PROCESSING AND PROPERTIES OF BIODEGRADABLE POLYMER BLENDS BASED ON GELATINIZED POTATO STARCH

By

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ABSTRACT

The development of environmental friendly polymers from renewable resources, specifically for short term packaging and disposable applications, has been recognized as an important alternative to synthetic polymer based packaging materials. In this work, we focus particularly on the use of potato starch, because there is a significantly large by-product stream of potato starch from potato waste after food processing in Canada.

Poor processability and flowability are the main restrictions against the application of starch in granular form. Hence, thermoplastic starch (TPS) has been developed using starch in the presence of water and other plasticizers (e.g. glycerol) typically by using heat and shear. A microcompounder extruder was used for blending TPS, with an injection molding machine to prepare samples for testing. The sample test results show that TPS has severe limitations due to poor mechanical properties and high water sensitivity.

To overcome the mentioned weaknesses, while maintaining material biodegradability, one method is to blend TPS with a high performance biodegradable polymer. Poly lactic acid (PLA) was added to TPS to improve the mechanical properties. The addition of PLA improved mechanical properties and reduced water sensitivity. In order to improve the compatibility between the main phases in the blend, maleic anhydride (MA) was grafted unto PLA as a reactive compatibilizer.

Other methods to improve hydrophobocity and reduce water uptake were also investigated. Natural fiber reinforced TPS biocomposites were processed in order to improve blend performance and water sensitivity. For this purpose, sisal fiber was added to the TPS and TPS/PLA blends, and had major effects on the blend properties.

The addition of paraffin wax was also investigated. The incorporation of paraffin wax also reduced the water sensitivity of the samples significantly and improved the mechanical properties compared to TPS only samples.

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Nomenclature

ASTM	American Society for Testing and Materials
DSC	differential scanning calorimetry
HCl	Hydrochloric acid
KOH	Potassium hydroxide
MA	maleic anhydride
MeOH	Methanol
PCL	polycaprolactone
PEG	poly (ethylene glycol)
PHAs	polyhydroxyalkanoates
PHB	Polyhydroxybutyrate
PHBV	poly (hydroxybutyrate-co-valerate)
PLA	poly (lactic acid)
PLAgMA	poly (lactic acid) grafted maleic anhydride
PPG	poly (propylene glycol)
PS	polystyrene
PVC	polyvinyl chloride
THF	Tetrahydrofuran
ΔH	enthalpy of fusion, J/g

CHAPTER 1

Introduction

Petroleum based polymer materials with brilliant mechanical properties, low cost, great durability, and low density are extensively being used in a wide rage of applications from simple packaging to heavy construction. Although these petro-based plastics play an essential role in the quality of the life, they generate some major problems in our ecosystems: environmental pollution as well as consuming our finite petroleum resources. Economic growth leads to an extreme increase in the amount of waste over the past decade. Despite exhaustive efforts made to reduce the amounts of plastic waste, this quantity of the waste is significantly increasing all over the world, particularly in developing countries (Yu, 2006).

In the United States, the total generation of solid waste since 1980, has constantly grown by more than 50% per year until 2003, which was 236.2 million tons per year. In European Union, this number has increased from 204 million tones in 1995 to 243 million tones in 2003. It is important to mention that containers and packaging materials made up the largest part of the solid waste which is about 75 million tons in the United States, and only 9% of this may be recycled (Rudnik, 2008).

In order to solve problems generated by plastic waste and reduce the amount, development of recyclable and/or biodegradable plastics is seriously needed. Biodegradable polymers with low cost, which have been designed to degrade after their useful life time, are an attractive alternative for petroleum-based polymers, using such native materials as polysaccharides, e.g. starch.

Starch is a biodegradable natural carbohydrate polymer obtained from a large variety of sources such as the tubers of plants (potato), seeds of cereal grains (corn, wheat and rice), the pith of tapioca palm, and the pulse of plants (bean, pea and lentil)(Swinkels, 1985). Starch, due to its relatively low price and its availability has attracted extensive interest. However, in practice, the applications of starch in granular form are limited by its poor flowability and processability. Therefore, thermoplastic starch (TPS) has been developed from starch in presence of water and some other plasticizers and typically by using heat and shear (Donovan, 1979; Van Soest, 1997; Ma, 2005; Averous, 2008).

However, by itself starch is a poor alternative for petroleum-based plastics in any application which is suffering from severe limitations such as poor mechanical properties and high water sensitivity (Van Soest, 1997; Averous, 2000; Ma, 2005; Smith, 2005; Cyras, 2007; Rudnik, 2008; Averous, 2008). The water sensitivity and poor mechanical properties of the materials have been improved by the addition of high performance biodegradable polymers into the TPS such as poly (caprolactone) (PCL) (Averous, 2000; Wang, 2003), poly (lactic acid) (PLA) (Martin, 2001; wang, 2003; Huneault, 2006,) and poly(hydroxybutyrate) (Zhang, 1997; Averous, 2000; Yu, 2006).

Poly (lactic acid (PLA) is linear and biodegradable aliphatic polyester derived from renewable resources such as cornstarch and sugarcane. PLA as a high performance bio-based polymer has been considered as an alternative to petroleum-based plastics for disposable substances such as single use containers and cutlery, trash bags, and food containers. However, due to its expensive price compare to petroleum-based synthetic plastics, it is still not being used widely. In order to lower the material price, one way is to fill PLA with starch. The addition of starch into PLA matrix may also increase the PLA degradation rate (Bai, 2007).

The hydrophilic nature of starch, as compared to the hydrophobic nature of PLA and the lack of a reactive functional group between starch and poly (lactic acid) affect their compatibility and interfacial adhesion in TPS/PLA blends between the constituents. In order to obtain highly dispersed and compatible TPS/PLA blends, different compatibilizers have been investigated. Maleic anhydride (MA) is the most common compatibilizer being utilized to improve interfacial adhesion and compatibility between TPS and PLA in TPS/PLA blends (Carlson, 1998; Shin, 2006; Huneault, 2007; Jang, 2007; Ning, 2008; Orozco, 2009).

Commercially available biodegradable blends and composites materials have already been produced based on blending starch (from different sources) with high performance biodegradable polymers such as poly(lactic acid), poly (caprolactone), poly (hydroxybutyrate), and polyesteramides. The most common product is Mater-Bi from Novamont and Ecostar from National starch. In Table 1.1, a number of most well known starch based products which are commercially available in the market are listed.

Table 1.1 Commercially available starch based plastics

Trade name	Structure	Supplier	Origin	website
Solanyl	Starch Based	Rodenburg Biopolymers	Netherlands	www.biopolymers.nl
Bioplast TPS	TPS Based	Biotem	Germany	www.biotec.de
EverCorn	Starch Based	Japan Corn Starch	Japan	www.japan-cornstarch.com
Plantic	Starch Based	Plastic technologies	Australia	www.plantic.com.au
Biopar	Starch Based	BIOP Biopolymers Technologies AG	Germany	www.biopag.de
Placorn	Starch Based	Nihon Shokuhin Kako	Japan	www.nisshoku.co.jp

Another approach to improve the mechanical and water sensitivity properties of thermoplastic starch materials is the use of natural fibers. By incorporation of natural fibers into the TPS and TPS/PLA blends, both the mechanical properties and water sensitivity of the materials are significantly improved (Alvarez, 2005; Mao, 2005; Torres, 2007; Cao, 2008; Pejic, 2008). The chemical similarities between starch and natural fibers, as well as hydrogen bonding interactions between the fibers and the matrix, provide good compatibility in the composite (Ma, 2005; Cao, 2008).

In addition to the above mentioned materials, the addition of paraffin wax as a new biodegradable additive into TPS matrix was investigated. Paraffin wax is a super hydrophobic wax which consists of a complex mixture of hydrocarbons. Paraffin wax can be dispersed in many different kinds of matrixes, in either polar or non-polar solvents, e.g. water (Michelman, 2009).

CHAPTER 2

LITERATURE REVIEW

2.1 Biodegradable Polymers

In the 1980s, biodegradable polymers were commercially introduced in the U.S. The first generation of biodegradable polymers was usually a mixture of polyolefin and at least one other organic substance (e.g. starch) either blended or used as filler. Consumers realized that the products at best were only "biodisintegradable" and not totally compostable or biodegradable (Rudnik, 2008). Since that time, questions appeared about the biodegradability and/or compostability of polymers.

There are different international organizations that have established standards and testing methods for biodegradation and compostability of polymers. American Society for Testing and Materials (ASTM) and European Standardization Committee (CEN) are the two most significant standards. The following definitions contained herein are offered by American Society for Testing and Materials and according to ASTM D6400 (ASTM D 6400-04, ASTM publications):

Degradable Plastic

> "Degradable plastic is a plastic designed to undergo a significant change in its chemical structure under specified environmental conditions, resulting in a loss of some properties that may be measured by standard test methods appropriate to the plastic."

Biodegradable plastic

> "Biodegradable plastic is a degradable plastic in which the degradation results from the action of naturally occurring microorganism such as bacteria, fungi, and algae."

Compostatble plastic

> "Compostable plastic is a plastic that undergoes degradation by biological process during composting to yield carbon dioxide, water, inorganic compounds, and biomass at a rate consistent with other known compostable materials and leaves no visually distinguishable or toxic residues."

Polymers can be degradable without being necessarily biodegradable, and might be biodegradable without being necessarily compostable. A polymer may biodegrade at a rate which is too slow to be considered compostable (Stevens, 2002).

Averous (2004) also defined biodegradable plastics based on ASTM standard D-5488-94d as *"materials able of undergoing breakdown into carbon dioxide, water, methane, inorganic compounds, or biomass in which the main mechanism is the enzymatic action of micro-organisms. Biodegradation can be measured by definite standard tests, over a specific period of time."*

Biodegradable polymers can be either natural or synthetic. The natural products are usually come from different sources such as plant origin and animal origin. Averous (2004) classifies biodegradable polymers by way of their production into four categories where three of them are made from renewable resources (categories 1 to 3):

1. To make use of polymers from biomass such as the agro-polymers (e.g. starch polymers and cellulose).
2. To produce polymers by microbial production (e.g. the polyhydroxyalkanoate or PHA).
3. To produce monomers from agro-resource by fermentation and then polymerize them (e.g. poly lactic acid, PLA).
4. To produce polymers whose monomers are made from renewable agricultural sources and polymers are made by chemical synthesis.

Table 2.1 A brief look at some biodegradable polymers (Halley, 2005)

Base polymer	**Source type**	**Advantages**	**Disadvantages**
Starch	Renewable	Low cost Fast biodegradation	Poor mechanical properties Hydrophilicity
Polyhydroxyalkonoates (PHAs)	Renewable	Water stable Quick biodegradation	High cost
Poly lactic acid	Renewable and non-renewable	High strength	Brittle
PCL	Non-renewable	Water stable hydrolysable	Low melting point
Polyglycolic acid	Non-renewable	High strength Soluble in water	brittle
PVOH	Non-renewable	Good performance High strength	High cost

Biodegradable products are finding uses in many applications, including packaging, paper coating, fibers, bags, films and some dishware that is oven and microwavable.

2.2 Biodegradable polymers from renewable resources

2.2.1 Native starch

Starch is the storage polysaccharide of many seeds, roots and tubers and is relatively inexpensive and ubiquitous polymer. Starch provides soluble macromolecules which display high viscosity, and adhesion (Barsby, 1996). Starch ($C_6H_5O_{10}$) is a polysaccharide carbohydrate composed of a mixture of two α-glucose monomeric units named *amylose* and *amylopectin* with some other minor components such as *lipids* and *proteins*.

Depending on the source, starch generally contains 15-30% amylose and 70-85% amylopectin. Amylose is a polymer which consist of several thousands of $(1 \rightarrow 4)$-linked α-D-glucopyranosyl units linked in a linear fashion. Typically, it has a molecular weight of approximately 1×10^5 to 1×10^6 G mol^{-1} (Buleon, 1998).

Amylopectin is a highly branched polymer which is made of 250 to 500 glucose units. These glucose units are linked in a linear fashion by $\alpha\ (1 \rightarrow 4)$ linkages which are interlinked by $(1 \rightarrow 6)$

linkages. Amylopectin is a super large and branched molecule which its molecular weight ranging from 1×10^6 to 1×10^8 $Gmol^{-1}$ (Buleon, 1998).

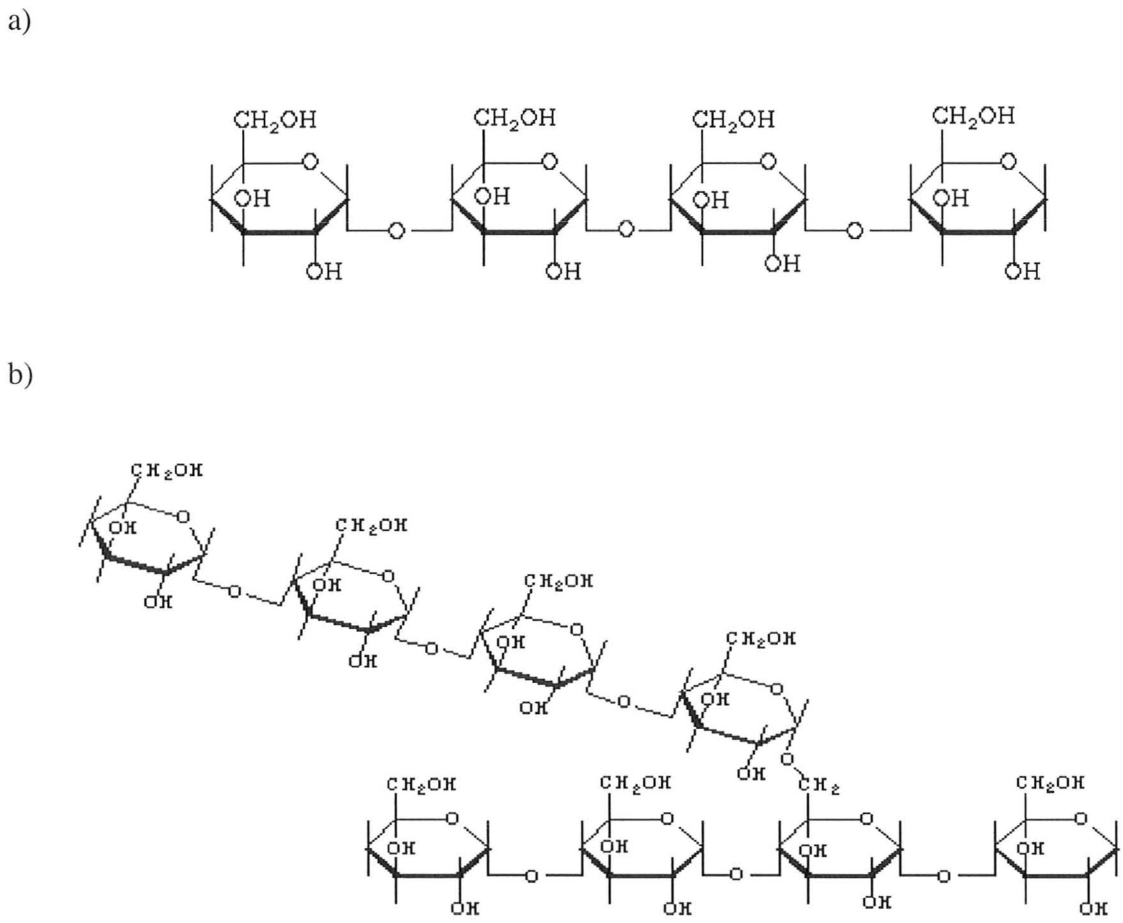


Figure 2.1 Schematic structures of a) amylose and b) amylopectin (Rudnik, 2008)

Starch granules from different botanical sources differ in size, shape, and morphology, e.g. starch granules are ranging from 2 to 30 μm depending on the plant origin.

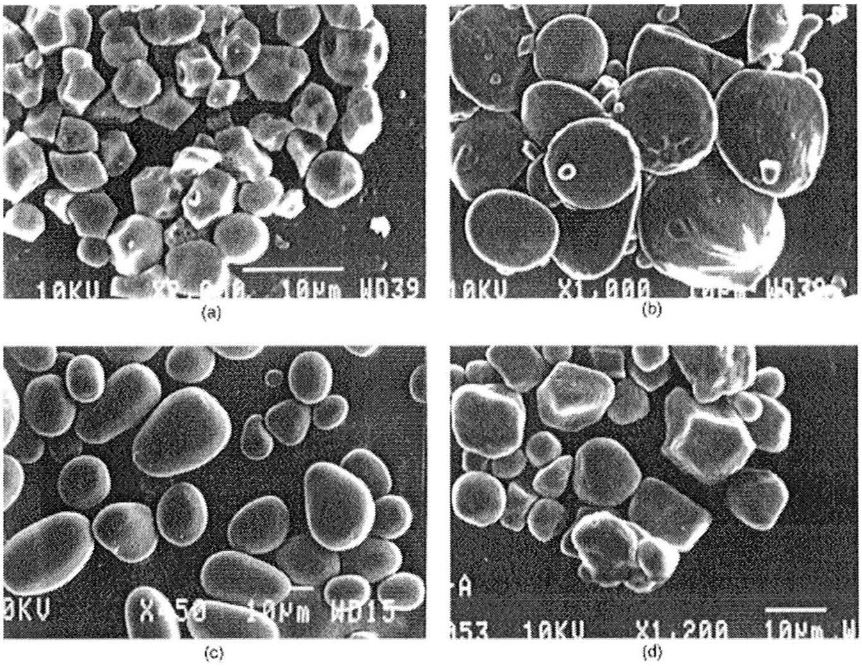
Dry starch due to its low price and its availability, was first used as filler materials in order to reduce the cost of a blend with more expensive materials. Since natural starch can be biodegraded in water and soil, many researchers have tried to find methods to use starch as a biodegradable substitute for petroleum-based polymers (Bai, 2007).

2.2.1.1 Potato Starch

The potato was first used for domestic cultivation in South America by the ancient civilizations. The Spaniards arrived in South America in 1525 and started using and exporting potato. They brought this new food to Spain and it quickly spread all over Europe. The production of potato starch first took place in factories of The Netherlands (Grommers, 2009). Potato starch is mainly being produced in Europe and China, and the major starch product in North America is corn starch. Generally, potato is the world's fourth most important food crop after wheat, corn and rice with annual word production of 312 million tonnes in 2006 (Singh, 2009).

As reported, about 30% of the potato starch manufactured in the US is being used in food industry. Potato starch granules are relatively large, swell easily and more water soluble than other kinds of starches. Cooked and gelatinized potato starch is more sensitive to shear than cereal starches.

Potato starch typically has 20-25% amylose and 75-80% amylopectin, since for many applications including making plastic from starch, amylose weakens the mechanical properties of the products, so amylose is not desired. Therefore, amylose-free potatoes have been also developed. Torres et al (2007) investigated the mechanical properties if thermoplastic potato starch and stated that potato starch shows the highest tensile test results among all kinds of other starches (Torres, 2007).



(a) (b) (c) (d)

Figure 2.3 Scanning electron micrographs (SEM) of starches from different sources: (a) rice, (b) wheat, (c) potato, and (d) corn (Singh, 2003)

The major difference between potato starch and other kinds of starch is having larger granules, greater amylopectin content, and hence, higher molecular weight (Hegenbart, 1995). Potato starch typically has larger granules with an ellipsoidal shape (Grommers, 2009). Although starches from different sources mainly show similar properties, they are different in many aspects. Table 2.4 shows the main differences between different commercial native starches.

Table 2.2 Differences between different native starches (Grommers, 2009)

Characteristics	Potato	Maize	Wheat	Tapioca	Waxy maize
Shape of granules	oval	Round	round	truncated	Round
Diameter, μm	5-100	2-30	0.5-45	4-35	2-30
Number of granules per gram of starch *10 6	100	1300	2600	500	1300
Swelling power at 95°C	1153	24	21	71	64
Solubility at 95°C	82	25	41	48	23
Paste resistance to shear	low	Medium	medium	low	Low
Film strength	high	Low	low	high	high
Film flexibility	high	Low	low	high	high
Film solubility	high	Low	low	high	High
Rate of retrogradation	medium	High	high	low	very low

2.2.1.2 Crystallinity of native starch

Since the mechanical properties of thermoplastic starch highly depend on crystallinity and gelatinization conditions (Van Soest, 1996a), understanding the mechanism of starch gelatinization and thermoplastic starch crystallinity will lead to better control of the structure development of thermoplastic starch during processing.

Starch is a semi-crystalline polysaccharide with a crystallinity of 15-45% (Huang, 2005). It shows a particular molecular organization, macromolecules are mostly oriented according to the radial axis. Inter-macromolecular hydrogen links, which are located between hydroxyl groups, along with the participation of water molecules result in the macrostructure in starch. The branch chains of amylopectin which are the dominating crystalline component in native starch are partially in the form of a double helix organization (Averous, 2007). We can also find co-crystallization of single helical amylose molecules and outer branches of amylopectin in a form of hybrid amylose-amylopectin helix, which gives radially oriented crystalline bundles (Huang, 2005), and single helical crystallization between amylose and free fatty acids or lipids (Averous, 2007).

Starches differ in the packaging of the double helices in the unit cell (Huang, 2005) depending on the source. As a result, several types of crystallinity are observed in the X-ray diffraction pattern. They are the 'A' type mostly cereal starches such as wheat, rice and maize, 'B' type mainly found in tuber starches such as potato and soga; and 'C' type in root starches (bean).

Technically the 'C' type structure is an intermediate structure between 'A' type and 'B' type (Van Soest, 1996a).

The other type is the Vh-type, which is the association of amylose, fatty acids and monoglycerides (Halley, 2005). The main difference between 'A', 'B' and 'C' type crystallinity is in the packing density of the double helices in the unit cell as well as chain lengths. 'A' type crystalline structure shows a denser packing of the helices with a double helix in the centre of the arrangement, whereas in the 'B' type crystalline structure, this double helix is replaced with a column of water molecules. The other difference between these two types of crystallinity is the difference between chain lengths. Starches with 'A' type crystallinities are made from shorter chains while starches with 'B' type crystallinities are formed from longer chains (Van Soest, 1996a).

2.2.2 Thermoplastic starch

2.2.2.1 Starch gelatinization

In the 1980s, an important development occurred by processing raw starch at its natural water content, approximately 15%, in a closed volume at a temperature above 100°C (Rudnik, 2008). Using single or twin extruders or intensive batch mixers, thermoplastic starch (TPS) polymers are obtained with moduli much the same as those of polypropylene and high density polyethylene (Rudnik, 2008). Starch gelatinization is the disruption of the internal bonding between the starch granules. Destruction of hydrogen bonds between the macromolecules causes the semi-crystalline structure of granules to transform into a homogeneous, amorphous material (Averous, 2004).

When raw starch, with water content more than 5%, is gelatinized under heat and pressure, a de-structured starch due to a series of irreversible changes is formed. Thermoplastic starch is a modified starch that has been processed to destroy the crystalline structure of native starch and form an amorphous thermoplastic. Starch gelatinization is the disruption of molecular organization of starch granules, which is directly affected by starch-water interactions. The starch swells and forms a viscous paste with destruction of the inter-macromolecule hydrogen bonds. During gelatinization, the water molecules enter the starch granules under the action of mechanical energy and thermal energy leading to the disruption of the granule structure (Huang, 2005).

Starch gelatinization is usually described in two steps (Halley, 2005). In the first step the addition of water breaks apart crystallinity of starch structure and disrupts helices. In the next step, addition of heat and more water causes starch granules which are made up of amylose and amylopectin molecules to swell and amylose leaves the granules. Starch granules, mainly containing amylopectin collapse and are held in a matrix of amylose (Halley, 2005).

As mentioned above, water has a remarkable role in starch gelatinization. It acts as an effective plasticizer and decreases the gelatinization temperature of thermoplastic starch as well as the melting temperature of starch. With decreasing amounts of water in TPS (less than 20%) the melting temperature of starch approaches the degradation temperature of native starch (Averous, 2007). For instance, the DSC thermogram for pure potato starch shows the melting temperature somewhere between 220°C and 240°C, while the starting temperature of starch degradation is 225°C. To overcome this drawback, a high boiling and nonvolatile (at the processing temperature) plasticizer is added, e.g. glycerol. The glycerol content may control the TPS rigidity in solid state and its viscosity in the melt state (Huneault, 2006).

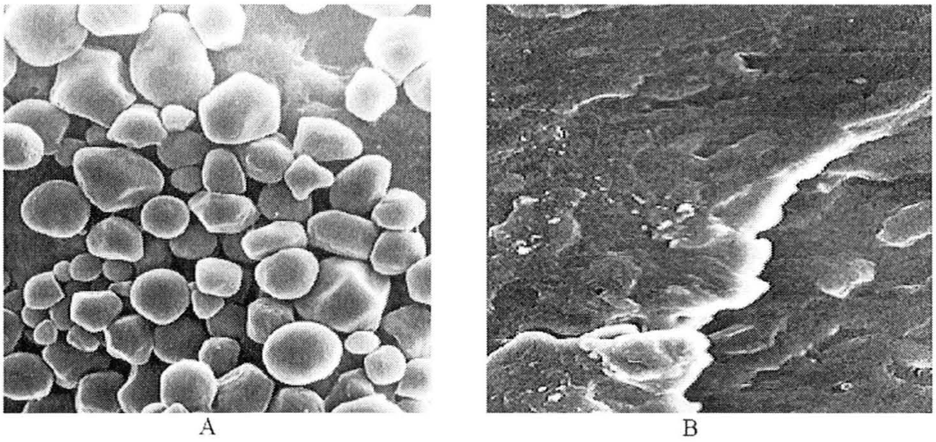


Fig.2.2 SEM images: (a) native starch; (b) thermoplastic starch (Yu, 1996)

Since there are many hydrogen bonds between the hydroxyl radicals of native starch, the tensile strength of pure starch is high. During starch gelatinization, water and glycerol disrupt the molecular organization of starch granules, which leads to a decrease in the interaction of molecules. Thus, the tensile strength and modulus of starch decrease after plasticization. On the other hand, the plasticizers improve the segmer and macromolecule movements, and these result in an increase in elongation (Halley, 2005).

The glass transition temperature (T_g) of dry pure starch is not exactly clear, but most studies show it to be in the range of 240 °C to 250 °C (Poutanen, 1996). Since starch gelatinization is the break up of the molecular organization within the starch granules, the glass transition temperature and the melting temperature both decrease (refer to Table 2.5) (Averous, 2004).

The most important deficiencies of TPS, for packaging applications, are its high hydrophilicity, low temperature resistance, weak mechanical properties and retrogradation of starch over time (Huneault, 2006). TPS is a very moisture sensitive material and readily decomposes on contact with water. To overcome this drawback and improve the poor mechanical properties of thermoplastic starch, one effective strategy is to blend TPS with other biodegradable polymers (Averous, 2004). Thus, numerous works have investigated the blending of TPS and other biopolymers, including: aliphatic polyesters such as polycaprolyctone (PCL), polylactic acid (PLA), and polydroxy-butyrate-co-valerate (PHBV), and polyesteramid**.**

2.2.2.2 Plasticizers

Adding plasticizers to polymers normally results in a decrease of the intermolecular force and increase segmental mobility of polymer's chains (Ke, 2004). Plasticizers are used in order to improve the flexibility and decrease the glass transition temperature of amorphous parts and the melting point of crystalline domains (Ke, 2004).

