fiber length will make molding difficult. This study involves the processing techniques of internal mixer for homogenous mixing between the TPS matrix and cellulose fibers and compression molding machine for hot pressing the non-reinforce TPS and composites to thick sheets.

Curvelo *et al.* (2001) prepared TPS samples, produced by corn starch, plasticized by glycerol as the matrix, and reinforced by *Eucalyptus urograndis* fibers. The composites were prepared in an internal mixer connected to a torque rheometer equipped with roller rotors at 170°C operating at 80 rpm for 8 min. Then, the resulting materials were compression molded at 160°C to produce 10x10 cm sheets with 2.5 mm thickness.

According to the research of Corradini *et al.* (2007) the TPS were produced from starch and zein plasticized by glycerol. These materials were mixed in an internal mixer connected to a torque rheometer operating at 50 rpm for 6 min. After that, these mixtures were hot pressed for 5 min at 160°C to produce 150x120x2.5 cm molded sheets.

Additionally, Teixeira *et al.* (2009) prepared the TPS composites from cassava starch plasticized using either glycerol or a mixture of glycerol and sorbitol. These matrixes were reinforced by cellulose cassava bagasse nano-fibers. These mixtures were processed at 140±10°C in an internal mixer equipped with roller rotors rotating at 60 rpm for 6 min. These processed materials were then compression molded 140°C into one and two millimeter thick plates.

6. Properties of Green Composites

Properties of green composites based on TPS and cellulose fibers are represented as following.

6.1 Mechanical properties

The increase of mechanical properties, i.e. ultimate tensile strength (UTS) and elastic modulus (E), of green composites when compared with pure TPS confirms the interfacial adhesion and the strong interaction between matrixes and cellulose fibers (Martins *et al.*, 2009) as shown in Figure 5; green composites prepared from corn starch (CS) plasticized by glycerol (30% wt/wt of glycerol to starch) as matrix that was reinforced with recycled paper cellulose fibers (NF) and newspaper fibers contents ranging from 0-8% (wt/wt of fibers to matrix) (Wattanakornsiri *et al.,* 2011). These results are favored by the chemical similarities between starch and cellulose fibers (Ma *et al.*, 2005). However, the percent elongation at break decreased with respect to those of pure TPS. These results could be due to the high crystallinity of the cellulose fibers, then providing higher stiffness of the green composites when compared to the pure TPS (Prachayawarakorn *et al.*, 2010).

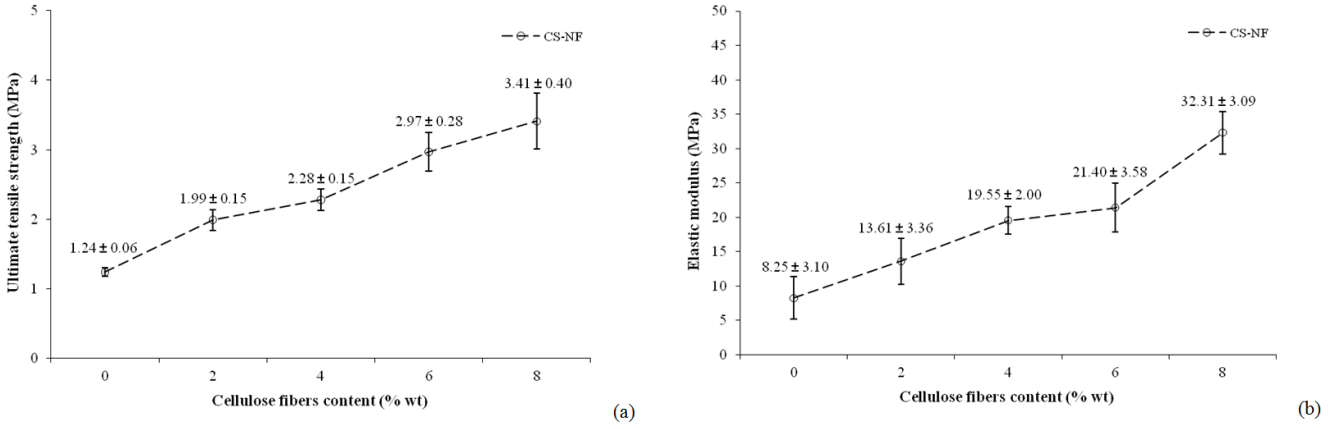

Figure 5. Effect of cellulose fibers content on mechanical properties, (a) ultimate tensile strength and (b) elastic modulus, of non-reinforced TPS and green composites (Wattanakornsiri *et al.*, 2011).

In addition, the amount and structure of amylose and amylopectin molecules of the various starch sources play an important role in the UTS, E and percent elongation at break including the formed network of TPS (Van Soest and Borger, 1997). With higher amylopectin contents the UTS and E increased but the percent elongation at break decreased. These can be explained as following that the large content of amylopectin with the branched structure is less ordered and therefore has a greater degree of entanglement, which is physical interlocking the polymer chains, being a direct consequence of chain overlap (Shenoy *et al.*, 2005), and causing higher stress and lower elongation (Janssen, 2009). Another explanation might be that the higher content of linear amylose molecules makes that the entanglement between matrix chains not quite strong; they will slide easily along each other with lower stress and higher elongation (Graff *et al.*, 2003). Besides, glycerol gave the chains more mobility and the interactions between the chains of linear amylose molecules are lowered.

6.2 Thermal properties

Generally, two glass transitions (Tg) are detected in the green composites (Shi *et al.*, 2006). Figure 6 represents differential scanning calorimetry (DSC) thermal traces in the case of green composites studied by Wattanakornsiri *et al.* (2011), where the terms CS-NF0 and CS-NF4 and 8 are used to define the non-reinforced TPS, and green composites containing 4 and 8% wt/wt of fibers to matrix, respectively. The two glass transitions were related to phase separation phenomena that can take place in starch-glycerol system with glycerol/starch ratio larger than 0.2 (Lourdin *et al.*, 1997). The lower transition temperature (T_{t1}) is clearly attributed to starch-poor phase and hence related to the glycerol glass transition (Averous *et al.*, 2001), whereas the higher one (T_{t2}) is attributed to starch-rich-phase and hence referred to the TPS glass transition (Ma *et al.*, 2008). Depending on the type of TPS/cellulose fiber composites the T_{t1} values occur in the range of -50 to -70°C (Averous and Boquillon, 2004) that is close to the glycerol glass transition, which is about -75°C (Teixeira *et al.*, 2009). Similarily, the T_{t2} values are characterized by the broad temperature transition range of 60 to 100°C that is the expected values for starch conditioned at 23°C and 50%RH (Kalichevsky *et al.*, 1992).

Higher amylopectin TPS composites have higher Tg values than those of lower amylopectin composites. The lower molar weight of amylose and its lack of branches result in a larger free volume of the lower amylopectin TPS composites, so parts of polymer chains can move easier (Graff *et al.*, 2003). This can be ascribed for the lower Tg of amylose in relation to the branched amylopectin. Thus, the green composites with lower amylose contents gave higher Tg values (Janssen, 2009).

Generally, thermogravimetric analysis (TGA) is used to study thermal degradation of green composites as Figure 7 represents TGA results in the case of green composites studied by Wattanakornsiri *et al.* (2011). The behavior of TGA mass loss curves was similar for the non-reinforced TPS and green composites and the weight loss gradually decreased with raising of fibers contents. The degradation temperatures increased with the presence of cellulose fibers in green composites. These are described by the higher thermal stability of fibers compared to starch, and especially the good compatibility of both polysaccharides (Martins *et al.*, 2009). The degradation temperatures of composites are between the values of matrixes and fibers with an additional effect by following the rule of matrix (Averous and Boquillon, 2004). In general, the degradation temperatures of crystalline cellulose fibers occur at higher values in comparison to TPS matrixes (Teixeira *et al.*, 2009).

Moreover, the percentage weight losses decrease with the addition of cellulose fibers. This is explained by the fact that at equilibrium the composites had lower water content when compared to the pure matrixes and the fibers crystallinity decreased their polar character. Hence, the presence of fibers in the matrixes decreased the inside water content and the diverse interactions brought by the fibers

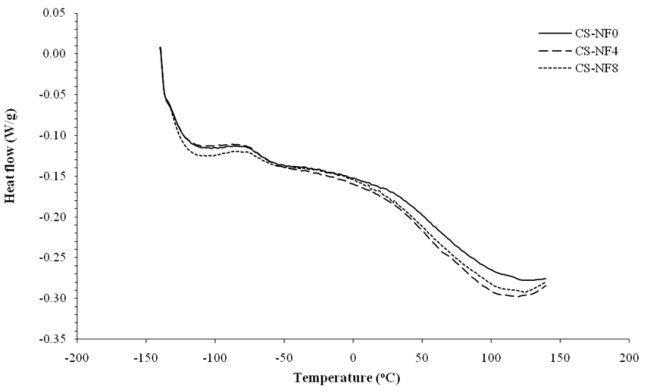

Figure 6. DSC scans for non-reinforced TPS and composites (Wattanakornsiri *et al.*, 2011).