The effect of plasticizers on the inter-molecular mobility of semi crystalline polymers affects the molecular organization and eventually leads to lower T_g of the amorphous domains and T_m of the crystalline phase (Halley, 2005). The efficiency of plasticizers is evaluated by measuring the reduction of glass transition temperature and considering the improvement in mechanical properties (Martin, 2001).

The necessity of the application of the final product restricts the choice of plasticizers. There are various requirements that plasticizers must fulfill, (Ljungberg, 2002):

1. Plasticizers should not have any tendency to migrate to the surface of polymer, e.g. lactic monomers are great plasticizers for Poly (lactic acid), but the monomers have a tendency to migrate to the material surface, causing the surface to become sludgy.
2. Plasticizers should be miscible with the polymer; otherwise, the plasticizer behaves as an antiplasticizer, e.g. soy bean oil (SO) as a plasticizer for PHB increases the glass transition temperature.
3. Polymer material should not be saturated with plasticizer. If so, the glass transition temperature of the blend does not decrease further with increasing plasticizer content.
4. Plasticizers should not be extremely volatile. Plasticizer with lower molecular weight (Mw) has more ability to reduce glass transition temperature. The plasticizing efficiency of poly ethylene glycol (PEGs) as a plasticizer for poly (lactic acid), increases with decreasing molecular weight (Baiardo, 2003.

Most plasticizers used for biopolymers contain hydroxyl groups which form hydroxyl bonds between the plasticizer and the polymer. These hydroxyl bonds increase the free volume of the polymer and decrease the stiffness of the polymer matrix (Han, 2005).

Among a number of models which have been used to describe the mechanism of plasticization, three are cited more than others. The *free volume* model which involves intermolecular spaces and the *gel and lubricity* models which focus on the plasticization process (Han, 2005).

Lubricity theory: In lubricity theory, plasticizers play the lubricant role and reduce the mobility forces and let the chains to move freely. Plasticizers help polymer chains to move over each other easily (Wypych, 2004).

Gel theory: Plasticizer molecules adhere to the polymer chains and polymer-plasticizer interactions are taking the place of polymer-polymer attachments. This weakens the forces that are holding chains together, resulting in a decrease in the T_g of the polymer and leads to gel flexibility (Liong and Wong, 2002). Gel theory also states that the group of plasticizers molecules that are not attached along the polymer chains, make a compacted plasticizer region which makes the movement of polymer chains easy (Han, 2005).

Free volume theory: The free volume theory originated few years later than the gel and lubricity theories. The free volume of a polymer is a space wherein molecules move vibrationally at temperature above absolute zero. This theory shows that between molecules and atoms there is nothing but free volume. Free volume is usually affected by temperature and plasticizers and has a direct effect on the motion of chains. The T_g of a polymer can be predicted based on free volume. In general, the fraction of free volume at T_g for all polymers was found to be around 2.5%. The other definition for free volume is the difference between the volume at absolute zero and the temperature of interest (Han, 2005). By decreasing the temperature, vibrational motion of the chains decreases.

Addition of plasticizer molecules into the polymer, implies not only the introduction of molecules with much lower T_g than that of the polymer, but also small plasticizer molecules bring a great free volume into the blend. Since plasticizer molecules usually are much smaller than polymer molecules, adding plasticizers is an effective way to increase free volume of polymers. (Wypych, 2004).

Native starch in granule form displays poor processibility and flexibility, because of the hydrogen bonds between hydroxyl groups of starch molecules. In the presence of plasticizers, semicrystalline granules of native starch are changed into amorphous materials due to break up of bonds between starch molecules (Donavon, 1997).

Several plasticizers have been used to gelatinize starch. Plasticizers which are used, include polyols such as glycerol, glycol, xylitol, sorbitol, and sugars and ethanolamine (Van Soest, 1996; Bai, 2007; Poutanen, 1996; Rodriguez-Gonzalez, 2004; Van Soest, 1996). And also plasticizers having amid groups such as urea, formamide and acetamide or a combination of plasticizers have been studied (Ma, 2006; Yang, 2006). Between the plasticizers, usually water is the most important one, and starch chain mobility highly depends on the water content (Hulleman, 1998; Ning, 2008).

2.2.2.3 Crystallinity of thermoplastic starch

During the gelatinization process the native granular structure of starch is destroyed and the crystalline structure of the amylopectin molecules melts. A complicated network is forming which contains amorphous amylose and amylopectin with some residual crystallinity.

Van Soest et al (1996a, b) implied that two types of crystallinity exist in thermoplastic starch after processing (Van Soest, 1996a, b):

1. Residual crystallinity: ' A',' B' or' C' type crystallinity as a result of incomplete melting of starch during processing; this type obviously depends on the crystalline structure in the native source. There is an observed residual 'B' type crystallinity in thermoplastic potato starch after processing.
2. Processing-induced crystallinity: amylose VH-, VA- or EH-type crystallinity caused by recrystallization of amylose during processing.

The amount of residual crystallinity depends on process parameters such as processing temperature, shear stress and mixture composition. The amount of glycerol and water content indirectly affects the residual crystallinity. The lower the amount of glycerol is the lower the residual crystallinity. In fact, decreasing the amount of glycerol increases the melt viscosity which leads to an increase in shear stress on the melt (Van Soest, 1996a,d).

Process-induced crystallinity, which is caused by the recrystallization of amylose, also is affected by processing conditions. Increasing the rotor speed or increasing the mixing time during processing causes an increase in single helical type crystallinity. The amount of recrystallized amylose is directly related to the amount of initial amylose, which is a function of crystalline structure in the native source (Soest, 1996a).

2.2.3 Poly (lactic acid)

Poly (lactic acid) (PLA) is biodegradable semi-crystalline linear aliphatic polyester, prepared from lactic acid (2-hydroxy propionic acid). It is a thermoplastic, high-strength, high-modulus polymer which is commercially available.

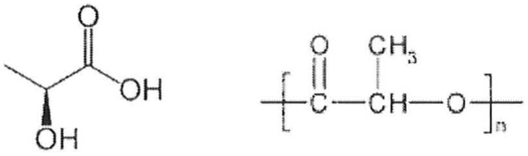


Figure 2.3 Structure of lactic acid (Rudnik, 2008), and Poly(lactic acid) (Averous, 2004; Averous, 2001)

Poly(lactic acid) is generally prepared through either polycondensation or ring-opening polymerization of lactic acid. High molecular weight poly lactic acid is usually being produced by the ring opening polymerization of the lactide monomers (Nijenhuis, 1992).

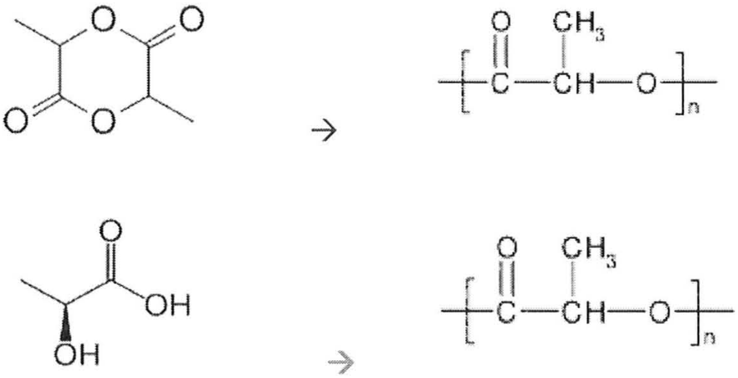


Figure 2.4 Preparing Poly (lactic acid) from lactic acid through a) poly condensation, b) ring opening

PLA exhibits better mechanical and thermal properties in comparison with the other biodegradable aliphatic polyesters, such as poly (hydroxyl butyrate) (PHB) and poly (ε-caprolactane) (PCL), made from renewable sources (Kulkarni, 1971). Its tensile strength is around 68 MPa and its modulus is around 2050 MPa, but the elongation at break (9%) is not high enough for many applications such as filming (Martin, 2001). PLA shows higher tensile strength and high modulus below T_g. For instance its tensile strength increases up to 68.4 MPa (Averous, 2001).

Martin et al (2001) investigated the thermal properties of PLA and reported that PLA is a semi-crystalline polymer with glass temperature (T_g) of 58°C and the melting temperature (T_m) of 152°C (Martin, 2001). The DSC testing results indicate PLA decomposes when the processing temperature exceeds 220°C. The thermal properties of PLA were also investigated by Wang et al (2003). Poly (lactic acid) exists as two stereo-isomers, Poly (levo-lactic acid) and Poly (dextro-lactic acid), which have the same chemical and physical properties. In addition to these two types of poly (lactic acid) that both are semi-crystalline in nature, there is an amorphous combination of D- and L- poly (lactic acid) with weak mechanical performance (Smith, 2005). Poly (lactic acid) properties and the stereo isomeric L- to D, L ratio are closely tied together, and deeply affect its thermal and mechanical performances, and also the degree of crystallinity. Thus, controlling the ratio of L- to D- monomers is an important issue (Rudnik, 2008). The glass transition temperature (T_g) of PLA is highly influenced by the ratio of two isomers (L-lactic acid and D-lactic acid). Pure L-PLA is a semi-crystalline polymer with a glass transition temperature (T_g) of 55 °C and melting point (T_m) of 180 ° (Lunt, 1998). PLA with high L-lactic acid content exhibits a high melting temperature and high crystallinity. PLA is almost an amorphous polymer when the amount of L-lactic acid decreases to 80% (Sinclair, 1996).

Generally, commercial Poly (lactic acid) is a mixture of Poly (L-lactic acid) (PLLA) and Poly (D, L-lactic acid) (PDLLA), but it is possible to find 100% L-PLA which has a high crystallinity (Averous, 2001).

By adding Poly (D, L-lactic acid) to pure L-PLA, the melting temperature and rate of crystallization are reduced, but there is no significant change in glass transition temperature (Drumright, 2000). PLA polymers range from amorphous glassy to semi-crystalline polymers and the melting point of PLA ranges from130 °C to 180 °C, glass transition temperature from 50 °C to 60 °C.

PLA is finding various applications in the packaging industry. Since PLA is a rigid material, it needs to be plasticized to be used in films. This means plasticized PLA shows good flexibility (Martino, 2006). Table 2.3 shows the influence of plasticization on some PLA properties, where Oligomeric lactic acid (OLA) and poly (ethylene glycol) were used as plasticizers.

Table 2.3 Effect of plasticization on PLA properties (Averous, 2004)

Material	T_g °C	T_m °C	E modulus (Mpa)	Elongation (%)
Pure PLA	58	152	2050	9
M-PEG 10%	34	148	1571	18
M-PEG 20%	21	146	1124	142
PEG 400 10%	30	147	1488	26
PEG 400 20%	12	143	976	160
OLA 10%	37	144	1256	32
OLA 20%	18	132	744	200

PLA applications

Poly (lactic acid) has various applications in many different areas, containing paper coating, fibers, clear films and packaging. In food packaging, PLA has the advantage that its monomers are produced naturally and from non-toxic materials.

Table 2.4 Main applications for PLA (Rudnik, 2008)

Packaging	Food packaging, films, rigid containers, carrier bags and labels, coated papers and boards, battery packaging
Agriculture	Sheet or moulded forms for time-release fertilizers, plant clips
Transportation	Parts of automobile interiors (head liners, spare tire covers)
Houseware	Carpet
Electric applications	CD, computer keys, cases for walkmans, wrappers for CD

2.2.4 Natural fibers

Natural fibers such as sisal, coconut, jute, and cotton have been attracted much attention lately as a reinforcement in synthetic and natural polymer matrices. Compared to inorganic fillers, natural fibers offer many advantages such as being renewable, offering low cost, low density, high specific strength, and high modulus (Kalia, 2009).

Commonly used natural fibers can be found in the following resources (Mishra, 2004):

1. bast (flax, hemp, jute, kenaf, and ramie)
2. leaf (sisal, abaca (banana),pineapple and palm)
3. seeds (cotton, coir and kapok) of the plants or
4. fruits (coconut, hemp, jute)

All natural biofibers, disregarding to their sources, are cellulosic in nature. The three main constituents in lignocellulosic systems are cellulose, lignin, and hemicellulose. In biofibers, the amount of cellulose can vary depending on the species and the age of the plant. Cellulose is a polymer consisting of various amounts of hydroxyl groups. These hydroxyl groups are in intramolecular and intermolecular hydrogen bonds with the macromolecule itself, with other cellulose macromolecules, and also with other polar molecules (Mohanty, 2005).

Throughout the synthesis of natural fibers cell walls, polysaccharides consisting of cellulose and hemicelluloses are formed. Lignin fills the free spaces between the polysaccharide fibers and binds them together (Mohanty, 2005). Cellulose microfibrills are boundtogether by an amorphous lignin matrix. Lignin, providing rigidity to the cell wall, keeps the water in fibers and also acts as a protection against biological attack (Kalia, 2009).

Hemicellulose found in the natural fibers is an amorphous and unoriented cell wall constituent. Hemicellulose is believed to be a compatibilizer between cellulose and lignin. Both hemicellulose and lignin can be more or less strongly hydrogen bound to cellulose micro fibrils (Pejic, 2008).

In natural fibers, the cell wall has a complex, layered structure consisting of a thin primary wall and a thick, three layered secondary wall. The middle layer of the secondary wall determines and influences the mechanical properties of the natural fiber (Kalia, 2009). The spiral angle between the fiber axis and the cellulose micro fibrils is called the spiral angle which determines the mechanical properties of the cellulose based natural fibers. The spiral angle is correlated with the strength and stiffness of natural fibers. The greater the spiral angle, the lower the mechanical properties. Table 2.3 summarizes some important natural fiber compositions and properties.

Table 2.5 Properties of different natural fibers (Kalia, 2009)

Fiber	Density (g/cm^3)	Tensile strength (Mpa)	Young's modulus (Mpa)	Elongation at break (%)
Jute	1.3-1.45	393-773	13-26.5	7-8
Flax	1.5-3	45-1100	27.6	2.7-3.2
Hemp	-	690	-	1.6
Ramie	1.5	400-938	61.4-128	1.2-3.8
Sisal	1.45	468-640	9.4-22	3-7
Palf	-	413-1627	34.5-82.5	1.6
Cotton	1.5-1.6	287-800	5.5-12.6	7-8

2.2.4.1 Sisal fibers

Sisal is a hard natural fiber extracted from the leaves of a plant named Agava sislana. Sisal is one of the four most widely used natural fibers in industry. Sisal fiber is mostly grown in tropical North and South America, and the tropical countries of Africa and West India. Sisal fibers are composed of 78% cellulose, 10% hemicellulose, 8% lignin, 2% wax, and about 1% ash by weight (Mishra, 2004). The chemical composition and structural parameters of sisal fibers are presented in Table 2.6.

Table 2.6 Chemical composition and structural parameters of sisal fiber (Mohanty, 2000)

Cellulose/wt%	67-78
Lignin/wt%	8-12
Hemicellulose/wt%	10-14.2
Pectin/wt%	10
Wax/wt%	2
Spiral angle/degree	10
Moisture content/wt%	11

2.2.5 Natural Waxes

Wax is an organic substance which is solid at room temperature and becomes liquid when melted (IGI wax Affilliate, 2009). Because wax is plastic in nature, it is capable to deform under pressure without applying heat (Michelman, 2009). In general, waxes are thermoplastic in nature and insoluble in water (IGI wax Affilliate, 2009).

Waxes are divided into two main groups. They can be "naturally" or "synthetically" derived. Natural waxes can be also divided into (IGI wax Affilliate, 2009) the following categories:

1. Animal waxes – e.g. Beeswax, Lanolin, Tallow

2. Vegetable waxes- e.g. Carnauba, Soy
3. Mineral waxes- e.g.
    - Fossil waxes- Montan
    - Petroleum waxes-Paraffin, Microcrystalline

Waxes can be dispersed in many different kinds of solvents. The dispersed wax particle size may range from tens of nanometers to micron sized particles (Michelman, 2009).

In particular, paraffin wax is a natural wax that consists of a complex mixture of hydrocarbons which is totally biodegradable. In general paraffin wax is non-reactive, non-toxic, with good water barrier properties and colorless (IGI wax Affilliate, 2009).

There are two main mechanisms for consuming wax in different products (Michelman, 2009). Wax can be added as a surface active agent, where the wax particles migrate to the surface of the product, and are usually described as a water repellant wax in this form. Wax particles can also be used dispersed in a coating on the surface of a product.

The goal of adding a wax to a product as an additive or as a coating on top of a product is to develop a biodegradable product that would exhibit water barrier properties over a wide range of relative humidity (Despond, 2005)

2.3 Thermoplastic starch blends

As already mentioned, thermoplastic starch suffers from weak mechanical properties as well as high water sensitivity. In order to reduce the water sensitivity and improve mechanical properties of TPS we focus on a few methods to improve the properties.

2.3.1 Properties of Thermoplastic Starch and PLA Blends

Among various biodegradable polymers, PLA possesses good mechanical properties and processability (Park, 2000), but PLA is very brittle and relatively expensive. In order to lower product price , one possible way is to mix starch with PLA (Martin, 2001). However, the addition of starch into such a brittle polymer, leads to an even more brittle material (Wang, 2003). The main problem with the blend is the poor interfacial interaction between the hydrophobic PLA and hydrophilic starch (Ning, 2008). Weak interfacial interaction leads to weak mechanical properties in polymer blends (Ning, 2008). Gelatinization of starch is a good method to get good interfacial affinity (Park, 2000) and improve dispersion in other polymers (Martin, 2001). As a result, for TPS/PLA blends, the mechanical properties are enhanced and stiffness is improved comparing to the blends of native starch/PLA (Park, 2000).

Thermal behaviors of starch/PLA blends through differential scanning calorimetry (DSC) were investigated (Ke, 2004; Wang, 2003; Park, 2000). The results indicate that by adding native starch to PLA, regardless of starch concentration almost no changes were observed in T_m and T_g, but T_c of the blend shifted to higher temperatures. These results would seem to show that the thermal behaviors of starch/PLA blends are very similar to that of pure PLA. We have obtained the same results by investigating the thermal properties of thermoplastic potato starch and PLA blends.

For blends of TPS/PLA, DSC results indicate that T_g, T_m, and T_c of the blend decrease to lower temperatures compared to PLA. The addition of plasticizers resulted in a decrease in T_g, T_m and T_c of the blend compared to pure PLA, and decreased more with increasing plasticizer content (Park, 2000).

2.3.1.1 Maleation of Poly lactic acid

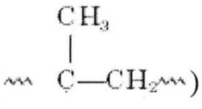
It has been reported that starch and PLA are thermodynamically immiscible (Zhang., 2004). One possible way to increase the compatibility between starch and PLA is the gelatinization of starch (Ning, 2008). The major drawback in the blend of TPS/PLA is its low elongation at break of the blend which is below 6% as soon as soon as the TPS concentration in the blend increases over 10% (Huneault, 2006). This The lack of interfacial affinity between TPS and PLA affects the mechanical properties of the blend, since the tensile strength and elongation at break of polymer blends are related to interfacial adhesion between the polymers in the blend (Carlson, 1998; Huneault, 2006; Zhang, 2004). This problem can be solved by grafting a reactive moiety in to the PLA; this moiety later reacts with TPS molecules in the blend (Carlson, 1998). Free radical initiated grafting of maleic anhydride into PLA is a well known grafting reaction. This reaction is performed in the presence of Lupersol 101 (2,5- dimethyl -2,5 di-(tret-Butylperoxy) hexane as an initiator (Carlson, 1998).

Interfacial modification in the blend is expected to change the mechanical properties. Hunealt et al (2006) have investigated the effect of interface modification of TPS/PLA blend on its mechanical properties. Results indicate that the tensile modulus, even after interface modification, decreases with increasing TPS fraction. Compared to the unmodified blend, the modulus and tensile strength are almost unaffected. In terms of elongation at break, for the unmodified blend, elongation is in the range of 10-20% which is a little higher than elongation of pure PLA, while for the modified blend elongation at break exceeds 150% (Huneault, 2006). Also, Orozco et al has reported maleic anhydride as an effective compatibilizer for thermoplastic starch and poly lactic acid blends (Orozco, 2009). Therefore, in this work, MA was grafted to poly lactic acid in order to improve the mechanical properties of TPS/PLA blends. After grafting MA, no significant effects were observed on mechanical properties of the blends, neither the tensile and modulus nor the elongation.

2.3.1.2 Coupling agent

In recent years various studies on the grafting reaction of maleic anhydride on poly lactic acid have been conducted. These studies imply that during the grafting reaction some desirable and undesirable reactions occur. For the grafting of maleic anhydride on to PLA, peroxide acts as the initiator (Carlson, 1998). By increasing the temperature, peroxide starts to decompose and breaks into two initial radicals. These radicals abstract hydrogen from the PLA chain and form polymers macroradicals which react with the maleic anhydride (Zhang, 2004).

The mechanism proposed for the grafting reaction is envisioned as follows.

In the reaction of the proposed mechanism for the grafting reaction, thermal decomposition of peroxide, ROOR, forms two initial alkoxy radicals ($RO\cdot$). These may decompose to secondary radicals. In continue, the primary radicals abstract hydrogen atom from PLA chain, so macromolecular radicals ( $\sim\overset{\overset{\displaystyle CH_3}{|}}{\dot{C}}-CH_2\sim$) are formed. Next, by reacting the maleic anhydride monomer with the macromolecular radicals, PLA g MA forms (Zhang , 2004).

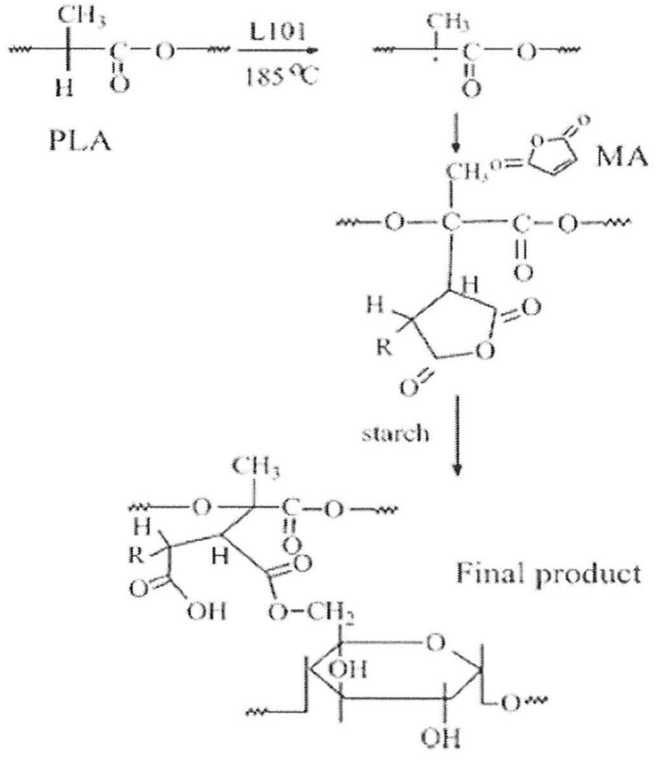


Figure 2.6 proposed reaction mechanism of PLA g MA (Zhang, 2004)

2.3.2 Thermoplastic starch reinforced with Sisal fibers

Since polar groups of starch molecules can react with the hydroxyl groups of lignocellulosic fibers, and make strong hydrogen bonding interactions, thermoplastic starch is an ideal matrix for the cellulosic fiber reinforcement (Cao, 2008). Acceptable compatibility between sisal fibers and TPS was ascribed to the strong hydrogen bonding interactions between the sisal and the matrix as well as the chemical similarities in starch and cellulose (Cao, 2008).

In this regard, the use of starch as a matrix for natural fiber reinforced composites has been reported by various authors (Cyras, 2004; Ma, 2005; Corradini, 2007; Torres, 2007; Pejic, 2008; Cao, 2008).

Some authors studied the mechanical properties of TPS and TPS reinforced with sisal fibers. They reported that with increasing sisal fiber content, increasing Young's modulus and tensile strength were observed (Corradini, 2009; Torres, 2007; Corradini, 2007). Torres et al (2007) reported that 100% increase in tensile strength was obtained by adding 10% sisal fiber to the matrix of TPS.

With the incorporation of sisal fibers into the TPS matrix, the water uptake at equilibrium of the composite decreased. This is probably due to the much less hydrophilic character of the lignocellulosic fibers compare to the super hydrophilic character of TPS matrix (Cao, 2008). Corradini et al (2009) observed a sharp decrease in the diffusion coefficient of the composite with the addition of only 5% sisal fiber.

CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 Experimental Materials

In this research work, potato starch was donated by Manitoba Starch. Glycerol with boiling point of 182°C and 99.5% purity was purchased from Sigma-Aldrich Canada LTD. Cargill-Dow poly (lactic acid) 4042D was used for the TPS/PLA blends. Maleic anhydride (99% purity) and Luperox 101 (2, 5- bis (tert-butylperoxy)–2, 5-dimethyl-hexane) were also supplied by Sigma-Aldrich Canada LTD. Sisal fiber was donated by Espartos Santos. High melt fully refined Paraffin wax was also donated by IGI (The International Group, Inc).

3.2 Preparation of Experimental Samples

3.2.1 Starch gelatinization

Five levels (0.16, 0.25, 0.33, 0.42, and 0.5 g water/ 1 g dry starch) of water content and two levels (0.5 and 0.66 g glycerol/ 1 g dry starch) of glycerol content were prepared in order to investigate the effect of plasticizers on starch gelatinization. The composition of these starch-water-glycerol mixtures are outlined in Table 3.1

Table 3.1 Compositions of starch-water-glycerol

Glycerol/Starch ratio	Water/Starch ratio	Starch wt%	Water wt%	Glycerol wt%
0.5 : 1	0.16	60	10	30
	0.25	57.1	14.3	28.6
	0.33	54.5	18.2	27.3
	0.42	52.2	21.7	26.1
	0.5	50	25	25
0.66 : 1	0.16	54.5	9.1	36.4
	0.25	52.2	13	34.8
	0.33	50	16.6	33.3
	0.42	48	20	32
	0.5	46.1	23.1	30.8

For each mixture, about 6 g of potato starch was mixed with water and glycerol. Each mixture was sealed in a plastic bag and kept at room temperature for a certain time (either one hour or 24 hours) prior to DSC testing.

3.2.2 Thermoplastic Starch (TPS)

Potato starch was dried in a vacuum oven in the presence of some Drierites (Anhydrous Calcium Sulfate) for 24 hours at 80°C prior to the mixing.