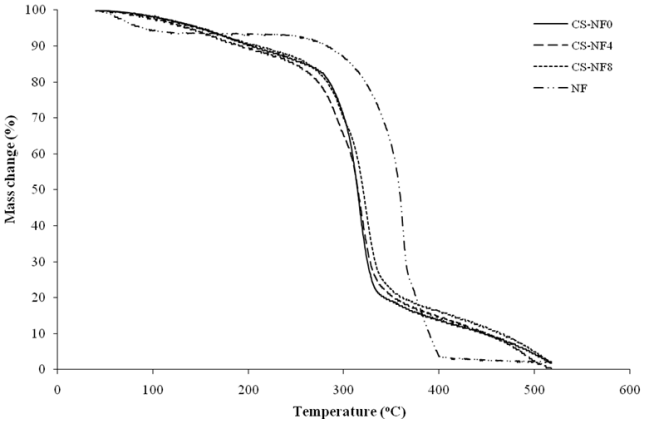

Figure 7. TGA scans for cellulose fibers, non-reinforced TPS and composites (Wattanakornsiri *et al.*, 2011).

took original water site of TPS matrixes (Averous and Boquillon, 2004). The addition of cellulose fibers improve the thermal resistance of the pure TPS due to the good thermal stability of crystalline structure for cellulose fibers and the good interaction between TPS matrixes and cellulose fibers (Ma *et al.*, 2008).

6.3 Water absorption properties

Low water resistance is a major drawback of TPS for many practical applications. In fact, TPS could absorb an amount of water from the environmental humidity; as a result, the mechanical properties could drastically drop down (Kalichevsky and Blanshard, 1993). The presence of cellulose fibers decreased the amount of water absorption. This can be mainly ascribed by the addition of the cellulose fibers; in fact, they are less hydrophilic in comparison to starch (Ma *et al.*, 2005) and can absorb a part of glycerol with a reduction of the hydrophilic behavior of TPS (Curvelo *et al.*, 2001). Besides, the presence of less hydrophilic cellulose fibers significantly reduced the water absorption of TPS probably also because of the constraint exerted by the fibers at the interface on the matrix swelling (Wattanakornsiri *et al.*, 2011). Besides, amylopectin-rich TPS are more sensitive to water absorption than amylose-rich TPS (van Soest and Essers, 1997).

6.4 Ageing properties

Ageing property (AP) is an important issue for TPS after processing (Averous *et al.*, 2001). The green composites are tested following the variation of mechanical properties during several weeks after molding (Shi *et al.*, 2006). The E was used to estimate the ageing properties as TPS stabilization that is the ratio of E at week six divided by the E at week two (Wattanakornsiri, 2012).

The presence of higher cellulose fibers contents in the green composites decreases or increases the ageing values that tends into the ageing stabilization value equal to one depending on the type of TPS and cellulose fiber composites (Wattanakornsiri, 2012). This is because of the fiber-matrix interactions that provide some kind of stabilizing three-dimensional network based on low intermolecular bonds (Averous and Boquillon, 2004) and due to the difference of re-crystallization or post-crystallization of starch chains between amylose and amylopectin molecules (Averous *et al.*, 2001).

Generally, in the TPS retrogradation takes place after cooling of gelatinized starch, while amylose re-crystallization is irreversible, amylopectin re-crystallizes reversibly. The crystalline structure of the higher amylose content composites is relatively stable (Yu and Christie, 2001), providing the higher ageing values. Concurrently, during ageing the amylose and amylopectin also co-crystallize to form cross-links between amylose and/or amylopectin and these cross-links can also increase the E (Yu and Christie, 2001). Besides, the re-crystallization of amylopectin could contribute to the ageing or making the life time of TPS relatively shorter. Thus, TPS should be composed of high amylose content due to the effect of retrodegradation (Ma *et al.*, 2005).

6.5 Functional groups

Fourier transform infrared spectroscopy (FT-IR) is a powerful technique for identifying types of chemical bonds of polymer composites in a molecule by producing infrared absorption spectrum, which is comparable to a molecular finger print. FT-IR spectra in the case of green composites, investigated by Wattanakornsiri *et al*. (2012), display the typical profiles of polysaccharide as illustrated in Figure 8, where CS-NF0, NF4, and NF8 are defined to non-reinforced TPS, and green composites containing 4 and 8% wt/wt of fibers to matrix. The peaks in the range of 1,026-1,027 and 1,079-1,155 cm^{-1} are attributed to C-O stretching of C-O-C group in the anhydroglucose ring and of C-O-H group, respectively. The wave numbers in the range of 1,414-1,454 cm^{-1} are designed for O-H bonding (Prachayawarakorn *et al.*, 2011). The peak positions in the range of 1,638-1,639 cm^{-1} are owing to the bound water present in the non-reinforced TPS and composites. The bands of 2,931 cm^{-1} are associated with C-H stretching. Besides, the bands belonging to hydrogen bonded hydroxyl (O-H) group appear in the range of 3,414-3,420 cm^{-1} that are attributed to the complex vibrational stretching, associated with free, inter and intra molecular bound hydroxyl groups (Galicia-Garcia *et al.*, 2011).

Especially in the last case, the bands slightly shifted to lower wave numbers by the presence of cellulose fibers; referring to an increase of intermolecular hydrogen bonding by the addition of cellulose fibers. This phenomenon is ascribed that when polymers are compatible, a distinct interaction, i.e. hydrogen bonding or dipolar interaction, exists between the chains of TPS matrix and cellulose fibers, providing the changes of FT-IR spectra on the composites, e.g. band shifts and broadening (Prachayawarakorn *et al.*, 2010).

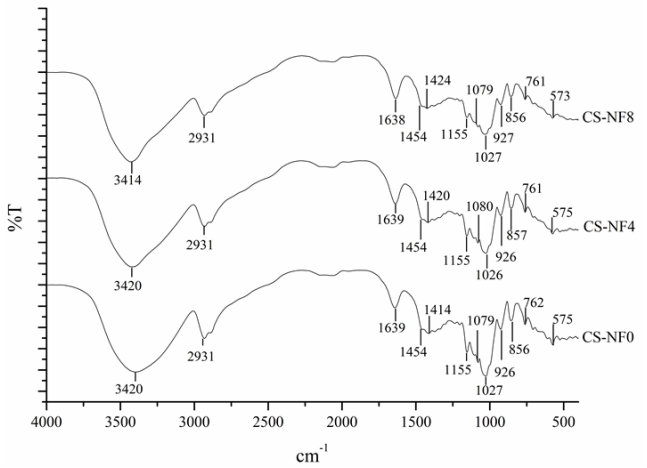

Figure 8. FT-IR spectra for cellulose fibers, non-reinforced TPS and composites (Wattanakornsiri *et al.*, 2012).

6.6 Morphology

Scanning electron microscopy (SEM) is one of the most worldwide using techniques for studying green composites' morphologies and compatibilities. SEM micrograph of the fractured surface of green composites studied by Wattanakornsiri *et al*. (2011) is illustrated in Figure 9. There, the cellulose fibers appear to be embedded in the matrix and good adhesion features, and also the TPS matrix remains tightly jointed to the fibers even after a cryo-fracture test without any evident debonding phenomena (Curvelo *et al.*, 2001). Moreover, the absence of fiber pullout indicates their good interfacial adhesion (Ma *et al.*, 2005).

6.7 Biodegradation

Starch is a nutrient for many microorganisms and once water is present in the starch structure of TPS it is readily biodegraded. Starch easily absorbs water, resulting in disintegration of green composites by partial solubility. Partially solubilised starch is even more readily biodegraded by enzymes principally from microorganisms (Shanks and Kong, 2012). The green composites prepared by TPS and cellulose fibers were fully biodegraded. Biodegradation rates showed that when fiber content increased the green composites degraded slower when compared to the pure TPS (Wattanakornsiri *et al.*, 2012). A more difficult biodegradability is related to the more hydrophobic cellulose fibers when compared to starch. Besides, this occurrence is due to the phase compatibility of TPS matrix and cellulose fibers (Prachayawarakorn *et al.*, 2011).