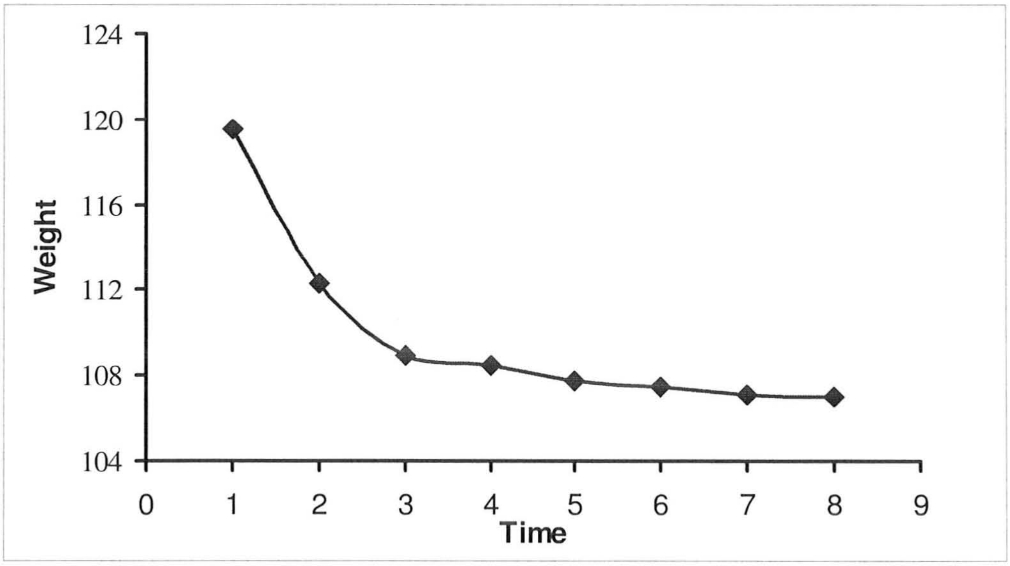


Figure 3.1 Drying Potato starch in vacuum in presence of Drierites

Dried potato starch was premixed with water and glycerol at room temperature. Different ratios of starch/glycerol/water are presented in Table 3.2. The basic formula of 60/30/10 was set for subsequent runs and for all the blends. The mixture of starch, glycerol and water was kept at room temperature for almost one hour before being loaded into either a Haake Rheomix 3000 batch mixer or micro compounder extruder (DSM Xplore).

Table 3.2 Different ratios of starch/glycerol/water

Starch wt%	Water wt%	Glycerol wt%
54.5	9.1	36.4
52.2	13	34.8
50	16.6	33.3
48	20	32
46.1	23.1	30.8

To mimic one form of extrusion processing, premixed samples were kept at room temperature for two different storage times (either one hour or 24 hours) prior to TPS preparation. Since there is little difference in the effects on thermal properties due to the two different sample preparation methods, the premixed samples were loaded to extruder after one hour.

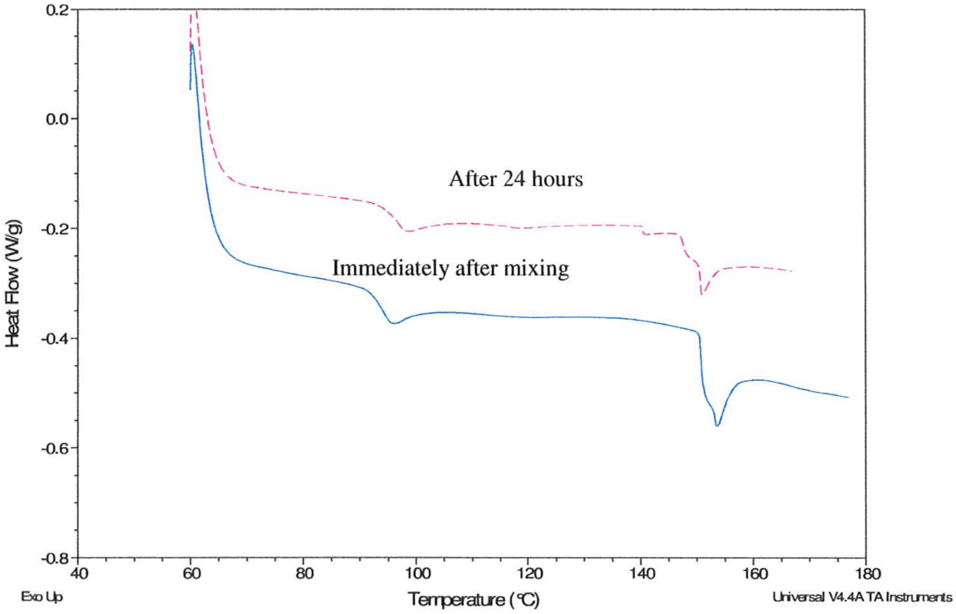


Figure 3.2 Effect of storage time prior to mixing on starch gelatinization temperature 52.2% starch-13% water-34.8% glycerol

Thermoplastic Starch (TPS) in open blending system

The blending conditions were 140°C at 75 rpm for 6 minutes. After processing the materials in Haake Rheomix Batch Mixer with roller rotors, the mixture was kept at room temperature for one week and then was ground into powder. Samples were molded into standard rectangle-shaped molds according to ASTM D 638-08 (type V with 2 mm thickness) in a hot press at 170 °C and 5-10 tons force and for 4 minutes.

Thermoplastic Starch (TPS) in closed blending system

The mixture of starch, glycerol and water was loaded into a micro compounder extruder (DSM Xplore). The blending conditions were 130°C at 75 rpm for 6 minutes. Dumbbell-shaped specimens according to ASTM D 638-08 (type V with 3.3 mm) thickness were prepared directly after extrusion. Specimens were sealed in plastic bags and kept at room temperature for 10 days prior to tensile testing.

3.2.3 Thermoplastic Starch (TPS)/PLA blends

Thermoplastic starch was prepared by aforementioned process in DSM. In order to prevent negative effects of moisture on mechanical properties of TPS/PLA blends (Wang, 2002) as well as thermal degradation of PLA (Bai, 2007), water must be removed from the TPS blends prior to mixing with PLA. The water removal was performed through venting for 4 minutes at 160°C. After venting, dried PLA was loaded to the extruder. The conditions were 160°C at 75 rpm for 4 minutes. Dumbbell-shaped specimens according to ASTM D 638-08 (type V with 3 mm thickness) were prepared directly after extrusion. Specimens were sealed in plastic bags and kept at room temperature for 10 days prior to tensile testing.

3.2.4 Thermoplastic Starch (TPS)/PLAgMA blends

3.2.4.1 Poly (lactic acid) grafted Maleic Anhydride (PLAgMA)

Maleic Anhydride (MA) chips were first ground into powder and then mixed with dried PLA pellets in an aluminum tray by hand and then Luperox 101 (L101) was added to the materials.

The blending ratio of PLA/MA/L101 was 100/2/0.25 (wt) (Carlson, 1998). The mixture was loaded into Haake Batch Mixer for blending under the conditions of 180°C and 75 rpm for 4 minutes. The mixture was grounded into powder and then was stored in a sealed plastic bag.

3.2.4.2 Characterization of the extent of Poly (lactic acid) maleation

It is not possible to get an accurate number for the extent of the anhydride grafted to the PLA without considering the fact that not only the maleated samples were titrated against the HCl, but also virgin PLA, THF-MeOH mixture, and even non-grafted MA which still left in the solution were titrated. To avoid obtaining the wrong values from the titration, back titration of 1 gr pure PLA with the same method is necessary.

The extent of maleation for PLA grafted MA samples was determined through titration. Since a direct titration of the samples is probably inaccurate, a back titration was performed. The following back titration method used is a close version of Carlson method (Carlson, 1998):

1. remove unreacted MA and L101 radicals by washing the samples for several times
2. samples were died in a vacuum oven at a temperature close to glass transition temperature of PLA until the samples totally dried
3. dissolve 1 gr of the maleated sample in a 20 ml mixture of THF-MeOH (5:1) under heat (40°C) and steer
4. when the samples were completely dissolved (about after half an hour) in the mixture, 30 ml of KOH solution (0.1N in MeOH) was added to the mixture

5. chemicals were left to react for 15 minutes
6. the sample was titrated with HCl 0.01N

After the titration the following calculations were performed to determine the quantity of grafted anhydride.

$$Anhydride(mole) = [(V_{KOH} \times N_{KOH}) - (V_{HCL} \times N_{HCl})]_{PLAgMA} - [(V_{KOH} \times N_{KOH}) - (V_{HCL} \times N_{HCl})]_{PLA}$$

(1)

$$\% Anhydride = Anhydride(mole) \times \frac{98.06 g / mol}{W_{sample} g} \times 100$$

(2)

3.4.2.3 TPS and PLAgMA Blends

The first two stages of the titration were performed on part of the PLAg MA samples called treated PLAgMA samples. Both treated and untreated PLAgMA samples were used as components to be mixed with TPS. Water free TPS and PLAgMA was prepared in DSM extruder with the same method and in the same conditions already mentioned for TPS/PLA blends preparation.

3.2.5 Thermoplastic Starch (TPS) reinforced with Sisal fibers

Sisal fiber was added to the TPS, one hour after the starch was premixed with water and glycerol at room temperature. The mixture immediately was loaded into a micro compounder extruder (DSM Xplore). The blending conditions were 130°C at 75 rpm for 6 minutes. Dumbbell-shaped specimens according to ASTM D 638-08 (type V with 3.3 mm) thickness were prepared directly after extrusion. Specimens were sealed in plastic bags and kept t room temperature for 10 days prior to tensile testing.

For the composites containing TPS/PLA/sisal fiber, TPS/sisal composite was first prepared with the aforementioned method, and then dried PLA was added after 4 minutes venting (in order to get water free TPS/sisal blend). In each composite, the amount of sisal fiber varied from 5-20% of total weight of the composite.

3.2.6 Thermoplastic Starch (TPS) blended with Paraffin wax

Paraffin wax as an additive was added to all the blends and composites. Paraffin wax before being loaded to the extruder was premixed with starch-water-glycerol mixture in all the blends. For each blend, the amount of Paraffin wax was 2% of total weight of the blend.

3.3 Characterization Measurements

3.3.1 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) experiments were operated using a 2920 Modulated DSC equipped with a refrigerated cooling system (RCS) (TA Instruments, USA) in order to investigate thermal properties of the samples. Samples used for DSC measurements were weighted (around 8 mgrs) in Tzero Aluminum pans which were sealed hermetically to eliminate water loss.

3.3.1.1 Starch gelatinization

Differential scanning calorimetry (DSC) has been used to investigate the effect of water and glycerol on the gelatinization and melting of potato starch. Samples were heated from 50°C to 180°C at a thermal scan rate of 10°C/min.

3.3.1.2 Thermal analysis

On order to investigate the glass transition temperature of pure TPS, samples were first hermetically sealed and then were heated from-10 °C to 180°C, after which the materials were quenched in liquid nitrogen and then reheated again from -10°C to 180°C. The thermal scan rate was 10°C/min.

For TPS/PLA or TPS/PLAgMA blends, quenching is not necessary. The sample were heated from 20°C to 180°C at a thermal scan rate of 10°C/min, and then cooled to -20°C at a thermal scan rate of 20°C/min. After equilibration at -20°C, the samples were reheated from -20°C to 180°C at the rate of 10°C/min. The curve of second thermal scan contains our favourite thermal information about the samples. A nitrogen flow (150ml/min) was applied throughout the experiments. The software of a TA Universal Analysis 2000 unit was used to analyze the results.

3.3.2 Tensile testing

The tensile tests were performed through an Instron tensile testing machine (Series IX Automated Material Testing System) according to ASTM D 638-08 at room temperature with a crosshead rate of 5 mm/min. 500 N load was used for TPS and TPS/Paraffin wax samples and a 5 KN load was used for TPS/PLA, TPS/PLAgMA, TPS/sisal fiber, and TPS/PLA/sisal with and without Paraffin wax. The type V test specimens with 3 mm thickness and 25.4 mm gauge length, prepared through injection molding in order to be used for tensile tests. For each measurement, at least 3 specimens were used. Actually, measurements were continued until 3 simillar results were obtained.

3.3.3 Contact angle measurement

Circular samples were prepared in a Carver hot press in order to measure the contact angle of the samples. The hot press was operated at 170°C for pure TPS samples and at 150°C for all TPS blends. The same method was used to prepare all the specimens, and also it was attempted to have a homogeneous surface for all the samples. A water droplet was deposited on the sample surface by a syringe. Contact angle is a tangent angle between the water droplet and the substrate, and the contact angle of hydrophobic samples is larger than that for hydrophilic ones.

The contact angle of each sample was recorded after 30 seconds. A Sanyo camera and goniometer along with a computer with drop shape analysis software (FTA200, Version 2.0) were used to determine the contact angle.

3.3.4 Water uptake measurements

The kinetics of water uptake was determined for the blends and composites. The samples used were thin dumbbell-shaped strips with dimensions of $63.5 \times 9.53 \times 3.3\, mm^3$. The samples were first perfectly dried at 80°C under the vacuum for 24 hours, and then kept at 75 % RH for one month. This situation was provided by placing the samples in a desiccator in presence of Sodium Chloride (NaCl). The samples were removed from the desiccator periodically and were weighted at particular time intervals. The water uptake (UW) of all the samples was determined as follows:

$$WU(\%) = \frac{W_t - W_0}{W_0} \times 100$$

(3)

Where W_0 is weight of a sample before exposure to 75% RH and W_t is weight of the sample after t h of exposure to 75% RH. For each sample, three replicates were tested, and average of three was reported.

3.3.5 Water vapour transition

In order to measure the water vapour transition (WVT) of the samples circular samples with 2 mm thickness were prepared through hot press. The hot press was operated under 10 tons force at 170°C for 4minutes and 150°C for 6 minutes respectively for pure TPS samples and for all TPS blends and composites.

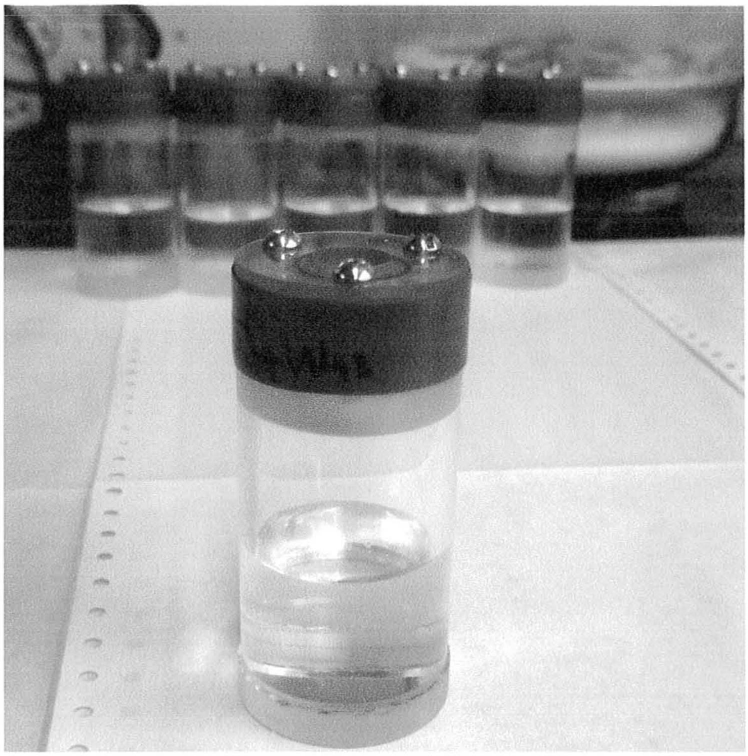


Figure 3.2 Water vapour transition test container

WVT tests were operated according to ASTM E 96 – 90. For each sample, three specimens were tested and the average WVT of them was reported. Specimens were attached to a cylindrical test dish. The test dish was filled with distilled water. The water depth should not be less than 3 mm to ensure coverage the dish bottom through the test. The surrounding of the specimens was thoroughly sealed to prevent the passage of vapour from anywhere else but the specimen. Each dish was weighted periodically for eight times during 2 weeks. Finally, the weight of each dish is plotted against the time. The slope of the straight part (steady state part) is the rate of WVT.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Starch Gelatinization

4.1.1 Effect of water on gelatinization temperature

Typical DSC thermograms of starch gelatinization consist of two transitions at low water content (15-40%) (Biliaderis,1980; Wang, 1991; Qu, 1994; Soest, 1996; Forssell, 1997; Nashed,2003). Many researchers consider that the gelatinization occurs in starch following two major transitions; gelatinization and melting (Van Soest , 1996c).

At higher water content, swelling of the amorphous region in starch granules destroys the crystalline regions by pulling the crystallites apart at lower temperatures, while at lower water content, crystallites melt at significantly higher temperatures (Wang, 1991). The concern of this study is to investigate the phase transition of potato starch at low plasticizer contents through the use of differential scanning calorimetry (DSC).

The phase transition of starch granules in a DSC thermogram has been characterized by using the onset temperature (T_o) and the peak temperatures (T_p) of the two endothermic transitions named gelatinization and melting. In Table 4.1 and Figure 4.2, it is shown that the gelatinization and melting peak temperatures decrease as water content of samples increases. This trend continues until the water content is in excess of 60% (Figure 4.1)(Wang, 1991).

Table 4.1 Effect of water content on gelatinization of potato starch when starch/glycerol ratio:2/1 (T1, associated with the first transition which is concerned as gelatinization, T2, associated with the second transition which is concerned as melting)

Starch%	**Water%**	**Glycerol%**	**$T_{1(gelatinization)onset}$ °C**	**T_{1peak} °C**	**ΔH_1J/g**	**$T_{2(melting)onset}$ °C**
54.5	9.1	36.4	93.73	97.43	1.38	150.91
52.2	13	34.8	92.37	95.62	1.432	148
50	16.6	33.3	87.66	90.68	1.373	147.51
48	20	32	85.14	88.51	1.814	142.35
46.1	23.1	30.8	79.25	83.47	5.993	141

All thermoplastic starch mixtures with water content higher than 60% (w/w) are assumed to have excess water. Wang et al. (1991) found that regardless of the starch source, when starch is gelatinized with a water content higher than 60%, complete gelatinization takes place and only one peak can been seen on the associated DSC thermogram (Wang, 1991). We examined two (2) samples with 55.3% and 65% water content in DSC and the thermograms show peak temperature of 61°C for both samples and only one for each was observed.

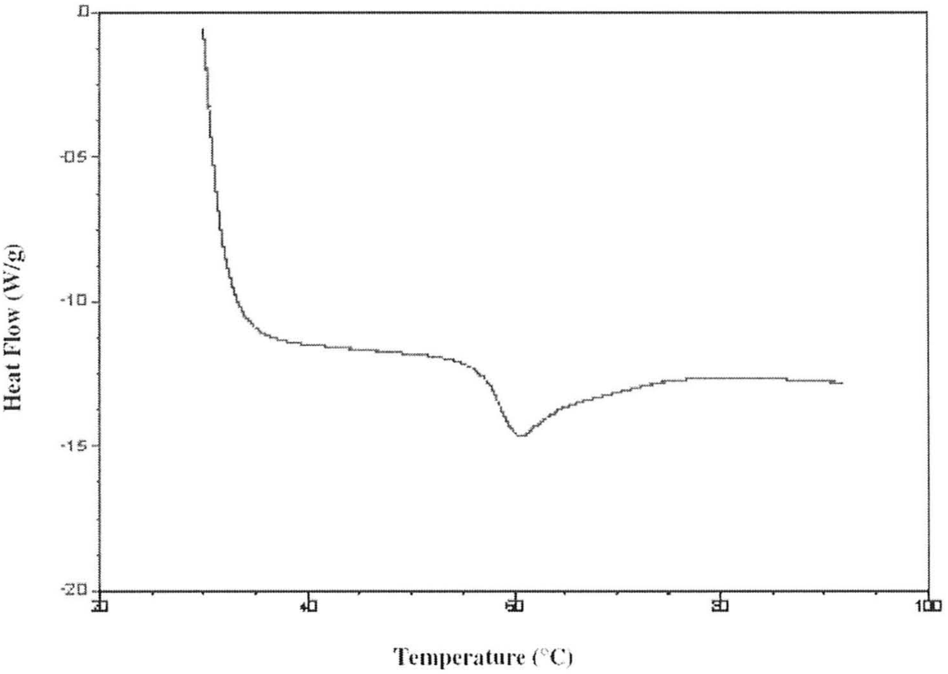


Figure 4.1 Thermogram of potato starch gelatinization with excess water

However, from results obtained from DSC, it can be concluded that a single peak endotherm observed for excess water changes to double peak endotherms with decreasing water content. As the water content of the samples decreases from excess water to lower water amounts, the peak temperature increases from 61°C to about 233°C for a bone dry starch. The effect of water addition to potato starch on the onset temperature and peak temperature for gelatinization at different water contents are shown in Figure 4.2.

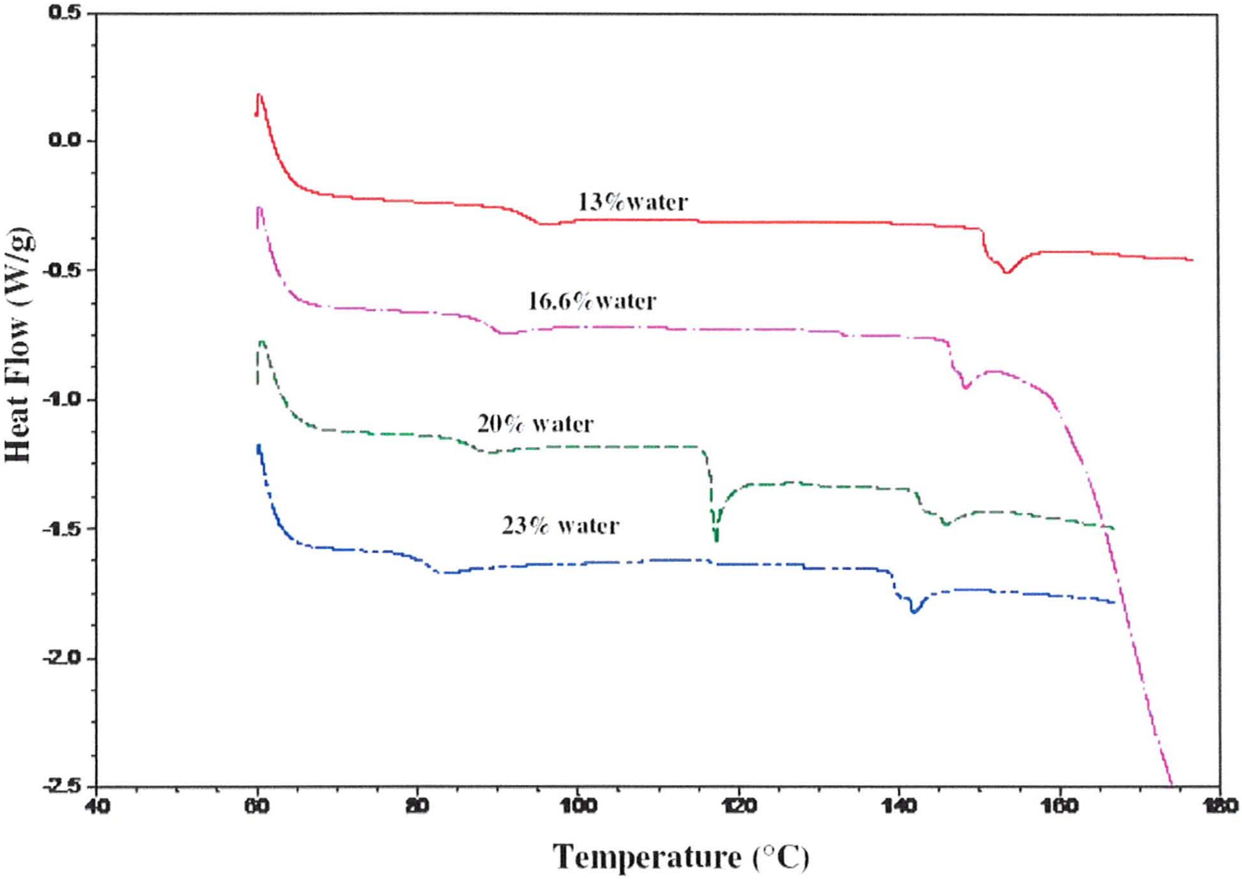


Figure 4.2 Effect of water content on gelatinization and melting temperature of starch while starch/glycerol ratio is constant and equal to1.5/1

As expected, increasing the water content in constant glycerol level leads to a linear decrease in the gelatinization temperature. This can be described with the following equations, where W is the percentage of moisture content (wt/wt).

For constant 20% glycerol content:

`Gelatinization temperature = 161 - 1.47 Water content,` R-sq=98%

For constant 25% glycerol content:

Gelatinization temperature = 160 - 1.37 Water content, R-sq = 96%

4.1.2 Effect of glycerol on gelatinization temperature

In the thermoplastic starch, glycerol plays an important role as an additive, to reduce thermoplastic starch brittleness and to increase flexibility (Nashed, 2003). Glycerol also affects gelatinization and melting behavior of starch. As previously mentioned, glycerol shifts melting temperature of starch toward lower temperatures (Van Soest, 1996c). In this section, the effect of glycerol on the gelatinization of potato starch is investigated through DSC.

At very low water contents and low glycerol content, no gelatinization peak is observed and only a broad melting peak is visible at relatively high temperatures. By increasing the amount of glycerol, a gelatinization peak appears and both gelatinization and melting peaks are observed. Results from DSC also demonstrate that increasing the glycerol content leads to an increase in gelatinization peak temperature.

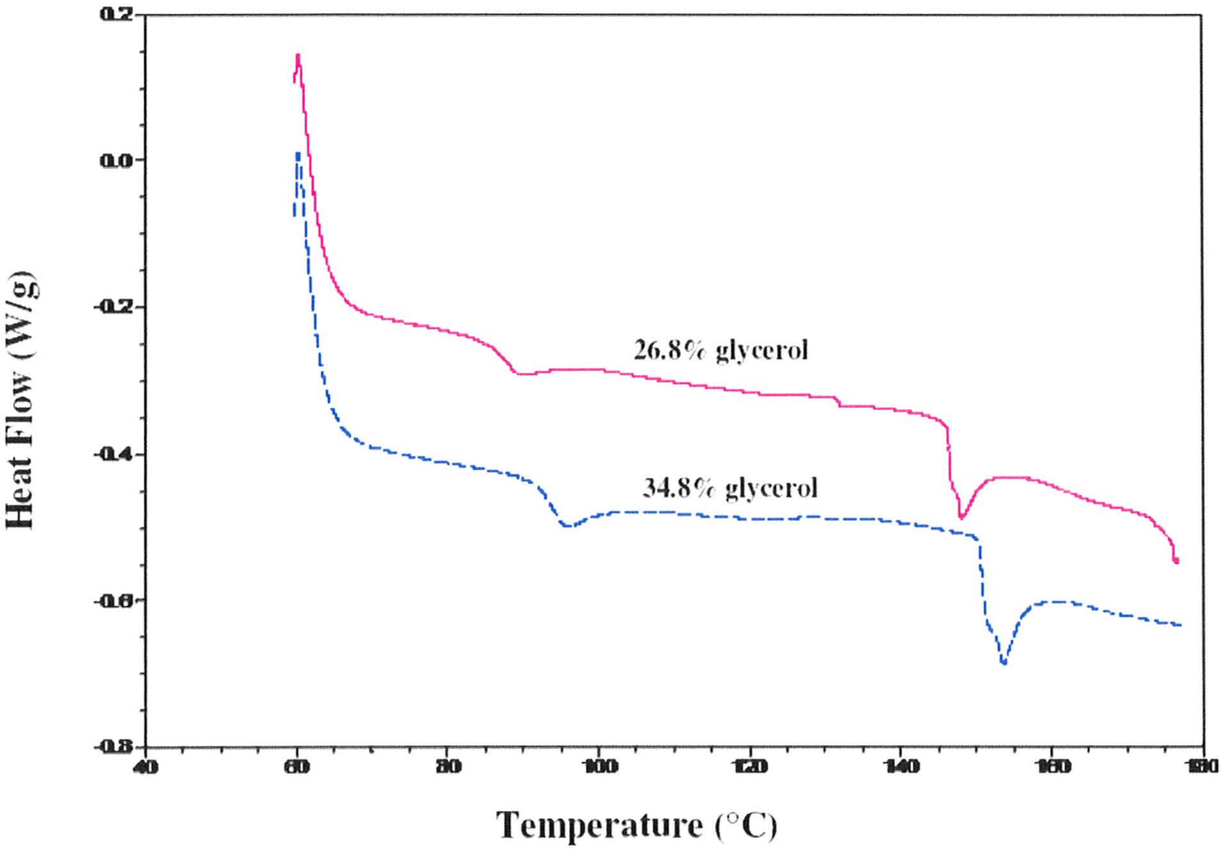


Figure 4.3 Effect of glycerol content on gelatinization and melting temperature of starch while starch/water ratio is constant and equal to4/1

The results of Van Soest et al. (1996c) are consistent with the present results, but also point out that the gelatinization temperature in thermoplastic potato starch linearly increases with increasing glycerol content at water contents higher than 33%.

DSC results illustrate that increasing the glycerol content increases the gelatinization temperature (Figure 4.3). In fact, glycerol at this point behaves as an anti-plasticizer as it shifts back the gelatinization process rather than facilitating. Rutgers et al. (2003) explain the anti- plasticizing effect of glycerol such that in a mixture of starch, water and glycerol, the hydrophilic nature of glycerol and its high tendency to absorb water faster than starch, decreases the effective amount of water for starch gelatinization. This leads to higher gelatinization peaks in the presence of glycerol. In Figure 4.3, an increase in the gelatinization temperature of potato starch by increasing the glycerol content can be seen.

4.1.3 Effect of glycerol on gelatinization

The effect of water and glycerol on the gelatinization of potato starch has been investigated. As expected, increasing the water content decreases the gelatinization onset temperature while increasing the glycerol content increases the gelatinization onset temperature.

Although glycerol as an effective plasticizer is being used to diminish the brittleness of TPS products and provide the desired flexibility (Wang, 2003), increasing its content in the blend increases the gelatinization onset temperature (Van Soest, 1996c; Rutgers, 2003; Qu, 1994).

The hydrophilic nature of glycerol and its tendency to absorb water more rapidly than starch put the glycerol and the starch in a competition to bind water. However, due to the more hydrophilic nature of glycerol, the presence of glycerol in the mixture results in reducing the effective amount of water available in the mixture for starch gelatinization (Van Soest, 1996; Rutgers, 2003; Qu, 1994).

Glycerol was added to the blend of starch and water at various time steps to investigate different forms of processing. The later adding glycerol to the mixture of starch and water attempted to minimize the glycerol water uptake in the mixture, while maintaining beneficial glycerol plasticization effects.

Glycerol was added to the mixture of starch and water

- at the same time with water
- 4 hours after adding water
- 24 hours after adding water
- 48 hours after adding water

From DSC thermograms it was observed that adding glycerol to the mixture of starch and water at different time steps does not affect the gelatinization peak significantly, neither in terms of onset temperature nor in terms of enthalpy changes (ΔH gelatinization). However, adding the glycerol at different time steps does affect both the onset melting temperature and melting enthalpy (ΔH melting).

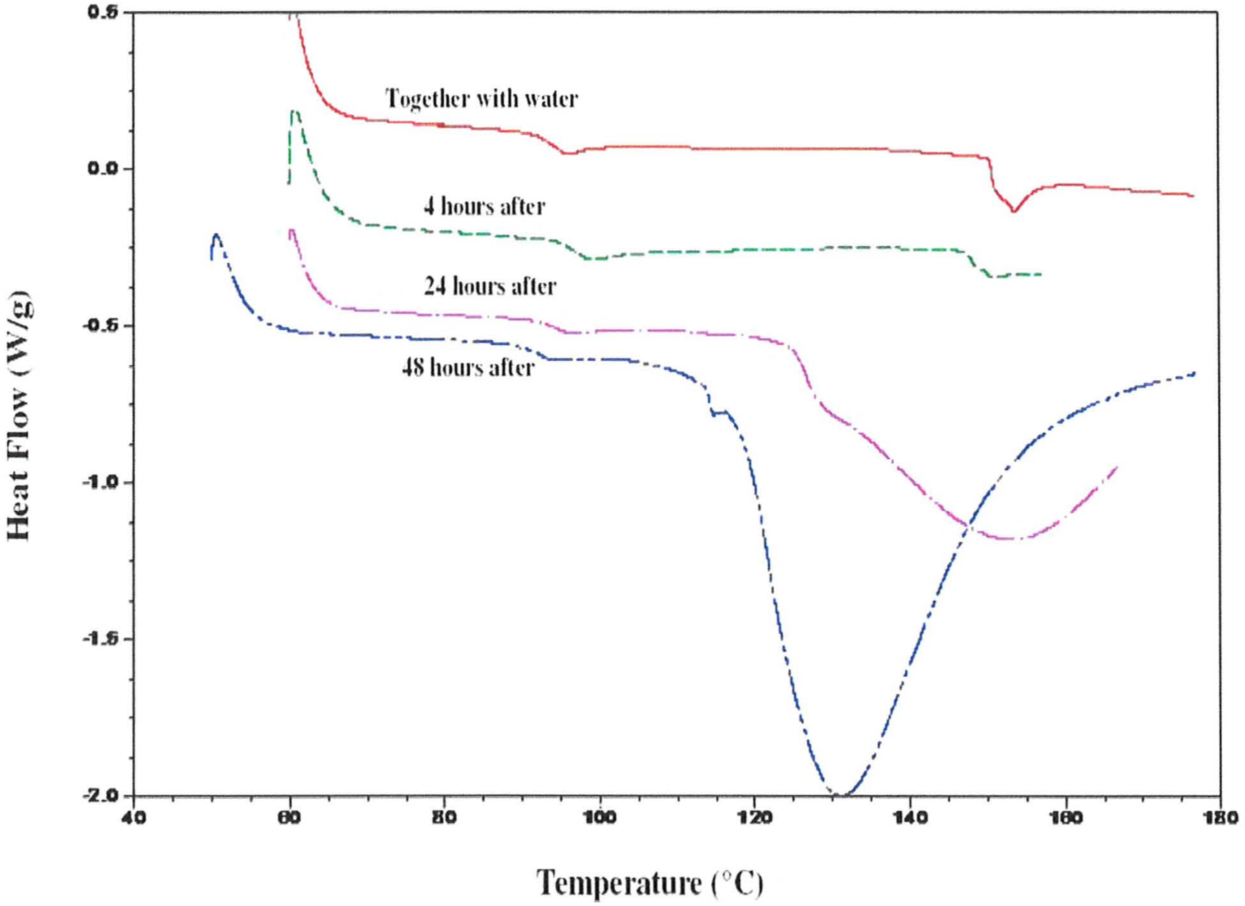


Figure 4.4 Add glycerol to the potato starch and water blend at different time steps (52.2% starch, 13% water, 34.8% Glycerol)

Figure 4.4 shows that by adding glycerol to the mixture of starch and water at different time steps after adding water, the melting onset temperature of the blend shifts to the lower temperatures. In the ratio of 52.2% starch, 13% water, 34.8% glycerol, adding glycerol to the mixture after 48 hours, the melting temperature decreases up to 35°C.

4.2 Properties of Thermoplastic Starch in closed system

4.2.1 Thermal Properties of Thermoplastic Starch

In both native starch and thermoplastic starch, the glass transition temperature is related with the amylose/amylopectin ratio. A higher percentage of amylose results in decreased glass transition temperature. Therefore, TPS samples made from starch with lower percentage of amylose exhibit higher glass transition temperature T_g, e.g. potato starch (Graaf, 2003).

The glass transition temperature is of great importance for the mechanical properties of the polymers, usually the higher the T_g, the tougher the materials. In starch based polymers, T_g is an important parameter giving information about the retrogradation behavior of the thermoplastic, with higher T_g indicative of long term thermal stability of the polymer.

As previously mentioned, at temperatures above the glass transition temperature, glycerol containing starch based bioplastics undergo retrogradation (Van Soest, 1996a,d). During storage, amylose is believed to get retrograded into single (E-type and V- type) and double helical (B-type) crystal structures while amylopectin only crystallized into double helical crystal structures (Van Soest, 1996a,d).

The rate of the retrogradation is a function of plasticizer content. In these products, increasing levels of plasticizer lead to higher amounts of water uptake, and the higher water content results in a decrease in glass transition temperature. The lower glass transition temperature of the products leads to an increase in retrogradation rate (Van Soest, 1996a). During storage, B-type crystallinity affects the mechanical properties of the products, and the products undergo aging becoming more rigid with higher modulus and tensile strength and lower elongation at break (Van Soest, 1996a, d).

The glass transition temperature plays an important role in mechanical properties of starch based polymers. The effects of different amounts of water and glycerol on the glass transition temperature of thermoplastic starch after 10 days of storage at room temperature in plastic bags were investigated.

Averous et al (2004) reported that it is difficult to determine the glass transition of plasticized starch through differential scanning calorimetry analysis due to the very low heat capacity changes at the glass transition. Glass transition temperatures of the samples were determined through DSC by heating the quenched molten TPS samples (Figure 4.5). The changes in water and glycerol content of the TPS affect the glass transition temperature. By increasing the amount of plasticizers the glass transition shifts to lower temperatures.

Previous studies on the T_g of thermoplastic pea starch reveal that the TPS materials plasticized with glycerol and water existed as a complex system composed of glycerol-rich and starch-rich domains, and each domain exhibits its own Tg (Cao, 2008; Averous, 2004). DSC thermograms of thermoplastic potato starch also exhibit the exact same trend as shown in Figure 4.5. The first transition which appears in lower temperature is associated with the glass transition temperature of glycerol-rich phase, while the second transition is associated with the glass transition temperature of starch-rich phase.

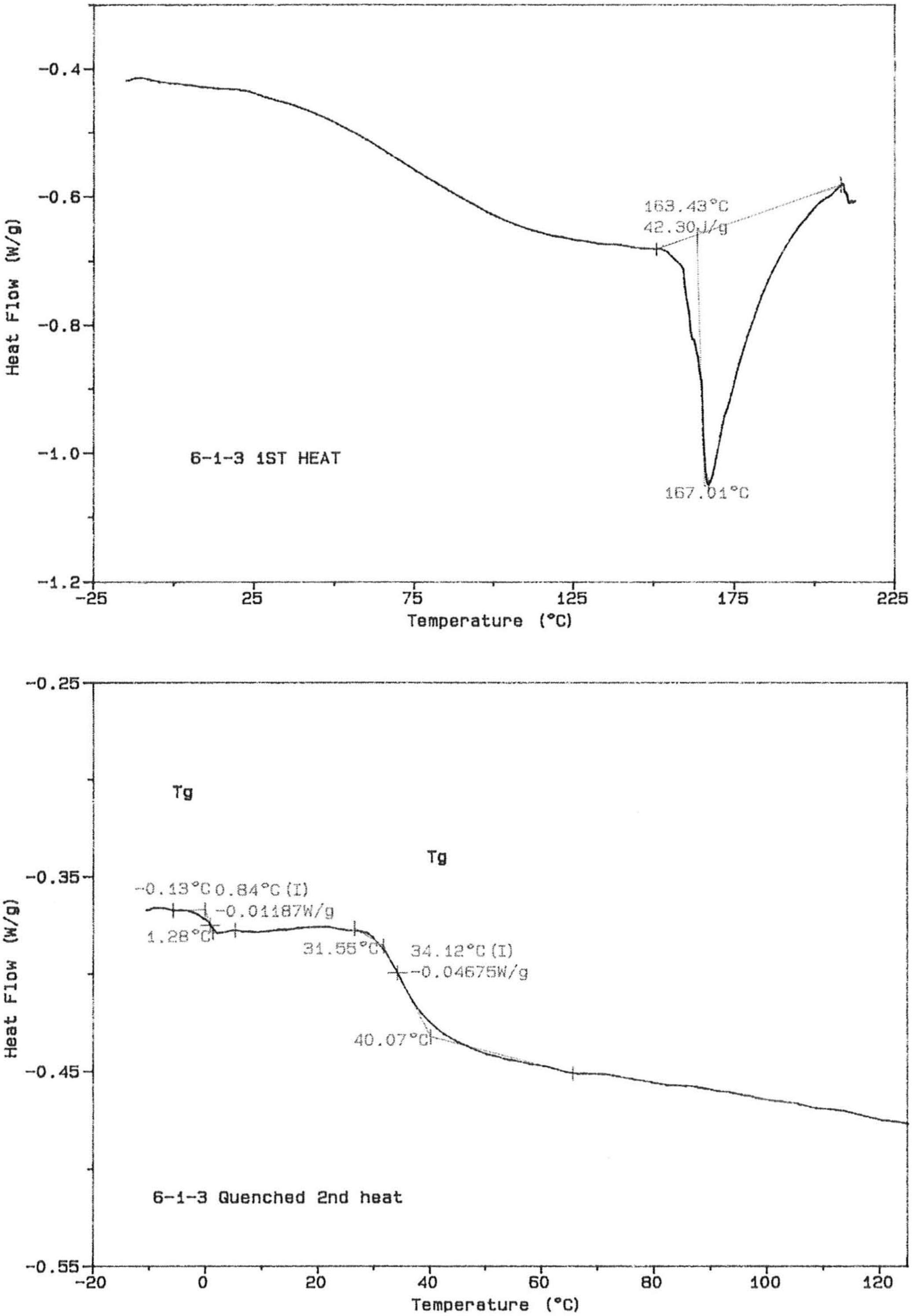


Figure 4. 5 Melting and glass transition temperature of extruded TPS after 10 days of storage

The effect of plasticizer content on Tg can be seen in the following table. Tg_1 °C, and Tg_2 °C are the glass transition temperatures for starch component in glycerol-rich and starch-rich domains, respectively.

Table 4.2 Effect of the plasticizer content on Tg

Starch%	Water%	Glycerol%	Tg_1 °C	Tg_2 °C
63.1	10.5	26.3	28.2	52
57.1	14.3	28.6	28.5	49
60	15	25	26.9	45.1
60	10	30	0	34.1
50	16.6	33.4	-11.3	32.3

4.2.2 Mechanical properties of Thermoplastic starch

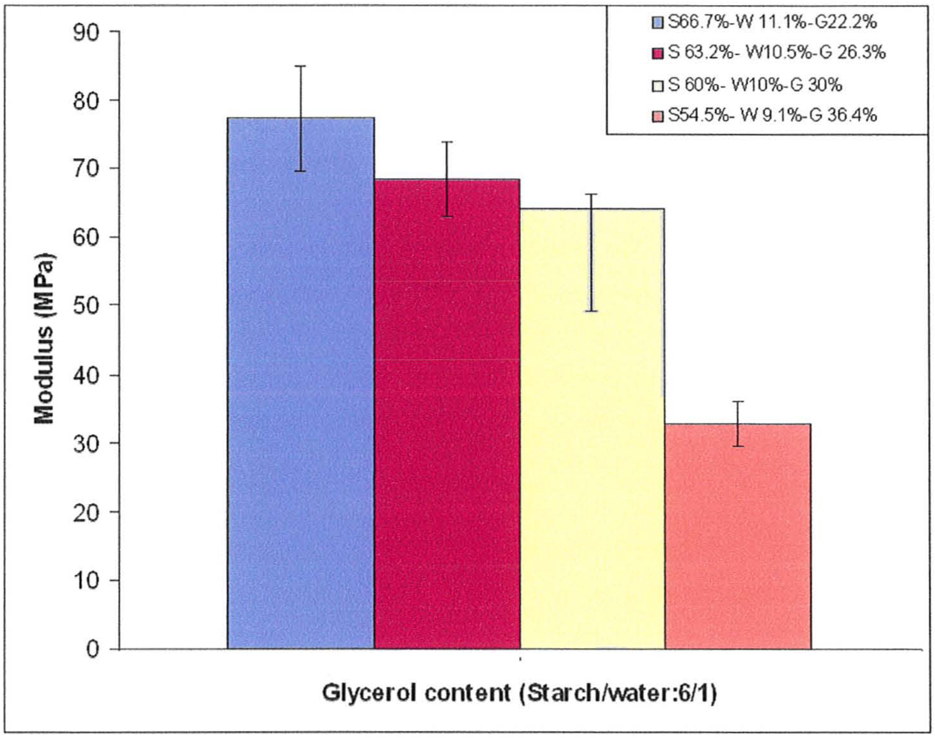
The mechanical properties of plasticized starch depend on the amount of plasticizer as well as storage time, relative humidity and starch source (Van Soest, 1996a; Van Soest, 1996d; Wang, 2003; Thnwall, 2006; Rudnik, 2008).

Yu et al (1996) investigated the mechanical properties of TPS plasticized with different plasticizers. The tensile strength of the TPS decreased as the plasticizer content increased, while the elongation at break of the samples increased with increasing the plasticizer content. You et al (2003) also reported the mechanical properties of thermoplastic starch with glycerol and urea.

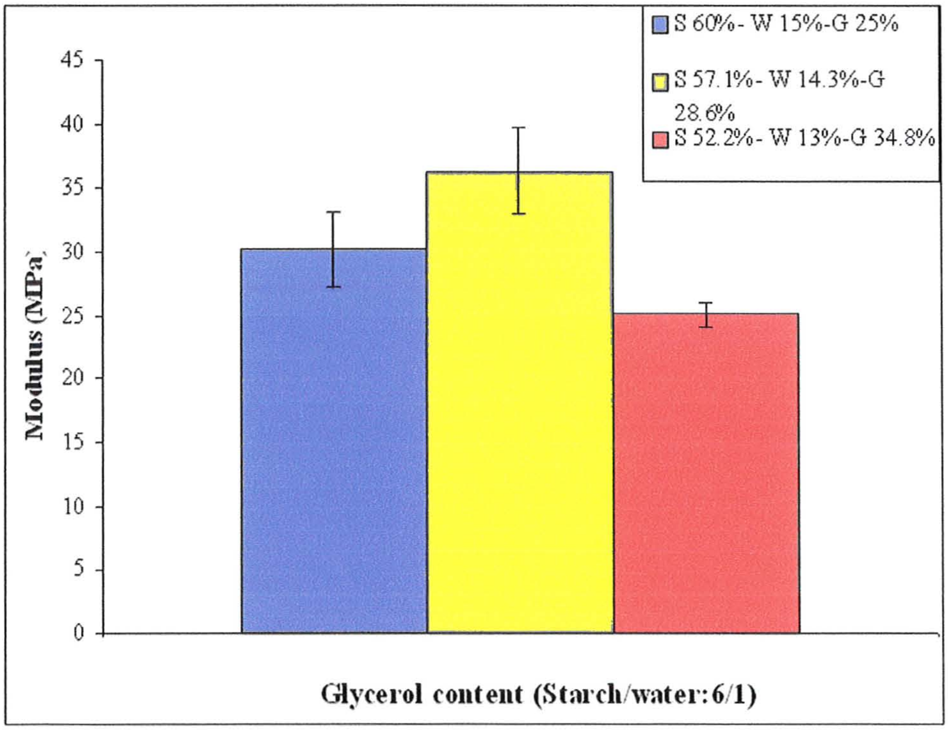
They reported that the tensile strength of the blend decreased from 5.7 MPa to 1.8MPa, while the elongation at break increased from 40% to 140% by changing the glycerol and urea content from 15 to19% and from 1to 5% respectively.

In Figure 4.6 the stress-strain properties of TPS materials prepared through DSM extruder at different ratios of starch/water/glycerol (wt %) are presented. The tensile strength, modulus and elongation at break of the thermoplastic potato starch are highly dependent on the amount of plasticizer. TPS blends with water content of c. 10 wt% containing c. 20-30% glycerol are relatively hard with an elastic modulus between 64 and 78 MPa and tensile strength between 1.9 and 2.95 MPa. The samples containing the same amount of glycerol with water content c. 15 wt% have more flexibility with an elastic modulus between 20 and 30 MPa and tensile strength between 1.3 and 1.6 MPa.

In terms of elongation at break of the samples, no specific trend is seen. But generally, for the TPS blends with water content of c. 15 wt%, elongation is higher than for the samples with water content of c. 10 wt%.



S66.7%-W 11.1%-G22.2%
S 63.2%- W10.5%-G 26.3%
S 60%- W10%-G 30%
S54.5%- W 9.1%-G 36.4%
Modulus (MPa)
0
10
20
30
40
50
60
70
80
90
Glycerol content (Starch/water:6/1)



S 60%- W 15%-G 25%
S 57.1%- W 14.3%-G 28.6%
S 52.2%- W 13%-G 34.8%
Modulus (MPa)
0
5
10
15
20
25
30
35
40
45
Glycerol content (Starch/water:6/1)

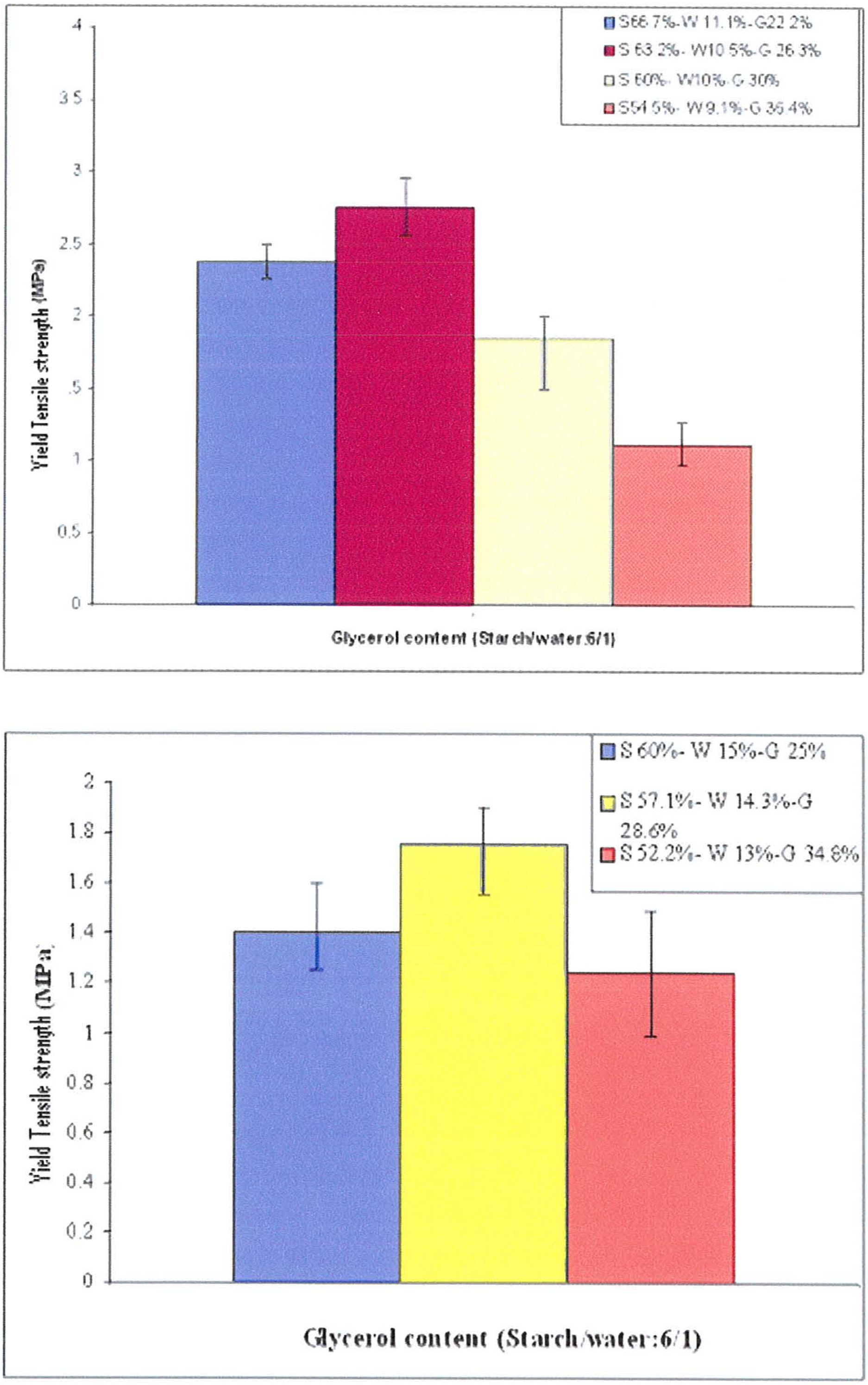


Figure 4. 6 Effect of glycerol content on mechanical properties of TPS at different starch/water ratios

Based on the processing limitations and mechanical properties of the TPS samples, for subsequent runs starch/water/glycerol (wt %) ratio was fixed at 60/10/30.