7. Concluding Remarks

Green composites have rapidly evolved over the last decade due to the approaching depletion of fossil fuels and worldwide environmental problems resulted from petroleum-derived plastics. The main advantage of green composites is their biological decomposition to organic wastes that can be returned to enrich the soil. Their use would be useful to the environment and lessen the labor costs for removal plastic wastes. In addition, their decomposition would help to increase the longevity and stability of landfills by reducing the volume of garbage as well as they could be recycled to useful monomers and oligomers by microbial activities. This review outlines the significance of research and development of green composites based on thermoplastic starch and cellulose fibers derived from naturally renewable resources. These composites could be used as commodity plastics like biodegradable artifacts, e.g. organic waste bags and seeding grow bags, being cheap, abundant and recyclable. However, the future growth and sustainability of green composites is reliant to continued research, in particularly related to the improvement of their hydrophobic character, surface modifications, and advanced processing techniques. These unresolved issues should be addressed as green composites are expected to replace petroleum-derived plastics in the future.

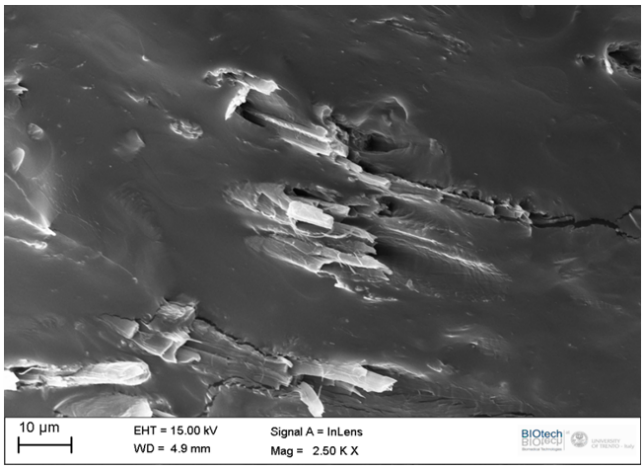

Figure 9. SEM micrograph of fragile fractured surface of green composites (Wattanakornsiri *et al.*, 2011).

References

Advani, S.G. and Sozer, E.M. 2002. Process Modeling in Composites Manufacturing, Marcel Dekker, New York, U.S.A.

Angellier, H., Molina-Boisseau, S., Dole, P. and Dufresne, A. 2006. Thermoplastic-waxy maize starch nanocrystals nanocomposites. Biomacromolecules. 7, 531-539.

Averous, L. and Boquillon, N. 2004. Biocomposites based on plasticized starch: thermal and mechanical behaviours. Carbohydrate Polymers. 56, 111-122.

Averous, L., Fringant, C. and Moro, L. 2001. Plasticized starch-cellulose interactions in polysaccharide composites. Polymer. 42, 6571-6578.

Bikiaris, D., Pavlidou, E., Prinos, J., Aburto, J., Alric, I., Borredon, E. and Panayiotou, C. 1998. Biodegradation of octanoated starch and its blends with LDPE. Polymer Degradation and Stability. 60, 437-447.

Bisanda, E.T.N. 2000. The effect of alkali treatment on the adhesion characteristics of sisal fibres. Applied Composite Materials. 7, 331-339.

Bismarck, A., Mishra, S. and Lampke, T. 2005. Plant fibers as reinforcement for green composites. In Natural Fibers, Biopolymers and Biocomposites, A.K. Mohanty, M. Misra and L.T. Drazl, editors. CRC Press (Taylor & Francis Group), New York, U.S.A., pp 37-108.

Carvalho, A.J.F.D., Curvelo, A.A.S. and Agnelli, J.A.M. 2002. Wood pulp reinforced thermoplastic starch composites. International Journal of Polymeric Materials. 51, 647-660.

Corradini, E., Carvalho, A.J.F.D. and Curvelo, A.A.D.S. 2007. Preparation and characterization of thermoplastic starch/zein blends. Materials Research. 10, 227-231.

Curvelo, A.A.S., Carvalho, A.J.F.D. and Angelli, J.A.M. 2001. Thermoplastic starch-cellulosic fibers composites:

preliminary results. Carbohydrate Polymers. 45, 183-188.

Chadehumbe, C. 2006. Tensile properties of thermoplastic starch and its blends with polyvinyl butyral and polyamides. Ph.D. dissertation, University of Pretoria, South Africa.