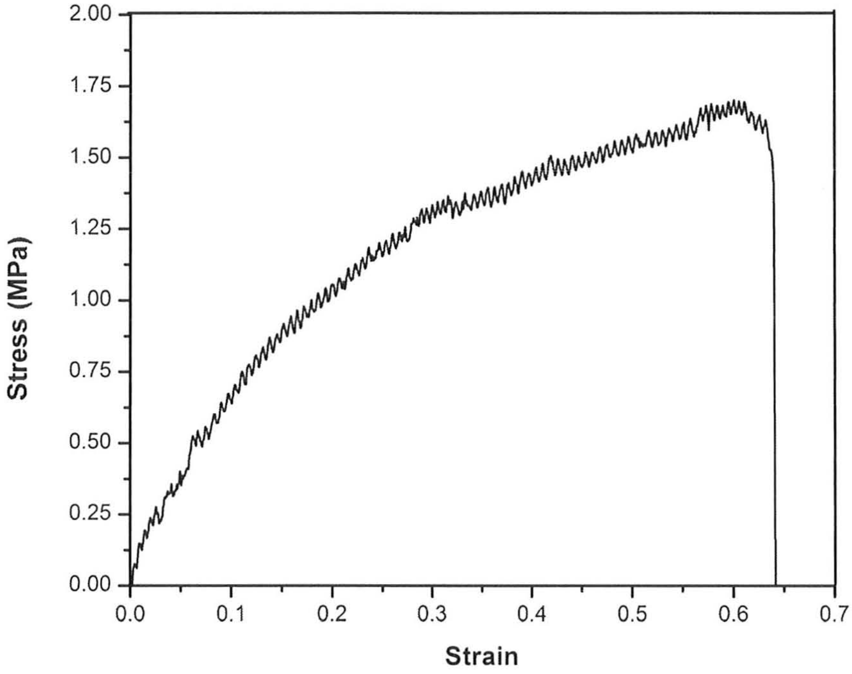
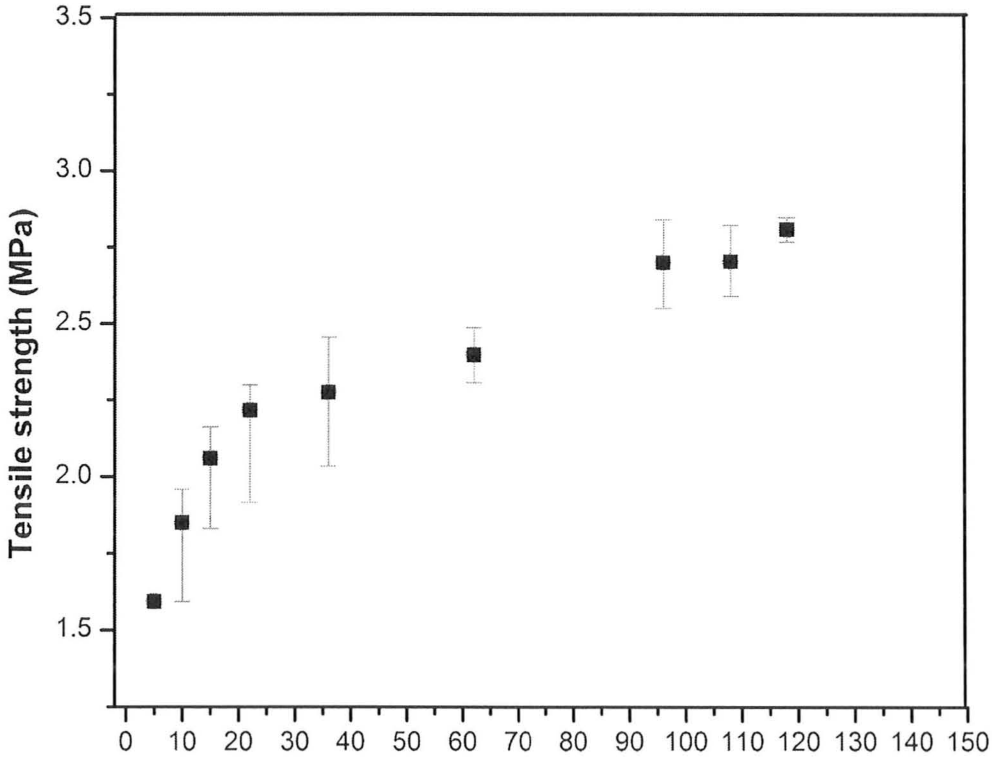


Figure 4.7 Stress-strain curve for TPS with 60 wt% potato starch, 10 wt% water and 30 wt% glycerol

4.2.3 Aging phenomena in thermoplastic potato starch

The changes in the mechanical properties of the TPS samples were investigated at 58%RH (in presence of Sodium Bromide in a desiccator) at specified holding times. The glass transition temperature of the samples for glycerol rich phase is 0 °C and for starch rich phase is 34.1°C. Therefore, the materials stored at 58% RH may show retrogradation during the storage, and as a result, big changes in mechanical properties occurred. The Young's modulus and tensile strength slightly increased from 15MPa and 1.59 to 42 MPa and 2.73 MPa respectively, while the elongation decreases slightly from 64.6% to 42% during the storage time.

It is illustrated that sample storage affects the mechanical properties of the samples. These effects are described by an increase in amylose and amylopectin B-type crystallization. The crystallinity reinforces the starch network resulting in an increase in the elastic modulus and the tensile strength and a decrease in the elongation at break.



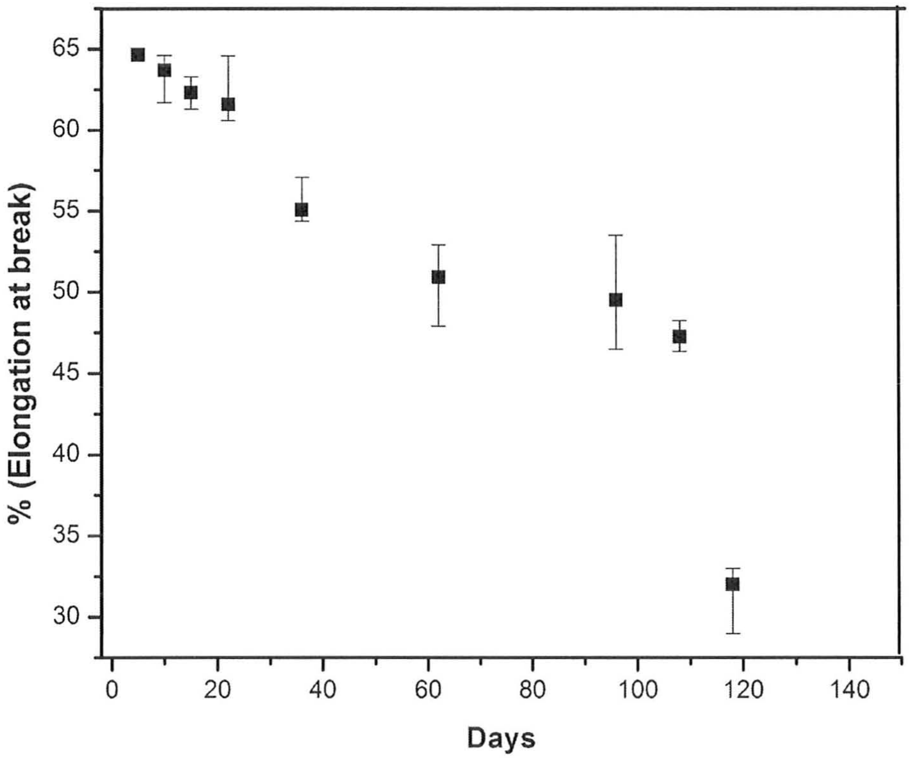


Figure 4.8 Changes in the mechanical properties of TPS materials during aging

4.3 Mechanical properties of Thermoplastic Starch in open mixing system

In addition to using DSM xplore extruder and injection molding for sample processing and preparation, a Haake Reomix 3000 Batch Mixer with roller rotorand hot press also were utilized. From a comparison of the TPS samples obtained from Haake mixer with the TPS samples obtained from DSM extruder, the Haake samples are less rigid with tensile strength between 0.213 and 0.3488 MPa, and elastic modulus between 4.7 and 15.7 MPa, which are much lower than the DSM extruder samples. However, the same behaviour as in mechanical properties of the samples attained from the DSM extruder were also observed in the samples obtained from the

Haake mixer. The elastic modulus and tensile strength are decreasing with increasing the amount of water and glycerol, while the elongation at beak does not show any clear trend.

Table 4.3 Stress-strain properties of the TPS samples prepared through Haake mixer at different ratios of starch/water/glycerol

Starch%	Water%	Glycerol%	Modulus (MPa)	Elongation%	Tensile (MPa)
60	15	25	13.9	69.44	0.3488
60	10	30	15.735	46.855	0.298
57.7	14.9	27.4	4.7325	231.5	0.3303
54.5	9.1	36.4	10.46	78.6	0.2241
52.2	13	34.8	6.375	69.4	0.256
50	16.6	33.4	6.53	30.53	0.2134

4.4 Properties of Thermoplastic Starch/ PLA blends

4.4.1 Thermal Properties of TPS/PLA

The DSC thermogram of pure PLA showed a glass transition temperature of 58.4°C, a crystallization temperature of 125.3°C and a melting temperature of at 153.3°C. The thermal properties of TPS/PLA blends are listed in Table 4.4. Results show that the TPS content does not affect the glass transition temperature and the melting temperature of the blend, while the heat of fusion was found to increase slightly by an increase in the PLA content. All the results from DSC thermograms of TPS/PLA blends demonstrate that the thermal transitions of the blends are also mainly from the PLA, not the starch. Since TPS/PLA blends are not completely miscible, visible transitions can be attributed to the PLA phase.

Table 4.4 Thermal properties of TPS/PLA blends

TPS%	PLA	T_g°C	T_c°C	T_m°C
0	100	57.6	130.4	151.9
30	70	58.75	123.4	148.9
50	50	57.5	125.71	149.6
70	30	57.8	123.67	148.9
100	0	34.1	/	/

As shown in Table 4.4, increasing the PLA content in the TPS/PLA blend, neither changed the crystallization temperature (T_c) nor the melting peak significantly. The enthalpy of crystallization and the heat of fusion were both found to increase with an increase of PLA content, showing that addition of PLA resulted in an increase of crystallinity. It has been reported (Jang, 2007) that the presence of the moisture during the mixing may lead to a decrease in the molecular weight of the blend due to PLA hydrolysis.

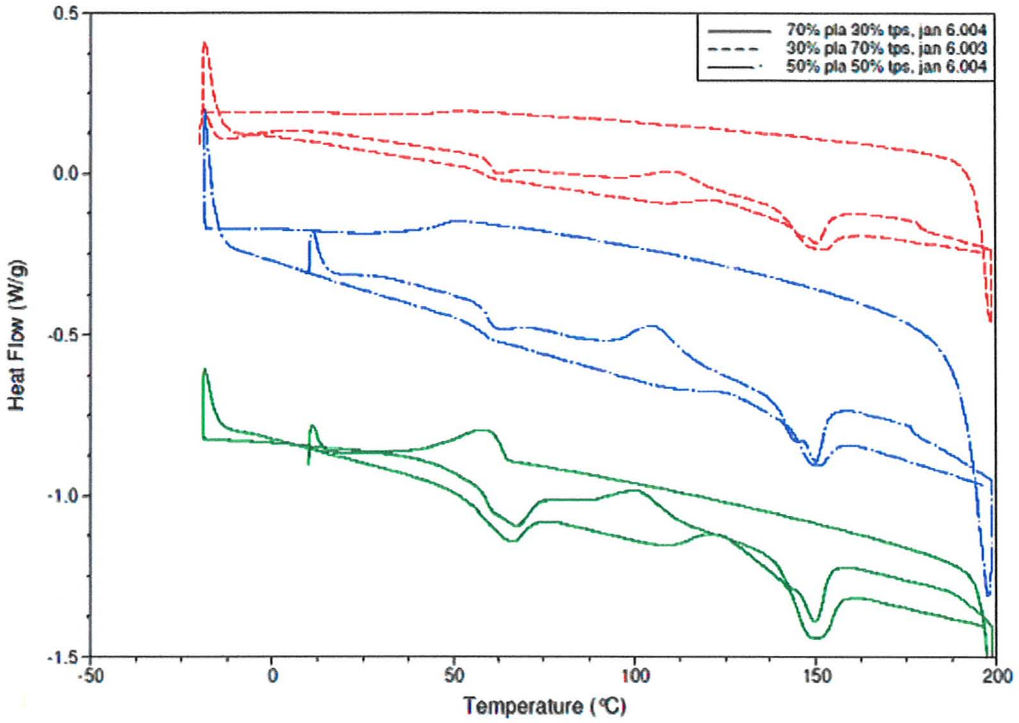


Figure 4.9 Thermal properties of the blend containing TPS and PLA at different ratio

4.4.2 Mechanical properties of TPS/PLA

Mechanical properties of thermoplastic potato starch blended with PLA in DSM mini extruder have been investigated on an Instron tensile testing machine.

Table 4.5 Mechanical properties of TPS/PLA blends

TPS %	PLA%	Elastic Modulus (MPa)	Elongation at break %	Tensile strength (MPa)
100	0	64	62.7	1.84
30	70	478	39.05	5.265
50	50	562	18.4	6.562
30	70	1088	16.53	12.592
0	100	3268	1.198	16.71

The tensile stress-strain behaviours of TPS/PLA were studied and the comparisons to the tensile properties of TPS, PLA and TPS/PLA with different ratios are shown in Table 4.5. By adding only 30% PLA to the TPS (based on the total weight), the tensile strength and modulus of the blend increased from 1.84 MPa and 64 MPa to 5.265 MPa and 478 MPa respectively, while the elongation at break of the samples decreased from 62.7% to 39%.

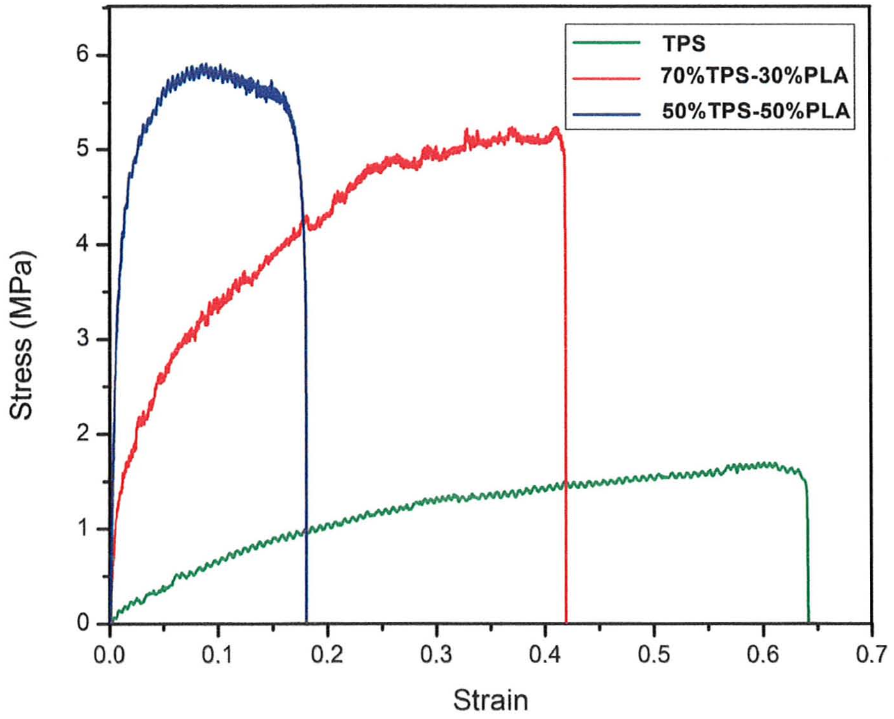


Figure 4.10 Effect of PLA content on stress-strain curve of TPS/PLA blend

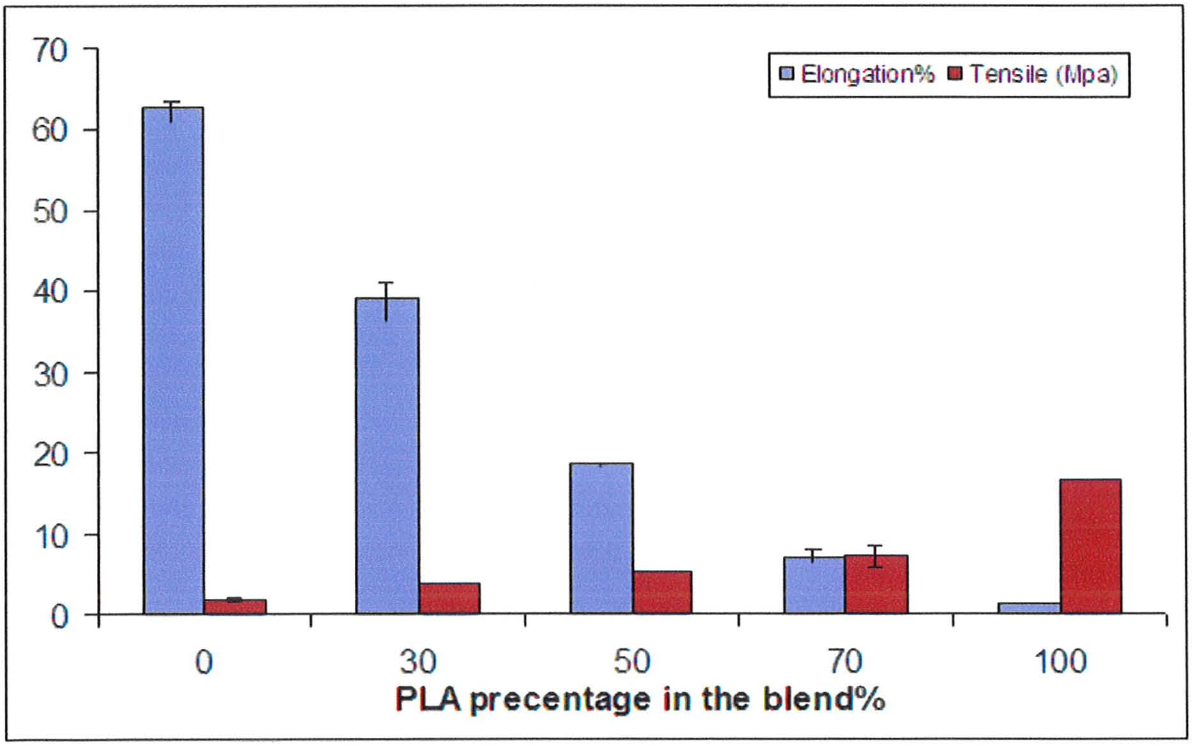


Figure 4.11 Mechanical properties of TPS/PLA blends at different ratios

4.5 Properties of Thermoplastic Starch/ PLAgMA blends

Polymer blends with immiscible components show poor properties due to the low capability of interdiffusion among molecules. Polymers miscibility and interfacial adhesion play an essential role in mechanical properties of polymer blends. In general, blends with high interfacial adhesion and better miscibility are expected to have better mechanical properties (Wool, 2005).

In order to improve the miscibility and interfacial adhesion between two immiscible polymers, applying reactive coupling agents into the material system is a common way. Introducing new functional groups onto each polymer backbone is an efficient way to prepare compatible polymer blends. Coupling agents containing certain reactive functional groups are being used to react with each polymer in the blend.

Starch and PLA are thermodynamically immiscible owing to the higher interfacial tension at the interphase between PLA and starch (Wang, 2001). Hydrophilic nature of starch and hydrophobic nature of PLA as well as lack of a reactive functional group will also affect their compatibility (Kim, 1998; Wang, 2008). Gelatinization of starch partially can solve this problem (Wang, 2008), but by applying both starch gelatinization and PLA maleation, better results can be obtained.

Maleic anhydride (MA) is considered as an effective coupling agent for the blend of thermoplastic starch and PLA (Huneault, 2007). In the presence of the initiator of Luperox 101, the functional groups of anhydride can highly react with starch hydroxyl groups to form ester linkages (Vaidya, 1994). Zhang and Sun (2004) reported that a PLA/starch composite with 1.0%

MA and in the presence of L101 (10% wt MA) exhibits a tensile strength of 52.4 MPa and 4.1% elongation, close to the mechanical properties of pure PLA.

MA was grafted to PLA at 180°C in the Haake Mixer. After the maleation of the PLA, a number of PLA molecules, MA molecules, and Luperix101 radicals may remain intact and un-reacted in the blend. In order to wash out the non grafted MA residuals, and un-reacted L101 free radicals which may chew up the PLA chains, and reduce the molecular weight of the polymer, the grafted materials (maleated PLA) was washed with a large amount of water. After the samples were rinsed thoroughly with water, they were put in water at 50-60°C in steer for 3 hours. After filtering the samples, they were placed in an oven at 60°C until perfectly dried out. By placing the grafted samples at temperatures above the glass transition temperature of poly (lactic acid), PLA chains are not frozen anymore, and non grafted MA free radicals get the chance to defuse out. Both treated and untreated maleic anhydride grafted poly (lactic acid) samples were utilized to be blended with thermoplastic starch.

4.5.1 Extent of Poly (lactic acid) Maleation

The grafting of maleic anhydride (MA) onto the PLA backbone at temperature of 180°C with an initiator concentration of 0.5 wt% was performed. The grafted samples were titrated in order to calculate the extent of MA which was successfully grafted to the PLA.

Since the initial percent of MA is small, it is obvious that the actual percentage of the MA grafted to PLA is very low. Because of this fact, any small disparity such as a contaminant may leads to a big error. Hence, a direct titration of the samples probably is not accurate and a back titration is needed in this case. Back titration of 1 gr PLAgMA was operated with the method which was described in chapter 3.

In the back titration, a known excess of base (KOH solution) first was added and then the base was titrated with acid (HCl). Actually, the KOH solution reacts with the solution of maleated samples in THF- MeOH , and then the base solution was titrated against the HCl.

It is not possible to get an accurate number for the extent of the anhydride grafted to the PLA without considering the fact that not only the maleated samples were titrated against the HCl, but also virgin PLA, THF-MeOH mixture, and even non-grafted MA which still left in the solution were titrated. To avoid obtaining the wrong values from the titration, back titration of 1 gr pure PLA with the same method is necessary.

After the required calculations, the quantity of grafted anhydride is as follows:

$$Anhydride(mole) = [(30\times0.1)-(10.1\times0.01)]-[(30\times0.1)-(30\times0.01)] = 0.289$$

$$\%Anhydride = Anhydride(mole)\times\frac{98.06g/mol}{W_{sample}g}\times100$$

$$\%Anhydride = 0.289\times\frac{98.06g/mol}{1\times10^{-3}g}\times100 = 2.85\%$$

The extent of maleation for samples grafted with MA is 2.85%.

4.5.2 Thermal properties of TPS/PLAgMA

The DSC thermogram of pure PLA showed a glass transition temperature of 58.4°C, a crystallization temperature of 125.3°C and a melting temperature of at 153.3°C. After grafting MA to the PLA, the transition temperatures do not change significantly. The DSC thermogram of PLAgMA illustrated a glass transition temperature of 57.6°C, a crystallization temperature of 130.4°C and a melting temperature of 151.9°C (Bai, 2007). Compared to PLA, the PLA grafted maleic anhydride (PLAgMA) showed lower Tg and Tm.

Table 4.6 Thermal properties of TPS/PLAgMA blends

TPS%	PLAgMA%	T_g°C	T_c°C	T_m°C
0	100	57.6	130.4	151.9
30	70	51.47	100.98	149.4
50	50	51.49	101.39	150.6
70	30	51.5	98	148.7
100	0	34.12	/	/

All the results from DSC thermograms of TPS/PLAgMA blends demonstrated that the thermal transitions of the blends are also mainly from the PLAgMA, not the starch, same as what we got for TPS/PLA blends (Wool, 2005). The glass transition temperature of the blends with maleated PLA, compared to the blends with pure PLA, decreased a bit to lower temperatures. Although MA was added to the blend as a coupling agent, it also may act as a plasticizer in the blend

(Jang, 2007). Therefore, the T_g depression observed is due to the plasticization effect of MA in the blend.

In comparison to TPS/ PLA blends, TPS/PLAgMA blends show lower crystallization exothermic peak. These results also show that the crystallization temperature decreases by increasing TPS content. The crystallization temperature happens at lower temperatures due to the easier movements of molecules. In this case starch acts as a nucleation agent (Jang, 2007).

As can be seen in Figure 4.12, in the blends of TPS/PLAgMA, there are double melting peaks, while in the DSC thermogram of PLA, there is a single melting peak. Jang et al (2007) reported that the double melting peaks are occurring because of the plasticizer effect of MA as well as nucleation effect of TPS. As a result, the heat of melting is affected by the addition of TPS. It is reported that the lower melting peak is related to plasticization effect of MA, while the higher one is related to nucleating effects of TPS. It is necessary to mention that the plasticized starch component in the TPS/PLA and TPS/PLAgMA blends acts as a nucleating agent in order to improve the kinetics of PLA crystallization, but it has no effect on the crystallization behaviour of PLA (Ke , 2003).

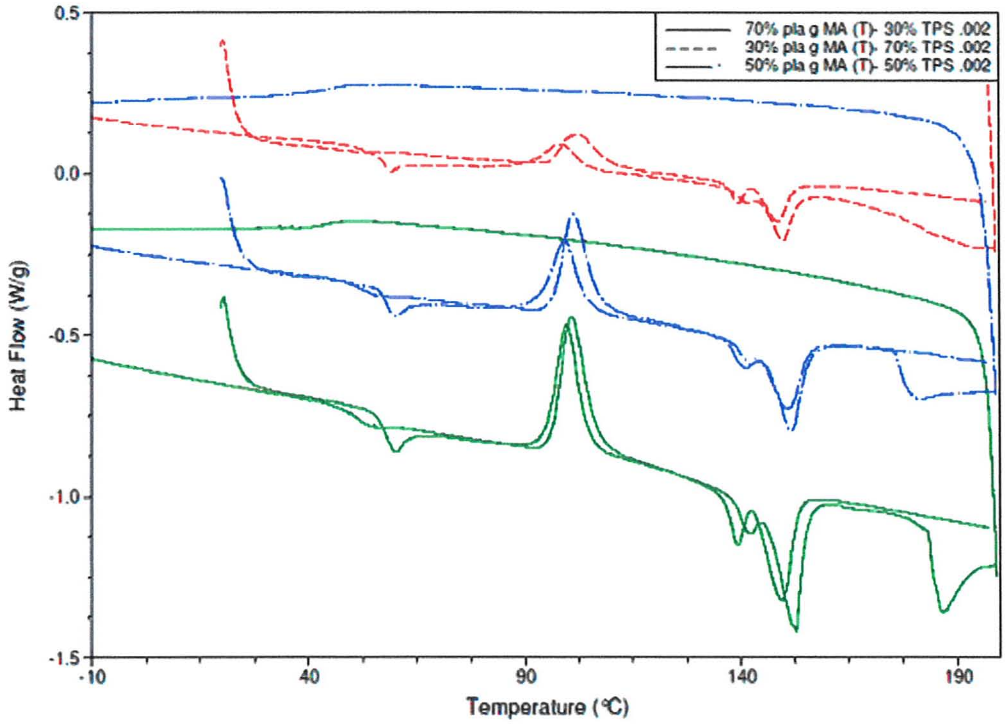


Figure 4.12 DSC thermograms of TPS/PLAgMA blends with different starch contents

4.5.3 Mechanical properties of TPS/PLAgMA

It has been reported that thermoplastic starch and PLA are not totally compatible, and without a compatibilizer their blends do not have sufficient interfacial adhesion. Orozco et al has reported MA as an effective compatibilizer for thermoplastic potato starch/PLA blends. Also MA is a common compatibilizer for blends of potato starch and/or thermoplastic potato starch with low density polyethylene (LDPE). Therefore, maleic anhydride (MA) as an effective coupling agent was used to improve interfacial adhesion and mechanical properties of the blend (Huneault, 2006; Averous, 2008; Orozco, 2009).

Thermoplastic starch was blended with both treated and untreated maleated poly (lactic acid). TPS was also blended with the mixture of PLA and treated PLAgMA.

The comparisons to the tensile properties of TPS/PLA, TPS/PLAgMA, and TPS/PLA & PLAgMA for the blends containing 70% TPS are shown in Figure 4.13. The modulus, elongation at break, and tensile strength of TPS/PLA were 478 MPa, 39.05%, and 5.265 MPa respectively. After adding the MA coupling agent, the elongation at break decreased significantly. Elongation at break decreased from 39.05% to 21.25% and 5.99% for the blend with treated and untreated maleated PLA respectively. After adding the MA coupling agent, the tensile strength and modulus did not change considerably for any of the blends, but for the blend of TPS with treated PLAgMA: the modulus increased from 478 MPa to 599.96 MPa.

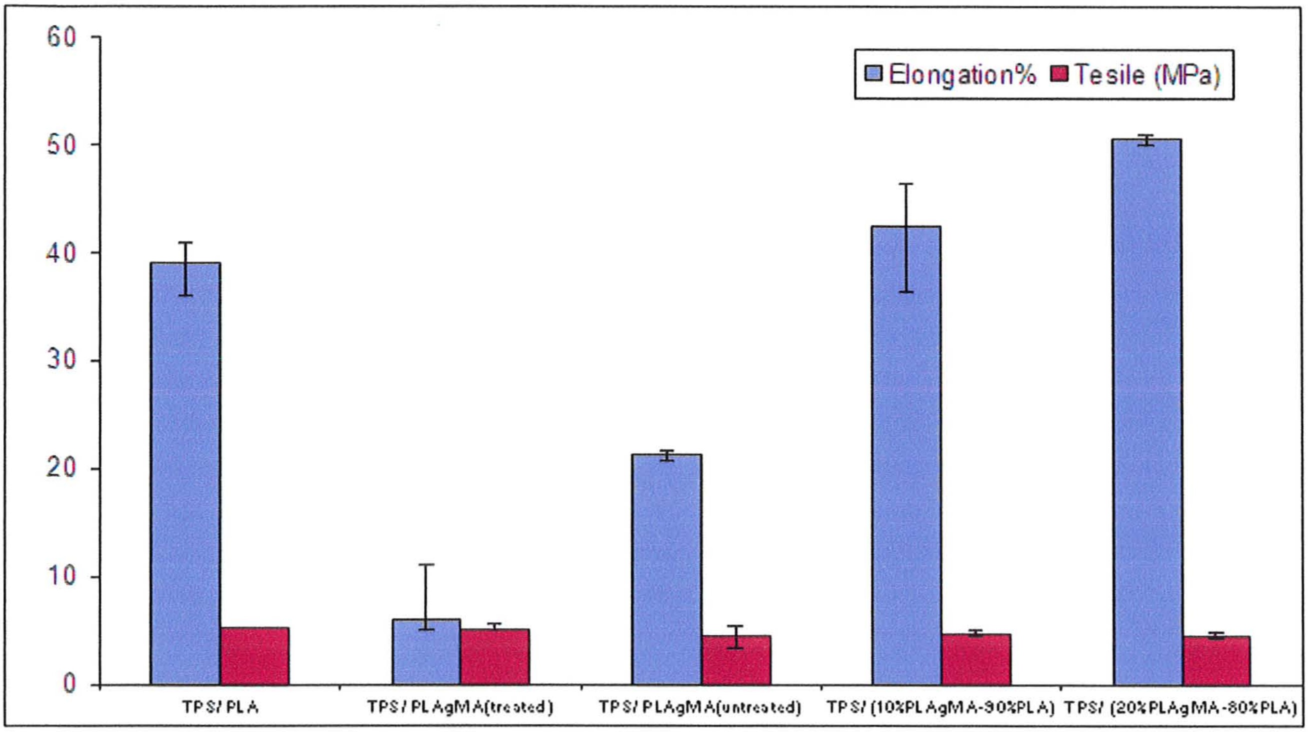
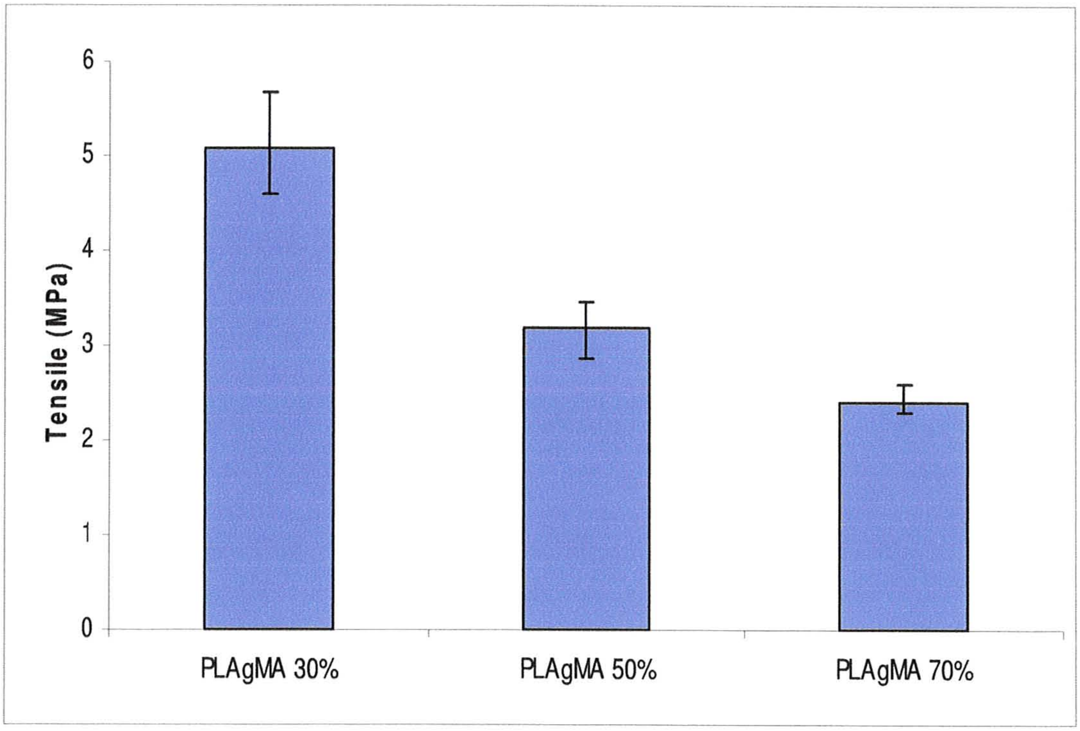


Figure 4.13 Changes in the mechanical properties of TPS/PLA blends by adding MA (70%TPS-30%PLA, or PLAgMA, or PLA & PLAgMA)

Results confirm the role of MA as an ineffective coupling agent for the blend of thermoplastic potato starch and PLA. From the results, it is clear that the blend of TPS with untreated PLAgMA exhibit the lowest elastic modulus and tensile modulus due to the presence of free MA radicals in the grafted materials which chewing up the PLA chains.

By increasing the amount of PLAgMA in the blend (both treated and untreated), all the elastic modulus, tensile strength, and elongation at break decreased to lower values.



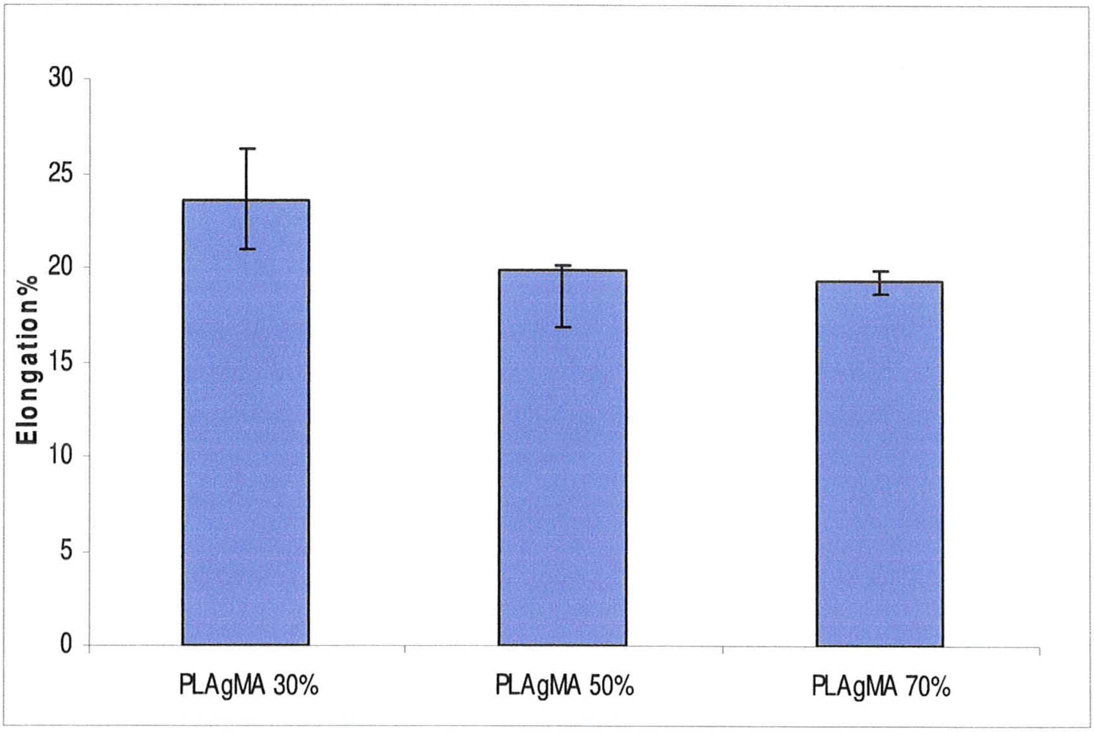


Figure 4.14 Changes in the mechanical properties of the TPS/PLAgMA blend by increasing the amount of PLAgMA

4.5.4 Water resistance properties of TPS/PLA & TPS/PLAgMA blends

4.5.4.1 Contact angle

Figure 4.15 shows the effect of PLA and PLAgMA content on the contact angle values for the TPS blends. The pure TPS blend with 10% water and 30% glycerol had a very low initial contact angle of about 17.4 ° after 30 seconds, and the water droplet was absorbed on the surface of the sample quickly. This behavior illustrates the hydrophilic characteristics of the TPS materials. With addition of 30% PLA into the TPS matrix, the contact angle of the blend increased considerably from 17.4° to 88.5 °.

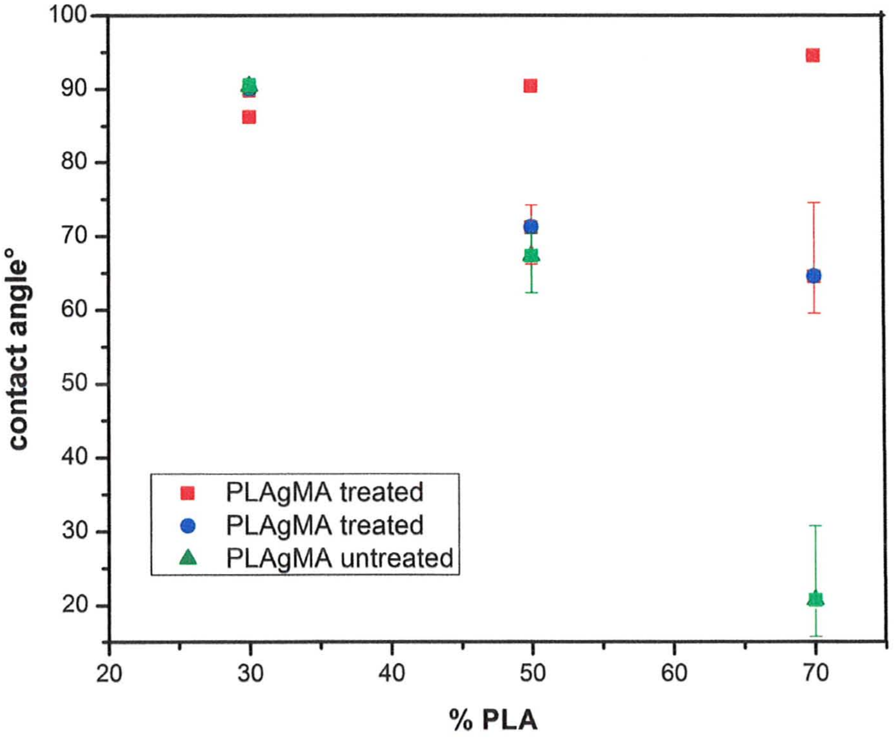


Figure 4.15 Effect of PLA, treated PLAgMA, and untreated PLAgMA content on their blends with TPS

The incorporation of treated PLAgMA into the TPS matrix also increased the contact angle value of the TPS blends, while the addition of PLAgMA into the TPS matrix, was only effective in low PLAgMA contents.

4.5.4.2 Water up take of TPS, TPS/PLA, and TPS/PLAgMA blends

The samples were kept in 75% RH at room temperature for 1 month. This situation was provided by placing the samples in a desiccator in presence of sodium chloride (NaCl). Figure 4.16 shows the moisture content ($w\%$) calculated as follows:

$$w\% = \frac{w_t - w_0}{w_0} \times 100 \qquad (3)$$

Where, w_t is the wet weight of a sample at each time and w_0 is the initial weight of the dry sample at the beginning of the test.

From the results it can be observed that after mixing the TPS materials with PLA or PLAgMA, the water up take significantly decreased. Among different blends of TPS with PLA and PLAgMA, the blends containing TPS and pure PLA, took the highest amount of moisture during storage, while the blends containing MA took the lowest amount of moisture. By grafting MA unto PLA backbone, hydroxyl groups of starch can react with anhydride functional groups and form ester linkages. These ester linkages compared to hydroxyl group significantly take lower amounts of moisture. Since the blends of TPS with untreated PLAgMA contains unreacted MA molecules that can also react with hydroxyl groups of starch and form ester linkages, the blends of TPS with unreacted PLAgMA take the lowest amount of moisture.

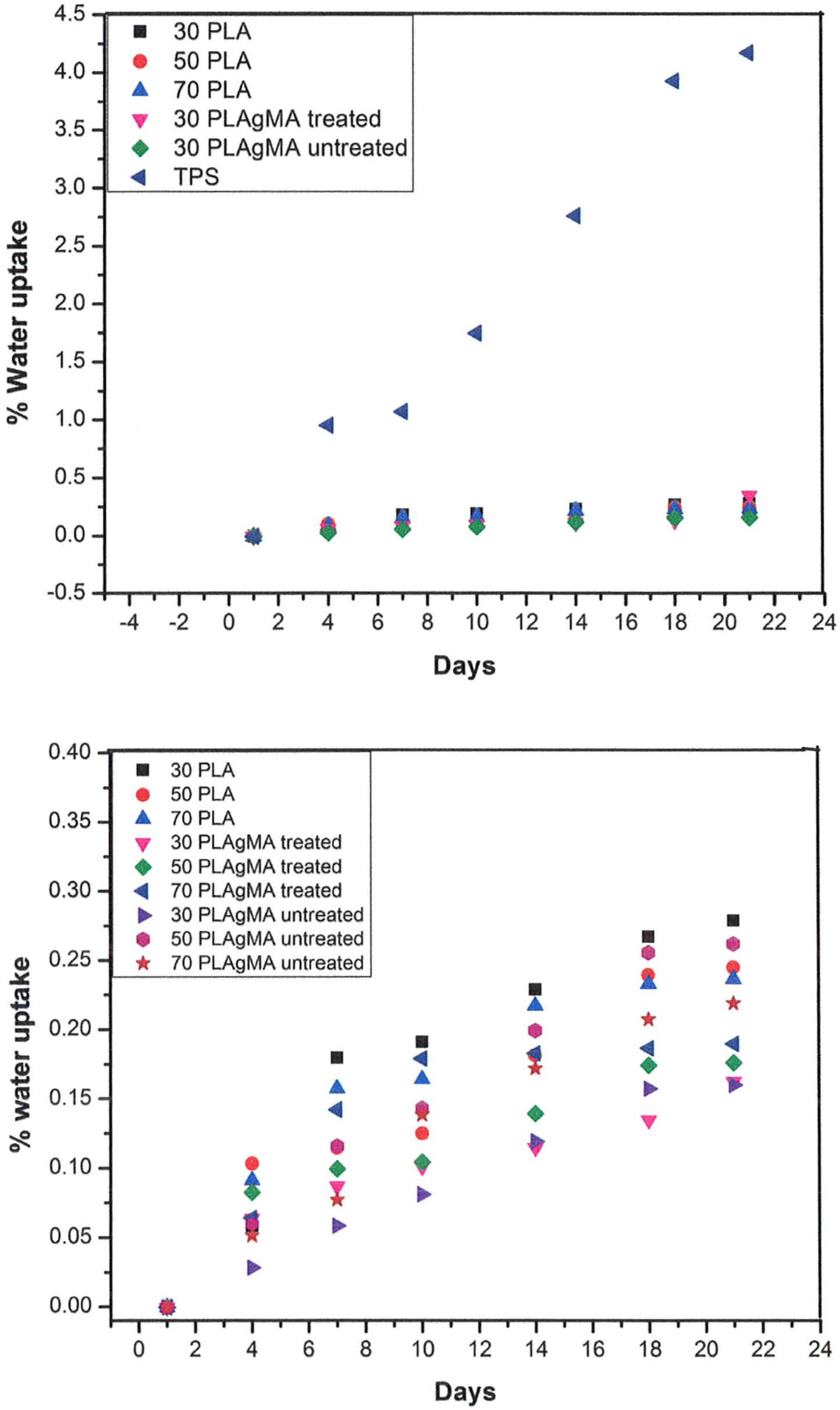


Figure 4.16 Water up take of TPS and TPS/PLA & TPS/PLAgMA

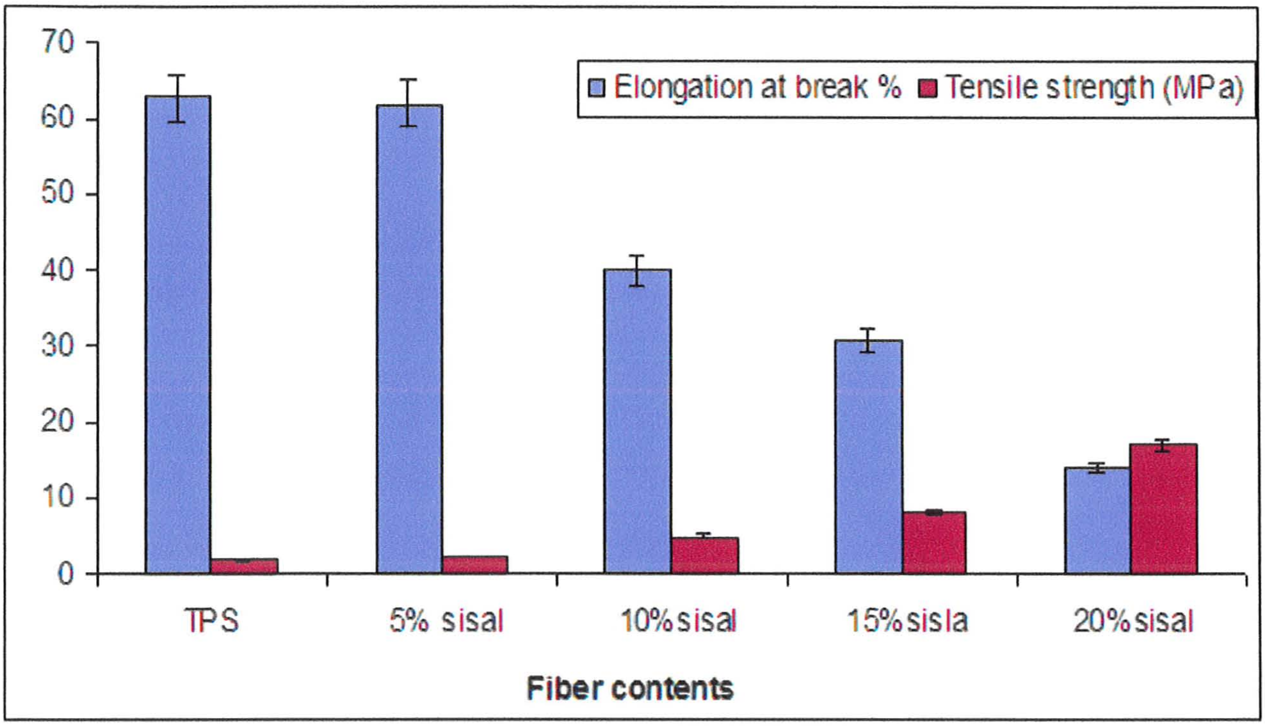
4.6 Effect of Sisal fibers on mechanical and water barrier properties of TPS and TPS/PLA blends

The effect of sisal fibers on the stress-strain behavior and water resistance properties of injection molded TPS matrix and TPS/PLA matrix has been investigated. Sisal fibers were taken under ambient and annealed conditions.

4.6.1 Mechanical properties

The mechanical properties of the unfilled TPS samples and the samples reinforced with various content of sisal fiber were studied by tensile testing at room temperature. The tensile strength, Young's modulus, and elongation at break are presented in Figure 4.17. From the results, it can be observed that the fiber content have an incredible effect on the mechanical properties of the TPS samples. In the samples contain 20% annealed sisal fiber, the tensile strength increased from 1.85 MPa to 16.26 MPa and Elastic modulus increased significantly from 64 MPa to 763.9 MPa. These results can be explained by strong hydrogen bonding interactions between sisal fiber and TPS molecules. Along with the increase in the elastic modulus and tensile strength of the reinforced samples, the elongation at break decreased from 62% to 12.3%, which indicates that the sisal fiber interfere with the motion of the TPS molecules and restrict their movements because of the strong interactions between the fiber and the matrix.

Note: The sisal content is based on TPS and/or TPS/PLA total weight in the composites.



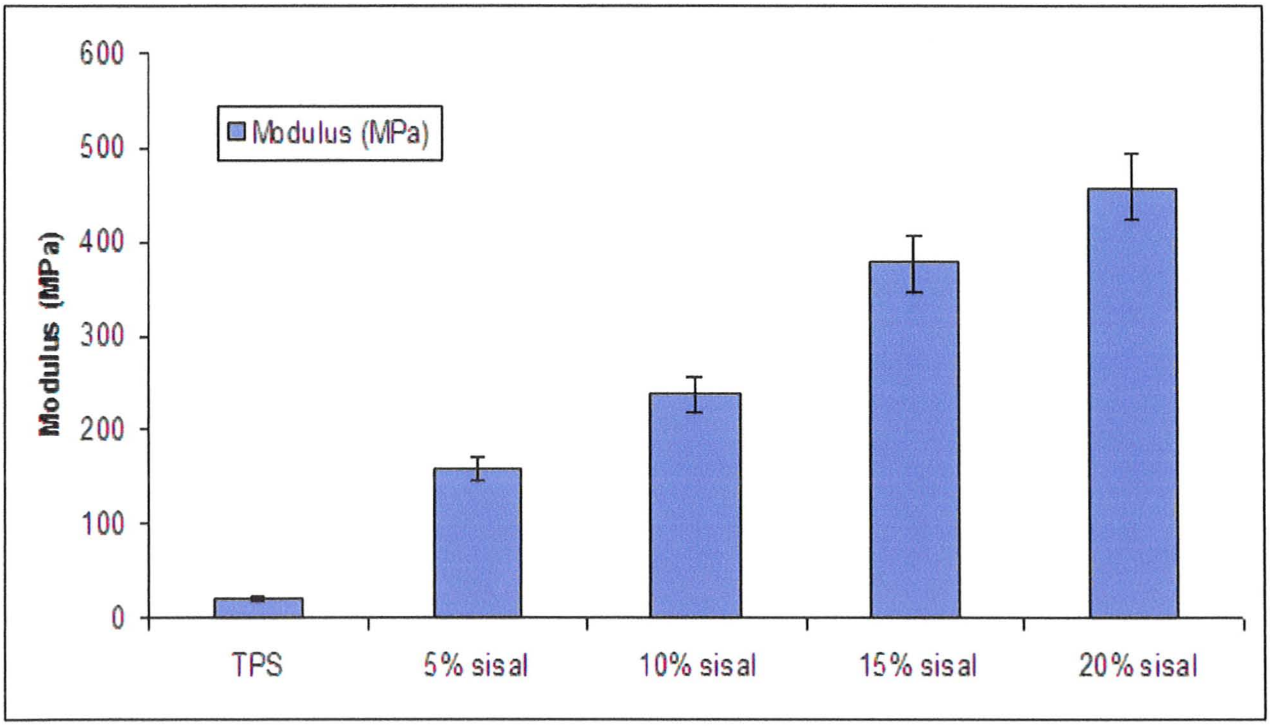


Figure 4.17 Effect of the fiber contents on the mechanical properties of TPS

The comparison between the TPS samples reinforced with ambient sisal fiber and the samples reinforced with annealed sisal fiber indicate that annealed sisal fiber significantly affects the mechanical properties. Sisal fiber contains 11-14% moisture content. This water acts as a placticizer for starch in the blend of TPS and sisal. As a rule, the higher the plasticizer content, the lower the mechanical properties of the blend. Annealing sisal fiber at almost 150° for 3 hours, leads to removing water from sisal. This is decreasing the plasticizer content in the blend.

The mechanical properties of TPS/PLA blends reinforced with sisal fiber with various contents of PLA were investigated. From the results, it can be observed that the tensile strength and elongation at break of the samples are significantly affected by sisal incorporation, as shown in Figure 4.19.

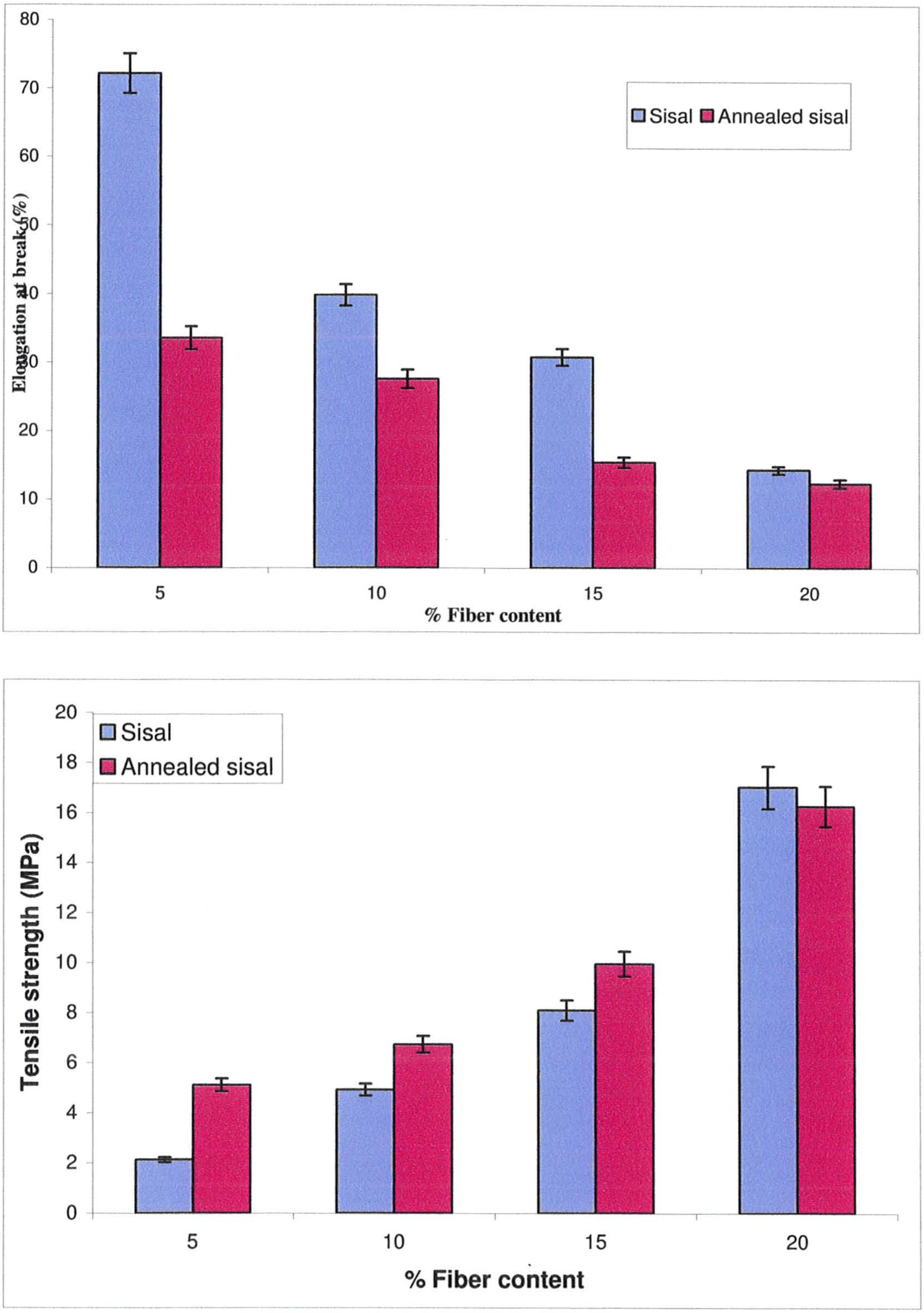


Figure 4.18 Effect of sisal annealing on mechanical properties the TPS/sisal composites

It can be seen that with addition of 20 wt% sisal to the blend of 70 wt % TPS with 30 wt% PLA, the tensile strength increased from 5.26 MPa to 27.03 MPa and elongation at break decreased from 39.05% to 8.9%. Results confirm the compatibility between sisal fiber and TPS/PLA matrix.