Chiou, B., Glenn, G.M., Imam, S.H., Inglesby, M.K., Wood, D.F. and Orts, W.J. 2005. Starch polymer: Chemistry, engineering, and novel products. In Natural Fibers, Biopolymers and Biocomposites, A.K. Mohanty, M. Misra and L.T. Drazl, editors. CRC Press (Taylor & Francis Group), New York, U.S.A., pp 639-669.

Dufresne, A., Dupeyre, D. and Vignon, M.R. 2000. Cellulose microfibrils from potato tuber cells: processing and characterization of starch cellulose microfibril composites. Journal of Applied Polymer Science. 76, 2080-2092.

Espigule, E., Puigvert, X., Vilaseca, F., Mendez, J.A., Mutje, P. and Girones, J. 2013. Thermoplastic starch-based composites reinforced with rape fibers: water uptake and thermomechanical properties. Bioresources. 8, 2620-2630.

Forssell, P.M., Mikkila, J.M., Moates, G.K. and Parker, R. 1997. Phase and glass transition behavior of concentrated barley starch-glycerol-water mixtures, a model for thermoplastic starch. Carbohydrate Polymers. 34, 275-282.

Galicia-Garcia, T., Martinez-Brutos, F., Jimenez-Arevalo, O., Martinez, A.B., Ibarra-Gomez, R., Gaytan-Martinez, M. and Mendoza-Duarte, M. 2011. Thermal and microstructural characterization of biodegradable films prepared by extrusion-calendering process. Carbohydrate Polymers. 83, 354-361.

Graff, R.A.D, Karman, A.P. and Janssen, L.P.B.M. 2003. Material properties and glass transition temperatures of different thermoplastic starches after extrusion processing. Starch/Starke. 55, 80-86.

Henson, F. 1997. Plastic Extrusion Technology (2nd ed.), Hanser, New York, U.S.A.

Hulleman, S.H.D., Jansen, F.H.P. and Feli, H. 1998. The role of water during the plasticization of native starches. Polymer. 39, 2034-2048.

Jacob, M., Thomas, S. and Varughese, K.T. 2004. Mechanical properties of sisal/oil palm hybrid fiber reinforced natural rubber composites. Composites Science and Technology. 64, 955-965.

Janssen, L.P.B.M. 2009. Influence of process conditions on the physical properties of TPS. In Thermoplastic Starch, L.P.B.M. Janssen and L. Moscicki, editors. WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, pp. 159-171.

Janssen, L.P.B.M. and Moscicki, L. 2006. Thermoplastic starch as packaging material. Acta Scientiarum Polonorum, Technica Agraria. 5, 19-25.

Jahn, A. 2002. Characterization of alkali treated flax fibers by means of FT raman spectroscopy and environmental scanning electron microscopy. Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy. 58, 2271-2279.

John, M.J. and Thomas, S. 2008. Biofibres and biocomposites. Carbohydrate Polymers. 71, 343-364.

Kalichevsky, M.T. and Blanshard, J.M.V. 1993. The effect of fructose and water on the glass transition of amylopectin. Carbohydrate Polymers. 20, 107-113.

Kalichevsky, M.T., Jaroszkiewicz, E.M., Ablett, S., Blanshard, J.M.V. and Lillford, P.J. 1992. The glass transition of amylopectin measured by DSC, DMTA and NMR. Carbohydrate Polymers. 18, 77-88.

Kaushik, A., Singh, M. and Verma, G. 2010. Green nanocomposites based on thermoplastic starch and steam exploded cellulose nanofibrils from wheat straw. Carbohydrate Polymers. 82, 337-345.

Ke, T. and Sun, X. 2001. Effect of moisture content and heat treatment on the physical properties of starch and poly (lactic acid) blends. Journal of Applied Polymer Science. 81, 3069-3082.

Kim, J., Kim, W. and Shin, M.A. 1997. Comparative study on the retrogradation of rice starch gels by DSC, X-ray and á-amylose methods. Starch/Starke. 49, 71-75.

Li, X. 2008. Development of flax fiber-reinforced polyethylene biocomposites by injection molding. Ph.D. dissertation, University of Saskatchewan, Canada.

Liu, J. and Huang, C. 2013. Biodegradable composites from rice straw and cornstarch adhesives. Advance Journal of Food Science and Technology. 5, 41-45.

Lourdin, D., Bizot, H. and Colonna, P. 1997. 'Antiplasticization' in starch-glycerol films?. Journal of Applied Polymer Science. 63, 1047-1053.