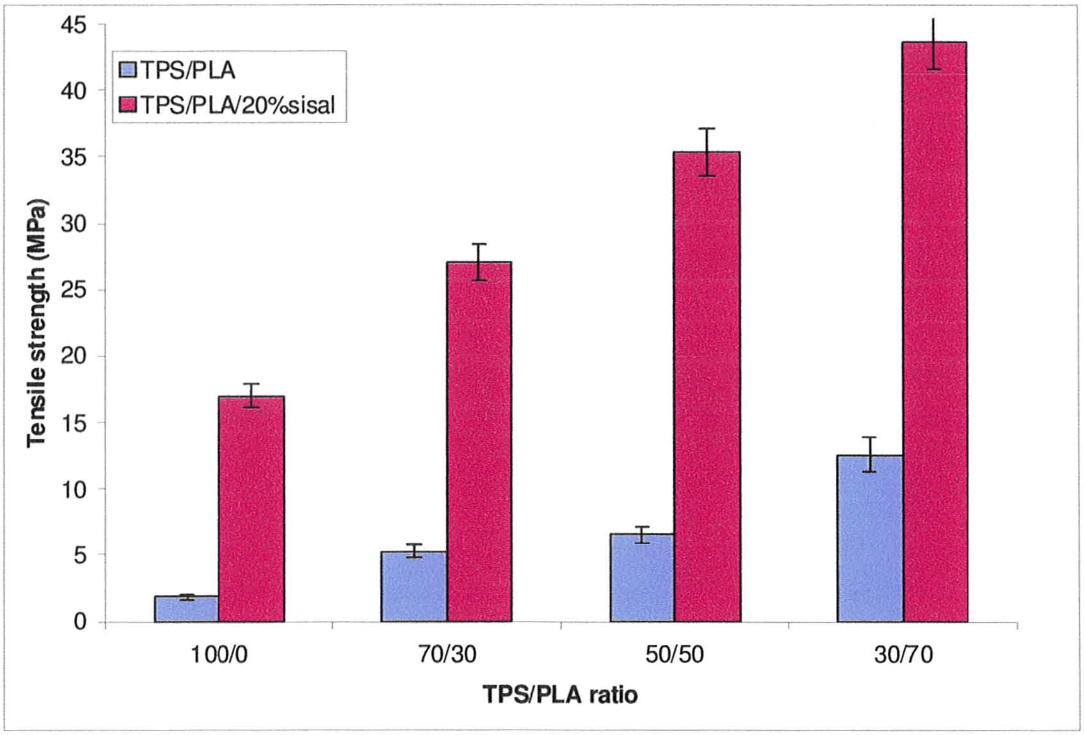


Figure 4.19 Effect of sisal addition into TPS/PLA blend on tensile strength properties

4.6.2 Water resistance properties of TPS reinforced with sisal fiber

4.6.2.1 Contact angle of TPS reinforced with sisal fiber

Figure 4.20 shows the effect of fiber content on the contact angle values for TPS blends reinforced with sisal fiber. The pure TPS blend with 10% water and 30% glycerol had a very low initial contact angle of about 17.4 °, and the water droplet was totally absorbed on the surface of the sample. This quick water absorption illustrates the super hydrophilic characteristics of the TPS materials. With addition of sisal fiber into the TPS matrix, the contact angle of the composites increased considerably from 17.4° to 65.2 °. The incorporation of annealed sisal fiber, is even more effective in terms of changing the contact angle.

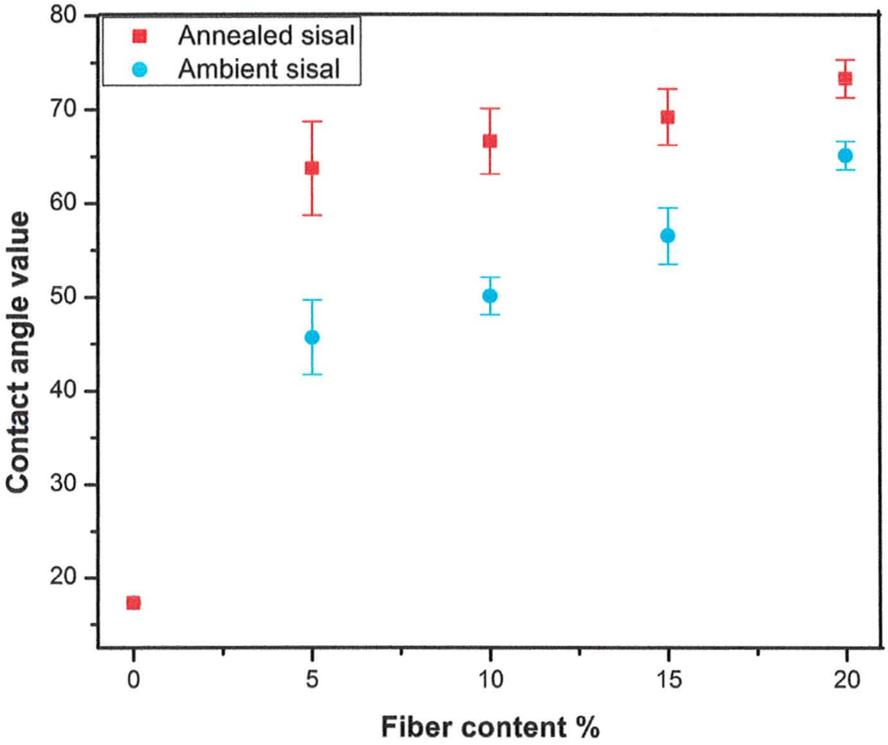


Figure 4.20 Effect of sisal content on the contact angle of TPS/sisal composites

Notice that the sisal content is based on TPS weight in the composites.

With incorporation of PLA into the blends of TPS reinforced with sisal fiber, contact angle value was changed significantly. At low PLA content, the contact angle increased with addition of PLA, by increasing the amount of PLA in the blend of TPS and sisal, the angle was decreased to smaller contact angle values. This can be owing to PLA and sisal immiscibility. It can also be related to exclusion effect of adding sisal and displacing PLA. In fact, since PLA is more hydrophobic than sisal, the less PLA would mean lower contact angle and more water uptake.

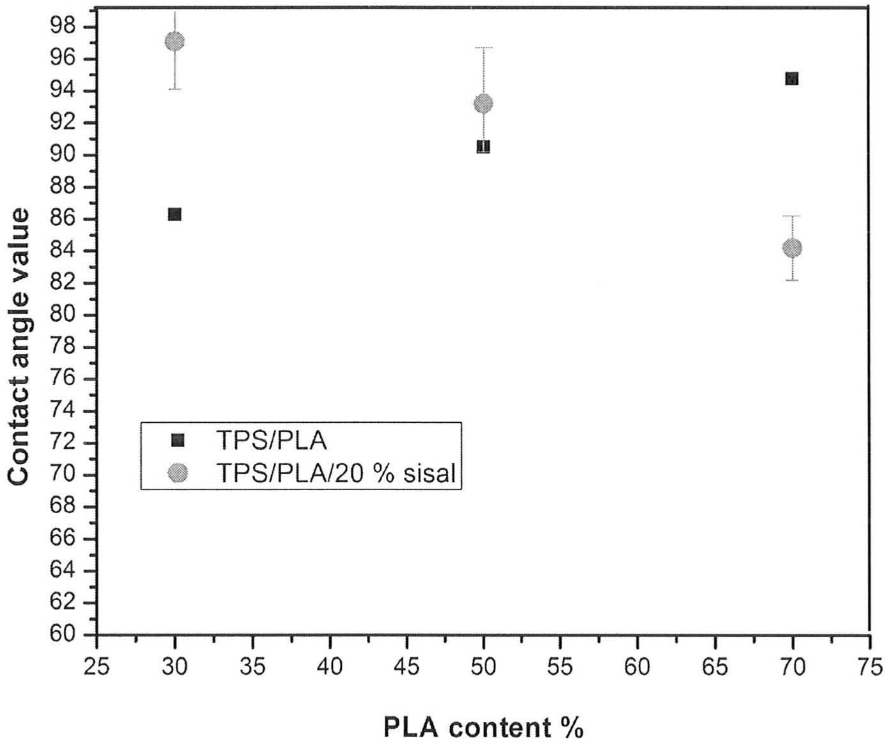


Figure 4.21 The contact angle of TPS/PLA and TPS/PLA reinforced with sisal after 30 seconds

4.6.2.2 Water up take of TPS reinforced with sisal fiber

The sisal fibers-reinforced thermoplastic starch composites samples were kept in 75% RH at room temperature for 1 month. The moisture up take as a function of time was determined in order to measure the steady state moisture content of TPS and sisal reinforced TPS samples. Figure 4.21 shows the moisture content ($w\%$) calculated as follows:

$$w\% = \frac{w_t - w_0}{w_0} \times 100$$

(3)

Where, w_t is the wet weight of a sample at each time and w_0 is the initial weight of the dry sample at the beginning of the test.

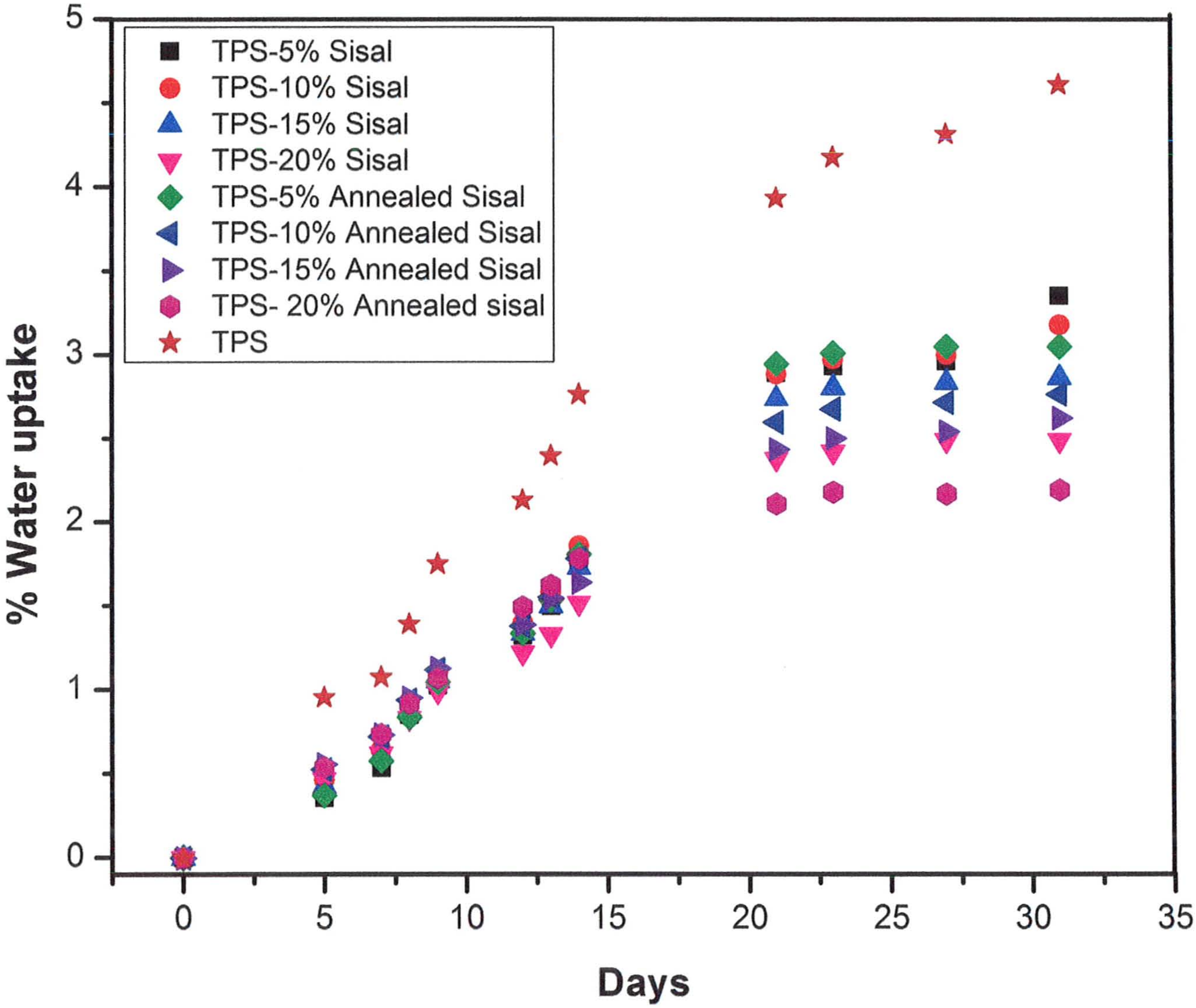


Figure 4.22 Water up take of TPS and TP/PLA samples reinforced with sisal fiber at 75%RH

The water up take of the TPS and TPS/PLA samples reinforced with sisal fiber conditioning at 75% RH after 3 weeks is shown in Figure 4.21. After 1 month, the water uptake of the TPS samples was around

4.5%, while those of reinforced with sisal fibers was around 3.5 %. Hence, it was concluded that in the presence of sisal fiber the swelling of the materials was decreased. This phenomenon demonstrated strong hydrogen bonding interactions between the sisal fiber and the TPS matrix. Also, the relatively hydrophobic characteristic (compare to super hydrophilic characteristics of starch) of the fiber and the lower glycerol content in the whole material are responsible for the water up take reduction. With incorporation of sisal fiber in to TPS/PLA blend, the water up take of the samples increased. This can be explained with the hydrophilic nature of the fiber compare to hydrophobic nature of PLA.

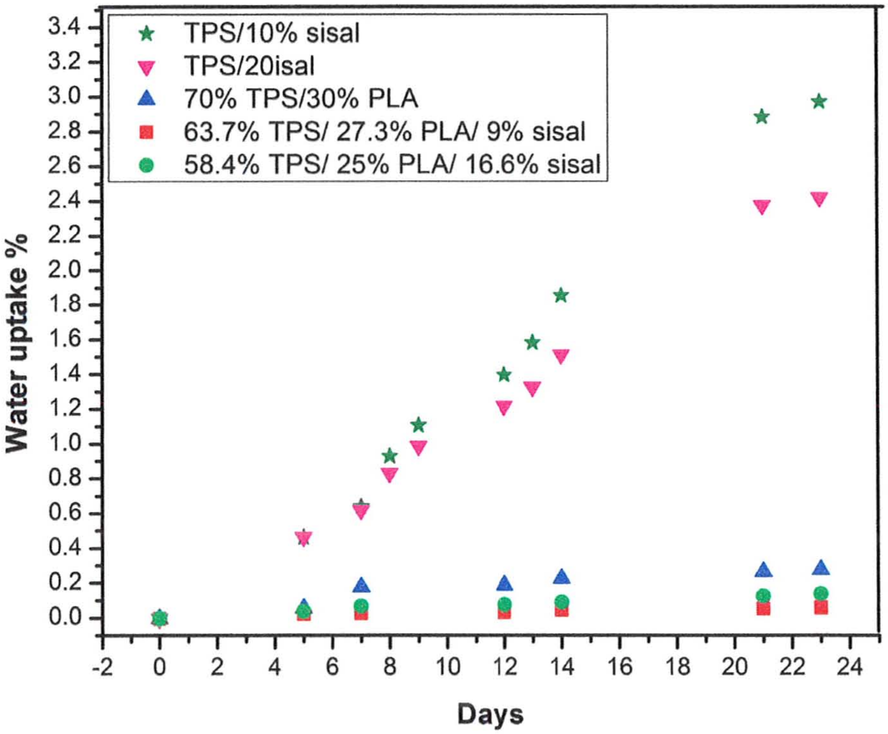


Figure 4.23 Comparison between the water up take of TP/PLA, TPS/sisal, and TPS/PLA/sisal samples at 75% RH

4.7 Effect of Paraffin Wax on mechanical and water barrier properties of TPS

4.7.1 Mechanical properties

Figure 4.23 shows the mechanical testing results for thermoplastic starch samples with and without paraffin wax. From the results, we observed that the incorporation of Paraffin wax did not significantly change the mechanical properties of the samples. With addition of 2% paraffin wax to the TPS samples, the Young's modulus and tensile strength changed from 64 MPa and 1.84 MPa to 47.1 MPa and 3.00 MPa respectively, while the elongation at break did not change notably and only had a slight decrease. We are not quite sure how paraffin wax affects starch based blends. If the paraffin wax is not totally compatible with TPS, then wax particles could be mobile in the blend. In this case, paraffin wax particles (as low viscosity material), could migrate to the surface and just end up on the product surface due to processing. If the paraffin wax is strongly adhered to TPS, then likely wax particles are not mobile anymore, and the wax will not bloom.

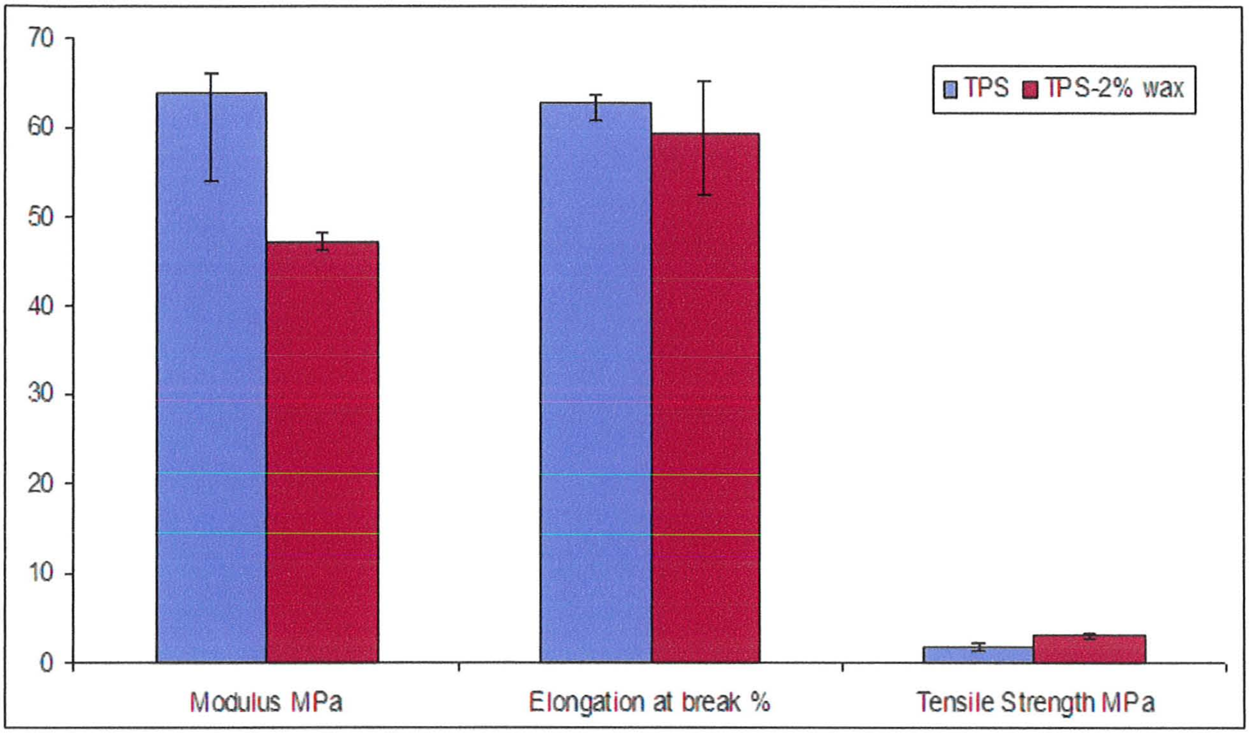


Figure 4.24 Effect of addition of 2% Paraffin wax on the mechanical properties of Thermoplastic starch

The mechanical properties of TPS/PLA samples, with and without paraffin wax were also investigated. The tensile strength, Young's modulus and elongation at break were determined form the tests and the data are presented in Table 4.7. Wax incorporation had relatively improved the mechanical properties of TPS/PLA blends. For the blends containing 70% TPS and 30% PLA, the tensile strength increased from 5.265 MPa to 7.318 MPa and Young's modulus increased considerably from 478 MPa to 573.75 MPa with addition of 2% Paraffin wax to the blend. Meanwhile, the elongation at break decreased from 39% to 7.4%, which indicates that the movements of the blend molecules restricted by the addition of Paraffin wax.

Table 4.7 Effect of addition of 2% Paraffin wax on the mechanical properties of Thermoplastic starch

TPS%	PLA%	Wax%	Modulus (MPa)	Elongation at break %	Tensile strength (MPa)
70	30	-	478	39.05	5.265
70	30	2	574	7.43	7.318
50	50	-	562	18.4	6.562
50	50	2	671	7.1	16.7
70	30	-	1088	16.53	12.592
70	30	2	1058	7.66	16.7

From the results, the negative effect of Paraffin wax on the TPS/PLA blends with high PLA content can be explained by the weak adhesion between the wax and PLA molecules. In low PLA contents, the wax is in a good incorporation with the blend since strong interactions exist between wax and starch molecules, as can be deduced from the results.

A comparison of the Young's modulus, elongation at break and tensile strength for the sisal fiber reinforced TPS with several different fiber contents to those of the sisal reinforced For TPS samples reinforced with 10% sisal fiber, the initial Young's modulus and tensile strength increased from 238 MPa and 4.927 MPa to 425 MPa and 9.167 MPa respectively, while the elongation at break decreases from 39.8% to about 18.7%, which is not an important change. The effect of Paraffin wax on the mechanical properties of TPS/sisal composites can be observed in Table 4.8(Sisal percentage is based on TPS).

Table 4.8 Effect of addition of 2% Paraffin wax on the mechanical properties of TPS reinforced with sisal fiber

Sisal	Wax	Modulus (MPa)	Elongation at break %	Tensile strength (MPa)
5%	-	158	72.2	2.125
5%	2%	304	14.42	5.814
10%	-	238	39.81	4.927
10%	2%	425	18.7	9.167
15%	-	378	30.77	8.104
15%	2%	534	17.82	10.01
20%	-	458	14.3	17.02
20%	2%	652	11.96	14.57

The wax incorporation in the composite has paramount effect on the mechanical properties in low sisal contents. Increasing the sisal content up to 20% reduces the effect of wax on the mechanical properties. For a composite containing 20% sisal fiber, wax incorporation has no significant effect on mechanical properties.

The mechanical properties of samples containing 70 wt % TPS and 30 wt % PLA, with incorporation of 20wt % sisal fiber and 2 wt % paraffin wax, were also investigated. The tensile strength, Young's modulus and elongation at break were determined form the tests. From the results, we observed that the incorporation of Paraffin wax had a slight effect on the tensile strength and the elongation at break and an opposite effect on the Young's modulus of the samples. The results indicate that addition of Paraffin wax not only did not improve the mechanical properties of the samples but also decreased it. This negative effect can be explained by the high content of sisal fiber in the composite in presence of Paraffin wax. Probably, at lower sisal contents, the wax incorporation may improve the mechanical properties of TPS blends containing PLA and sisal. (TPS and PLA percentages are based on total weight while the sisal and the wax content is based on TPS/PLA weight).

Table 4.9 Effect of addition of 2% Paraffin wax on the mechanical properties of TPS reinforced with sisal fiber

TPS%	PLA%	Sisal%	Paraffin wax%	Modulus (MPa)	Elongation at break%	Tensile strength (MPa)
70	30	10	-	495	20.65	10.79
70	30	10	2	854	6.2	13.35
70	30	20	-	1159	9.12	25.35
70	30	20	2	827	2.71	26.97

4.7.2 Water resistance properties of TPS based materials blended with paraffin wax

4.7.2.1 Contact angle of TPS based materials blended with paraffin wax

As previously mentioned, the pure TPS blend with 10% water and 30% glycerol exhibits a very low initial contact angle of about 17.4° after 30 seconds. With addition of PLA and sisal fiber, the contact angle of the TPS matrix increased to almost 90 °, which shows a significant reduction in the water sensitivity of the samples. At this point, paraffin wax was blended with the samples to obtain more water resistance.

With addition of 2% paraffin wax into the TPS, the contact angle increased to almost 50°, but it is still unacceptable. Paraffin wax was also added to TPS/PLA, TPS/sisal, and TPS/PLA/sisal matrixes. The wax incorporation into those matrixes which contain PLA did not change the contact angle, whereas it affects those which do not contain PLA, e.i. TPS, and TPS/sisal composites. From the results, paraffin wax increased the contact angle of pure TPS samples more than the other matrixes. With incorporation of wax to those samples which contained PLA, the contact angle not only did not increase, but also shifted to lower values. With incorporation of wax into the matrixes which contained sisal fiber, the contact angle did increase to higher values, but not significantly. The results indicate that wax achieves the best adhesion with pure TPS blend.

4.7.2.2 Water uptake of TPS based materials blended with paraffin wax

Different approaches to the reduction of moisture sensitivity of TPS based polymers have already been discussed. It was showcased that the water uptake of the TPS samples after addition of 30% PLA decreased considerably from 4.6% to less than 0.3% after 21 days in 75% RH. Also sisal incorporation had a huge effect on the water uptake of the TPS matrixes, such that the water uptake of TPS decreased down to almost half by addition of 20% annealed sisal.