Lu, D.R., Xiao, C.M. and Xu, S.J. 2009. Starch-based completely biodegradable polymer materials. Express Polymer Letter. 6, 366-375.

Ma, X., Chang, P.R. and Yu, J. 2008. Properties of biodegradable thermoplastic pea starch/carboxymethyl cellulose and pea starch/microcrystalline cellulose composites. Carbohydrate Polymers. 72, 369-375.

Ma, X., Yu, J. and Kennedy, J.F. 2005. Studies on the properties of natural fibers-reinforced thermoplastic starch composites. Carbohydrate Polymers. 62, 19-24.

Martins, I.M.G., Magina, S.P., Oliveira, L., Freire, C.S.R., Silvestre, A.J.D., Neto, C.P. and Gandini, A. (2009). New biocomposites based on thermoplastic starch and bacterial cellulose. Composites Science and Technology. 69, 2163-2168.

Mishra, S., Misra, M., Tripathy, S.S., Nayak, S.K. and Mohanty, A.K. 2001. Graft copolymerization of acrylonitrile on chemically modified sisal fibers. Macromolecular Materials and Engineering. 286, 107-113.

Mishra, S., Misra, M., Tripathy, S.S., Nayak, S.K. and Mohanty, A.K. 2002. The influence of chemical surface modification on the performance of sisal polyester biocomposites. Polymer Composites. 23, 164-170.

Mo, X., Zhong, Y., Liang, C. and Yu, S. 2010. Studies on the properties of banana fibers-reinforced thermoplastic cassava starch composites: preliminary results. Advanced Materials Research. 87-88, 439-444.

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

Mohanty, A.K., Misra, M., Drzal, L.T., Selke, S.E., Harte, B.R. and Hinrichsen, G. 2005. Natural fibers, biopolymers, and biocomposites: an introduction. In Natural Fibers, Biopolymers and Biocomposites, A.K. Mohanty, M. Misra and L.T. Drazl, editors. CRC Press (Taylor & Francis Group), New York, U.S.A., pp 1-36.

Muller, C.M.O., Laurindo, J.B. and Yamashita, F. 2009. Effect of cellulose fibers on the crystallinity and mechanical properties of starch-based films at different relative humidity values. Carbohydrate Polymers. 77, 293-299.

Mwaikambo, L.Y. and Ansell, M.P. 2002. Chemical modification of hemp, sisal, jute, and kapok fibers by alkalization. Journal of Applied Polymer Science. 84, 2222-2234.

Odling-Smee, L. 2007. Biofules bandwagon hits a rut. Nature. 446, 483.

Park, J.W., Im, S.S., Kim, S.H. and Kim, Y.H. 2000. Biodegradable polymer blends of poly (L-lactic acid) and gelatinized starch. Polymer Engineering and Science. 40, 2539-2550.

Patel, M. and Narayan, R. 2005. How sustainable are biopolymers and biobased products? The hope, the doubts, and the reality. In Natural Fibers, Biopolymers and Biocomposites, A.K. Mohanty, M. Misra and L.T. Drazl, editors. CRC Press (Taylor & Francis Group), New York, U.S.A., pp 833-853.

Prachayawarakorn, J., Chaiwatyothin, S., Mueangta, S. and Hanchana, A. 2013. Effect of jute and kapok fibers on properties of thermoplastic cassava starch composites. Materials and Design. 47, 309-315.

Prachayawarakorn, J., Ruttanabus, P. and Boonsom, P. 2011. Effect of cotton fiber contents and lengths on properties of thermoplastic starch composites prepared from rice and waxy rice starches. Journal of Polymers and the Environment. 19(1), 274-282.

Prachayawarakorn, J., Sangnitidej, P. and Boonpasith, P. 2010. Properties of thermoplastic rice starch composites reinforced by cotton fiber or low-density polyethylene. Carbohydrate Polymers. 81, 425-433.

Ray, D., Sarkar, B.K., Rana, A.K. and Bose, N.R. 2001. Effect of alkali treated jute fibers on composite properties. Bulletin of Material Sciences. 24, 129-135.

Rong, M.X., Zhang, M.Q., Liu, Y., Yang, G.C. and Zeng, H.M. 2001. The effect of fiber treatment on the mechanical properties of unidirectial sisal-reinforced epoxy composites. Composites Science and Technology. 61, 1437-1447.

Rowell, R.M., Young, R.A. and Rowell, J.K. 1997. Paper and Composites from Agro-based Resources, CRC Lewis, Boca Raton, Florida, U.S.A.

Shanks, R. and Kong, I. 2012. Thermoplastic starch. In Thermoplastic Elastomers, A. El-Sonbati, editor. InTech Europe, Rijeka, Croatia, pp 95-116.

Sarkar, B.K. and Ray, D. 2004. Effect of the defect concentration on the impact fatigue endurance of untreated and alkali treated jute-vinylester composites under normal and liquid nitrogen atmosphere. Composites Science and Technology. 64, 2213-2219.

Shenoy, S.L., Bates, W.D., Frisch, H.L. and Wnek, G.E. 2005. Role of chain entanglements on fiber formation during electrospinning of polymer solutions: good solvent, non-specific polymer-polymer interaction limit. Polymer. 46, 3372-3384.

Shi, R., Liu, Q., Ding, T., Han, Y., Zhang, L., Chen, D. and Tian, W. 2006. Ageing of soft thermoplastic starch with high glycerol content. Journal of Applied Polymer Science. 103, 574-586.

Souza, R.C.R. and Andrade, C.T. 2001. Processing and properties of thermoplastic starch and its blends with sodium alginate. Journal of Applied Polymer Science. 81, 412-420.

Sugih, A.K. 2008. Synthesis and properties of starch based biomaterials. Ph.D. dissertation, University of Groningen, The Netherlands.

Szegda, D. 2009. Experimental investigation and computational modeling of the thermoforming process of thermoplastic starch. Ph.D. dissertation, Brunel University, U.K.

Teixeira, E.D.M., Pasquini, D., Curvelo, A.A.S., Corradini, E., Belgacem, M.N. and Dufresne, A. 2009. Cassava bagasse cellulose nanofibrils reinforced thermoplastic cassava starch. Carbohydrate Polymers. 78, 422-431.

Thuwall, M., Boldizar, A. and Rigdahl, M. 2006. Extrusion processing of high amylase potato starch materials. Carbohydrate Polymers. 65, 441-446.

Van Soest, J.J.G. and Borger, D.B. 1997. Structure and properties of compression-molded thermoplastic starch materials from normal and high-amylose maize starches. Journal of Applied Polymer Science. 64, 631-644.

Van Soest, J.J.G. and Essers, P. 1997. Influence of amylose-amylopectin ratio on properties of extruded starch plastic sheets. Journal of Macromolecular Science, Part A. 34, 1665-1689.

Wattanakornsiri, A. 2012. Thermoplastic starch reinforced with recycled paper cellulose fibers. Ph.D. dissertation, Burapha University, Thailand.

Wattanakornsiri, A., Pachana, K., Kaewpirom, S., Sawangwong, P. and Migliaresi, C. 2011. Green composites of thermoplastic corn starch and recycled paper cellulose fibers. Songklanakarin Journal of Science and Technology. 33, 461-467.

Wattanakornsiri, A., Pachana, K., Kaewpirom, S., Traina, M. and Migliaresi, C. 2012. Preparation and properties of green composites based on tapioca starch and differently recycled paper cellulose fibers. Journal of Polymers and the Environment. 20, 801-809.

Willett, J.L. and Doane, W.M. 2002. Effect of moisture content on the tensile properties of starch/poly (hydroxyester ether) composite materials. Polymer. 43, 4413-4420.

Wollerdorfer, M. and Bader, H. 1998. Influence on natural fibers on the mechanical properties of biodegradable polymers. Industrial Crops and Products. 8, 105-112.

Yazdani, S.S. and Gonzalez, R. 2007. Aerobic fermentation of glycerol: a path to economic viability for the biofuels industry. Current Opinion in Biotechnology. 18, 213-219.

Yu, J., Chen, S., Gao, J., Huawu, Z., Zheng, H., Zhang, J. and Lin, T.A. 1998. Study on the properties of starch/glycerine blend. Starch/Starke. 50, 246-250.

Yu, J., Wang, N. and Ma, X. 2005. The effects of citric acid on the properties of thermoplastic starch plasticized by glycerol. Starch/Starke. 57, 494-504.

Yu, L. and Christie, G. 2001. Measurement of starch thermal transition using differential scanning calorimetry. Carbohydrate Polymers. 46, 179-184.