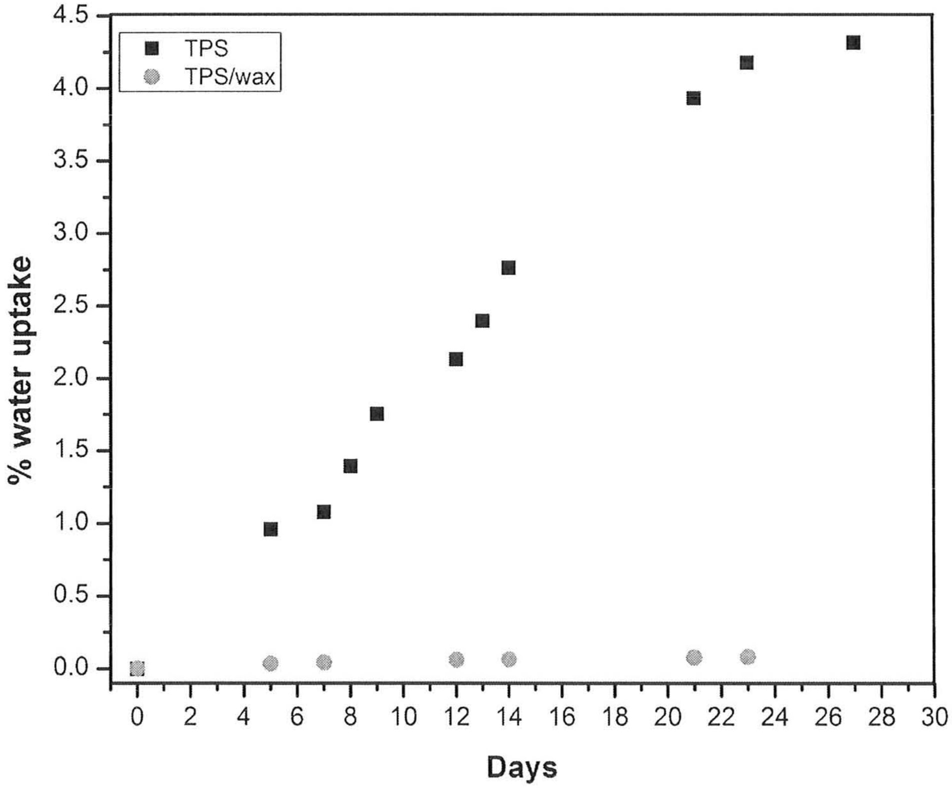


Figure 4.25 Comparison between the water uptake of TPS samples before and after 2% paraffin wax addition at 75% RH

In order to obtain the most possible decrease in moisture sorption of the samples, sisal fiber and 2 wt% paraffin wax was added to all the blends. Although wax incorporation had a significant effect on water up reduction of all samples, an incredible decrease in water uptake of pure TPS can be seen. Pure TPS samples containing only 2% paraffin wax absorbed the **lowest** amount of moisture between all other blends and composites. Significant reduction in water uptake of TPS blended with 2% paraffin wax reflects that the wax can provide excellent adhesion stability and dispersion in starch blends. The water uptake reduction was also obtained by the incorporation of paraffin wax into the other matrixes (TPS/PLA, TPS/sisal, and TPS/PLA/sisal), but not as significant as its addition to pure TPS.

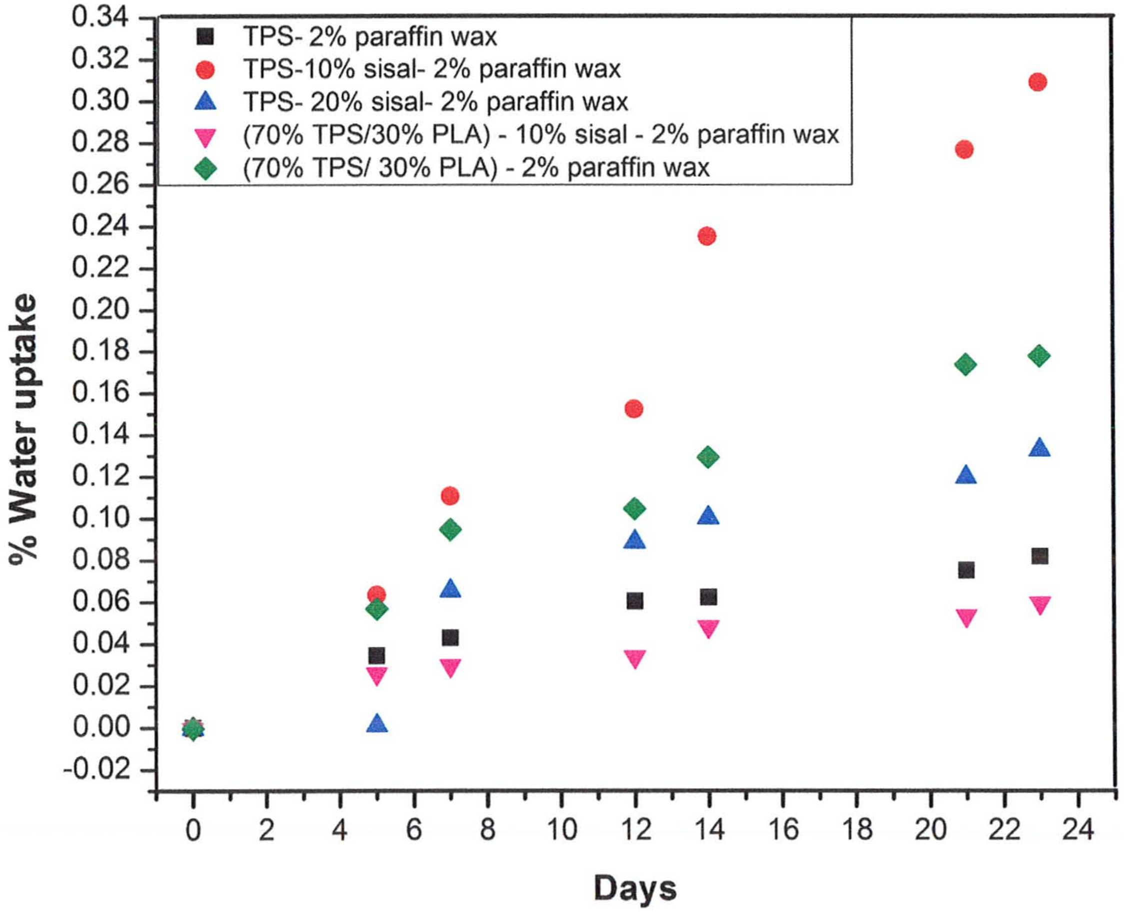


Figure 4.26 Comparison between the water uptake of different TPS based samples blended with 2%paraffin wax at 75% RH

4.8 Water vapor transition

The water vapor transition rate (WVTR) of some selected samples were evaluated to determine their suitability as water-resistant materials and to understand the role of each component in terms of water resistance. The tests were operated based on ASTM – E 96-90. The daily recorded weights for each specimen were first adjusted by calculating the weight change from initial to time of weighting. This adjustment was made by reversing the direction of the weight changes based on the initial weight of the specimen. The modified weights were plotted against the time of weighting. The slope of a line which fits the plot of at least six points is the rate of the water vapor transition.

$$WVT = \frac{G}{tA}$$

Where:

G = weight change, g

t = time, day

$\frac{G}{t}$ = slope of the straight line, g/day

A = test area (cup mouth area), m^2 and

WVT = rate of water vapor transition, $g/day \times m^2$

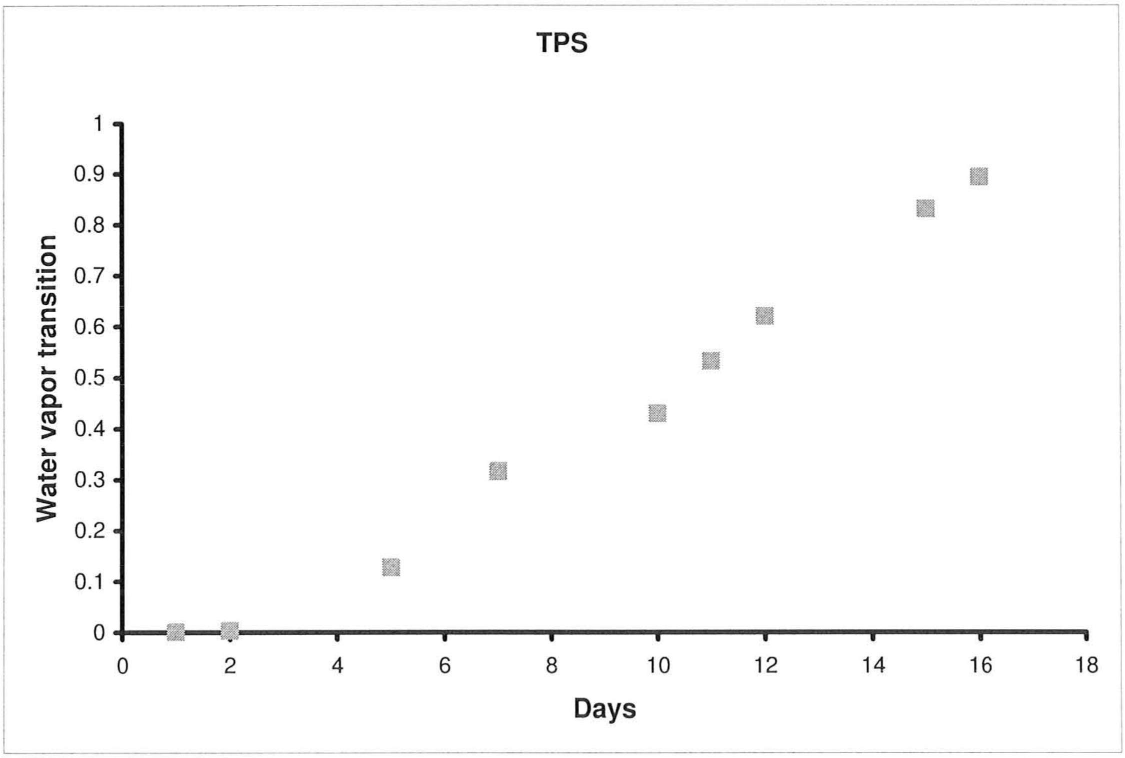


Figure 4. 27 Water vapor transition of TPS at room temperature from cylinder test container (cup mouth diameter, 1.5 cm)

WVTR data for TPS based samples are presented in Table 4.10. Values of WVTR for TPS decreased to less than half the initial value by addition of 30% PLA, 20% sisal, and 2% wax into the blend. However, this value compared to typical WVTR values for biodegradable polymers which are between 20 to 300 $g/day \times m^2$ at 25° is still higher (Shogren, 1997).

Table 4. 10 Water vapor transition rates of TPS based samples

Sample with 2 mm thickness	**WVTR** ($g/day \times m^2$)
TPS	1093
70%TPS- 30% PLA	967
TPS-20% sisal	746
TPS-20% sisal- 2% paraffin wax	723
(70%TPS- 30% PLA)-10%sisal-2%wax	757
(70%TPS- 30% PLA)-20%sisal-2%wax	530

CHAPTER 5

CONCLUSION

Potato starch was plasticized with water and glycerol. The DSC measurements indicated that as water content of the samples increased from 9 wt% to excess water, while the starch/glycerol ratio is constant, both the gelatinizatiom and melting temperatures decreased to lower temperatures. An increase in the glycerol content resulted in an increase in both gelatinization and melting temperatures. Addition of glycerol later to the mixture of starch and water, attempted to minimize the backward effect of glycerol on gelatinization temperature of the mixture while keeping glycerol plasticization effect. Although this attempt did not change the gelatinization temperature, it did affect the melting onset temperature significantly.

Potato starch was gelatinized with incorporation of water and glycerol in both Haake Reomix 3000 Batch Mixer and DSM Xplore microcompounder extruder. The reduction of both the melting and glass transition temperatures was obtained. By increasing the plasticizer content, T_g of both starch rich and glycerol rich domains in the blend shifted toward lower temperatures. For example, for a TPS blend with 10 wt% water and 25 wt% glycerol, the glass transition of glycerol-rich and starch-rich domains are 33.5°C and 52.1°C respectively. After increasing the plasticizers content to 20 wt% water and 40 wt% glycerol, these numbers decrease to -11.3°C and 32.3°C respectively. The mechanical properties of thermoplastic potato starch were investigated through Instron. The results indicated that the mechanical properties of the blends depend on the amount of plasticizers as well as storage time.

Thermoplastic potato starch was blended with a second polymer (PLA) to improve mechanical properties and reduce hygroscopy. In terms of mechanical properties and water sensitivity, incorporation of PLA had a major effect on both, such that, with incorporation of 30 wt% PLA into pure TPS, the Young's modulus increased from 64 MPa to 478 MPa, and also water uptake of the samples decreased from 4.5% after 24 days in 75% RH for TPS to 0.3% for TPS/PLA. Grafting MA unto PLA, in low PLA concentrations did not have significant effect on the TPS/PLA properties. Increasing the amount of PLAgMA in the blend weakened the mechanical properties and increased the water sensitivity.

The materials (TPS and TPS/PLA) were also blended with third ingredient (sisal and/or paraffin wax) to reduce hygroscopy. In comparison with that of the pure TPS, the Young's modulus and tensile strength of the sisal reinforced TPS composites(20 wt%) increased from 64 MPa and 1.84 MPa to 764 MPa and 16.3 MPa respectively. Also, compared with those of the unfilled 70 wt% TPS/ 30 wt% PLA blends, the Young's modulus and tensile strength of the TPS/PLA reinforced with 20% sisal increased from 487MPa to 850 MPa and from 5.2 MPa to 26 MPa respectively. Meanwhile, the incorporation of sisal fiber also decreased the water sensitivity of TPS/sisal composites.

The incorporation of 2% paraffin wax into the TPS, TPS/sisal, TPS/PLA and TPS/PLA/sisal matrixes, not only significantly reduced the water sensitivity, but also improved the mechanical properties of the blends. Paraffin wax incorporation partially increased the contact angle values of the blends and composites, while it had a considerable effect on the water uptake values of the samples.

The goal of this research was to make TPS basis materials appropriate for short term packaging and disposable applications. Based on the fact that the Elastic modulus and tensile strength of almost all the blends containing PLA and/or sisal fiber are equal or even greater than that of the LDPE, TPS materials from potato starch blended with PLA and/or sisal, are suitable for replacing materials currently used for applications requiring low elongation. However, for applications requiring high elongation such as filming, further research work is needed. In terms of water sensitivity, contact angles of most TPS/PLA, TPS/sisal, and TPS/PLA/sisal blends reach that of the LDPE. Water uptake of LDPE is around 0.01% per day. With addition of paraffin wax into all the blends, water uptake of the samples are even less than that of the LDPE. (Physical and mechanical properties of LDPE can be found in Appendix E).

References

Alvarez, V. V. (2006). Effect of microstructure on the tensile and fracture properties of sisal fiber/starch-based composites. *Journal of composite materials, Vol. 40, No. 1* , 21.

ASTM D 6400-04. (n.d.). *Standard Specification for compostable plastics* .

ASTM E 96 - 90. (n.d.). *ASTM* .

Averous, L. (2004). Biodegradable Multiphase Systems Based on Plasticized Starch: A Review. *Journal of Macromolecular Science, Vol. C44, No. 3* , 231.

Averous, L. (2007). - Bioplastics -Agro-polymers and Starch-based biomaterials. Retrieved from *http://www.biodeg.net/biomaterial.html.*

Avérous, L. F. (2001). Association between plasticized starch and polyesters:processing and performances of injected biodegradable systems. *Polymer engineering and science, Vol 41, No. 5* , 727.

Averous, L. F., & Fringant, C. (2000). Blends of thermoplastic starch and polyesteramide: processing and properties. *Journal of applied polymer science, Vol. 76, No. 7* , 1117.

Averous, L. H. (2009). Biocomposites based on plasticized starch. *Biofuels, Bioprod, Bioref, Vol.3* , 329.

Bai, Y. Q. (2007). Properties of thermoplastic starch/poly (lactic acid) blends. *Master Thesis*, McMaster University .

Baiardo, M. F. (2003). Thermal and mechanical properties of plasticized Ploly (L-lactic acid). *Journal of Applied Polymer Science,Vol. 90, No.7* , 1732.

Barsby, L. D. (1996). *Starch: advances in structure and function,* The Royal Society of Chemistry.

Biliaderis, C. M. (2006). Starch gelatinization phenomena studied by differential scannig calorimetry. *Journal of Food Science, Vol. 45, Issue. 6* , 1669.

Buleon, A. C. (1998). Starch granules: structure and biosynthesis. *International journal of biological macromolecules, Vol. 23* , 85.

Cao, X. C. (2008). Green composites reinforced with hemp nanocrystals in plasticized starch . *Journal of applied polymer science, Vol. 109* , 3804.

Carlson, .. N. (1998). Maleation of polylactide (PLA) by reactive extrusion. *Journal of applied polymer science, Vol. 72, Issue 4* , 477.

Corradini, E. J. (2009). Effect of Coconut, Sisal and Jute Fibers on the Properties of Starch/Gluten/Glycerol Matrix. *Journal of polymer and environment, Vol. 17, No. 1* .

Corradini, E. M. (2007). A Preliminary Study for the Use of Natural Fibers as Reinforcement in Starch-Gluten-Glycerol Matrix. *Macromolecular symposia, Vol. 245-246, Issue. 1* , 558.

Cyras, V. M.-T. (2008). Physical and mechanical properties of thermoplastic starch/montmorillonite nanocomposite films. *Carbohydrate Polymers, Vol. 73* , 55.

Cyras, V. P. (2004). Effect of chemical treatment on the mechanical properties of starch-based blends reinforced with sisal. *Journal of composite materials, Vol. 38, No.16* , 1387.

De Graaf, R. A. (2003). Material properties and glass transition temprature of different thermoplastic starches after extrusion processing. *Starch, Vol. 55* , 80.

Despond, S. C. (2005). Barrier properties of paper-chitosan and paper-chitosan-carnauba wax films. *Journal of applied polymer science, Vol.98* , 704.

Donavon, J. W. (1997). Phase transition of starch-water system. *Biopolymers, Vol. 18, No. 2* , 263.

Drumright, R. E. (2000). Polylactic Acid Technology. *Advanced materials, Vol. 12* , 1841 .

Forsell, P. M. (1997). Phase and glass transition behaviour of corn centrated barley starch-glycerol-water mixture, a model of thermoplastic starch. *Carbohydrate Polymers, Vol. 34* , 275.

Grommers, H. E. (2009). Potato starch, production, modification and uses. In J. W. Bemiller, *Starch: Chemistry and Technology* (p. 511). Elsevier.

Halley, P. J. (2005). Thermoplastic starch biodegradable polymers. In R. Smith, *Biodegradable Polymers for industrial applications* (p. 140). England: Woodhead publishing limited.

Han, J. (2005). *Innovation in food packaging.* Elsevier.

Hegenbart, S. (1995). *Building Texture with gums and starches.* Retrieved from http://www.foodproductdesign.com.

Huang, X. (2005). *Properties of thermoplastic starch/poly lactic acid*, Master Thesis, McMaster University.

Hulleman, S. H. (1998). The role of water during plasticization of native starches. *Polymer, Vol. 39* , 2043.

Huneault, M. L. (2006). Morphology and properties of compatibilized polylactide/thermoplastic starch blends. *Polymer, Vol.48* , 270.

IGI wax Affilliate, s. (2009). *http://igiwax.com/wax-basics/overview/*. Retrieved from http://igiwax.com/home/.

Jang, W. Y. (2007). Thermal properties and morphology of biodegradable PLA/Starch compatibilized blends. *Journal of Industrial and Engineering Chemistry* , 457.

Ke, T. S. (2003). Melting behavior and crystallization kinetics of satch and poly (lactic acid) composites. *Journal of applied polymer science, Vol. 89, Issue.5* , 1203.

Ke, T. S. (2004). Starch, Poly(lactic acid), and Poly(vinyl alcohol) blends. *Journal of polymers and environment, Vol. 11, No. 1* , 7.

Kulkarni, R. K. (1971). Biodegradable Poly lactic acid polymers. *Journal of Biomed mater* , 169.

Ljungberg, N. W. (2002). The effect of plasticizers on the dynamic mechanical and thermal properties of Poly (lactic acid) . *Journal of Applied Polymer Science,Vol. 81.No.5* , 1227.

Lourdin, D. B. (1996). Antiplasticization in starch-glycerol films? *Journal of applied polymer science* , 1047.

Lunt, J. (1998). Large-scale production, properties and commercial applications of poly (lactic acid) polymers. *Polymer degradation and stability, Vol. 59, No. 1-3* , 145.

Ma, X. Y. (2005). Studies on the properties of natural fibers-reinforced thermoplastic starch composites. *Carbohydrate polymers, Vol. 62* , 19.

Ma, X. Y. (2006). Yrea and formamide as a mixed plasticizer for thermoplastic wheat flour. *Carbohydrate Polymers, Vol. 60* , 218.

Martin, O. ,. (2001). Poly(lactic acid): plasticization and properties of biodegradable multiphase systems . *Polymer, Vol. 42, No. 14* , 6209.

Martino, V. ,. (2006). Thermal and mechanical characterization of plasticized poly (L-lactide-co-D,L-lactide) films for food packaging. *Journal thermal analysis and calorimetry, Vol 86, No. 3* , 707.

Michelman. (2009, September 13). *http://www.azom.com/Details.asp?ArticleID=4906.* Retrieved from Wax Emulsions - Modifying the Effects of Water on Aqueous-Based Coatings and Enhancing Secondary Properties in OEM Wood Coatings by Michelman.

Mishra, S. M. (2004). A review on pineapple leaf fibers, sisal fibers and their biocomposites. *Macromolecular materials and Engineering, Vol. 289, Issue. 11* , 955.

Mohanty, A. K. (2000). Biofibres, biodegradable polymers and biocomposites. An overview. *Macromolecular Materials and Engineering* , 1.

Mohanty, A. M. (2005). *Natural Fibers, Biopolymers, and Biocomposites.*

Narayan R., D. Y. (1994). Impact of goverment policies, regulations, and standards activities on an emerging biodegradable plastics industry. *Biodegradable plastics and polymers* , 261.

Nashed, G. R. (2003). The plasticization of glycerol and water on the gelatinization of wheat starch. *Starch, Vol. 55, Issue. 3-4* , 131.

Nijenhuis, A. J. (1992). Lewis acid catalized polymerization of L-lactide. kinetics and and mechanism of the bulk polymerization. *Macromolecules, 25* , 6419.

Ning, W. J. (2008). Preparation and characterization of compostible thermoplastic dry starch/ pol(lactic acid). *Polymer composites* , 551.

Ning, W. J. (2008). Preparation and characterizationof compatible thermoplastic dry starch/poly(lactic acid). *Polymer composites* , 551.

Orozoco, V. B. (2009). Preparatio and characterization of Poly(lactic acid)-g-Maleic anhydride+starch blends. *WILEY-VCH Verlag Gmbh & Co.*

Park, J. W. (2000). Biodegradable polymer of Poly(L-lactic acid) and gelatinized starch. *Polymer engineeringand science, Vol. 40, No. 12* , 2539.

Pejic, B. M. (2008). The effect of hemicelluloses and lignin removal on water uptake behavior of hemp fibers. *Bioresource technology* , 7152.

Pejica, B. M. (n.d.). The effects of hemicelluloses and lignin removal on water uptake behavior of hemp fibers .

Poutanen, K. F. (1996). Modification of starch properties with plastcizers. *Trends in Polymer Science, Vol. 4* , 128.

Qu, D. W. (1994). Kinetics of the formation of gelatinized and melted starch at extrusion cooking conditions. *Starch, Vol. 46* , 225.

Rieko, A. A. (2002). Studies on gelatinization and retrogradation of Katakuri starch by Differential Scanning Calorimetery. *Food Preservation Science, Vol.28, No. 6* , 299.

Rodriguez-Gonzalez, F. ,. (2004). Rheological and thermal properties of thermoplastic starch with high glycerol content. *Carbohydrate Polymers, Vol.58* , 139.

Rudnik, E. (2008). *Compostable polymer materials.* Elsevier.

Rutgers, R. N. *The plasticization effect of glycerol and water on the gelatinization of wheat starch.*

Schwartz, D. W. (2009). History and Future of starch. In J. W. BeMiller, *Starch: chemistry and technology.* elsevier.

Sears, J. K. (1982). *Technology of plasticizers.*

Shin, B. J. (2006). Properties of compatibilized PLA/Starch bleds. *Applied chemistry, Vol. 10, No. 1* , 77.

Shogren, R. (91). Water vapor permeability of biodegradable polymers . *Journal of Environmental polymer Degradation, Vol. 5, No. 2* , 1997.

Sinclair, R. (1996). The case for polylactic acid as a commodity packaging plastic. *Journal of macromolecular science. Pure and applied chemistry, Vol. 33, No. 5* , 585.

Smith, R. (2006). Thermoplastic starch biodegradable polymers. *Biodegradable Polymers for industrial applications* (p. 140). England: Woodhead publishing limited.

Stepto, R. (2006). *Understanding the processing of thermoplastic starch.* WILEY-VCH Verlag GmbH & Co.

Stevens, E. (2002). How green are green plastics? *BioCycle 43* , 42.

Torres, F. G. (2007). Processing and Mechanical Properties of Natural Fiber Reinforced Thermoplastic Starch Biocomposites. *Journal of thermoplastic composites materials, Vol. 20* , 208.

Vaidya, D. B. (1994). Properties of blends of starch and synthetic polymers containing anhydride groups. *Journal of applied polymer science, ol. 52, Issue. 5* , 617.

Van Soest, J. B. (1996c). Influence of glycerol on the melting of Potato starch. *Industrial Crops and Products, Vol.5* , 1.

Van Soest, J. B. (1996b). The influence of starch molecular mass on the properties of extruded thermoplastic starch. *Polymer, Vol. 37* , 3543.

Van Soest, J. J. (1996a). Changes in the mechanical properties of thermoplastic potato starch in relation with changes in B-type crystallinity. *Carbohydrate polymers, Vol 29* , 225.

Van Soest, J. K. (1996d). Influence of glycerol and water content on the structure and properties of extruded starch plastic sheets during aging. *Journal of polymer applied science, Vol. 64, Issue. 7* , 1411.

Van Soest, J. S. (1996f). Crystalliity in starch bioplastics. *Industrial Crops and Products, Vol. 5* , 11.

Van Soest, J. W. (1996e). Mechanical properties of thermoplastic maiz starch. *Journal of applied polymer science, Vol. 61* , 1927.

Wang, H. S. (2003). Properties of poly (lactic acid) blends with various starches as affected by physical aging. *Journal of applied polymer science, Vol. 90* , 3683.

Wang, H. S. (2001). Strengthening blends of poly (lactic acid) and starch with methylenediphenyl diisocyanate". *Journal of applied polymer science, Vol.82* , 1761.

Wang, X. L. (2003). Properties of starch blends with biodegradable polymers. *Polymer reviews, Vol. 43, Issue. 3* , 385.

Whistler, R. (1984). *Starch: chemistry and technology.*

Wojtowicz, A. V. (2005). The influence of water ad glycerol additionon thermal processig, reology and microstructure changes of potato starch. *Electronic Journal of Polish agricultural uiversites, Vol. 8, Issue. 4* .

Wool, R. P. (2005). *Bio-based polymers and composites.* Elsevier.

Wypych, G. (2004). *Hand book of plasticizers.* chem tec publishing.

Yang, J. Y. (2006). Study on the properties of ethylenebisformamide and sorbitol plasticized corn starch. *Carbohydrate polymer, Vol. 66* , 110.

Yu, J. G. (1996). Biodegradable thermoplastic starch. *Journal of applied polymer science, Vol. 62* , 1491.

Yu, L. D. (2006). Polymer blends and composites from renewable resources. *Progress in Polymer sciece, Vol.31, Issue. 6* , 576.

Zhang, J. S. (2004). Mechanical properties of polylactic acid/ starch composites compatibilized by maleic anhydride. *Biomacromolecules, Vol. 5* , 1446.

Zhang, J.-F. S. (2006). Poly(lactic acid)- based bioplastics. In R. Smith, *Biodegradable polymers for industrial applicaton* (p. 251). England: Woodhead publishing limited.

Zhang., L. D. (1997). Biodegradable polymer blends of poly(3-hydroxybutyrate) and starch acetate. *Polymer Int, Vol. 44* , 104.

Appendix A

Glass transition temperature of potato starch plasticized with different amount of water and glycerol

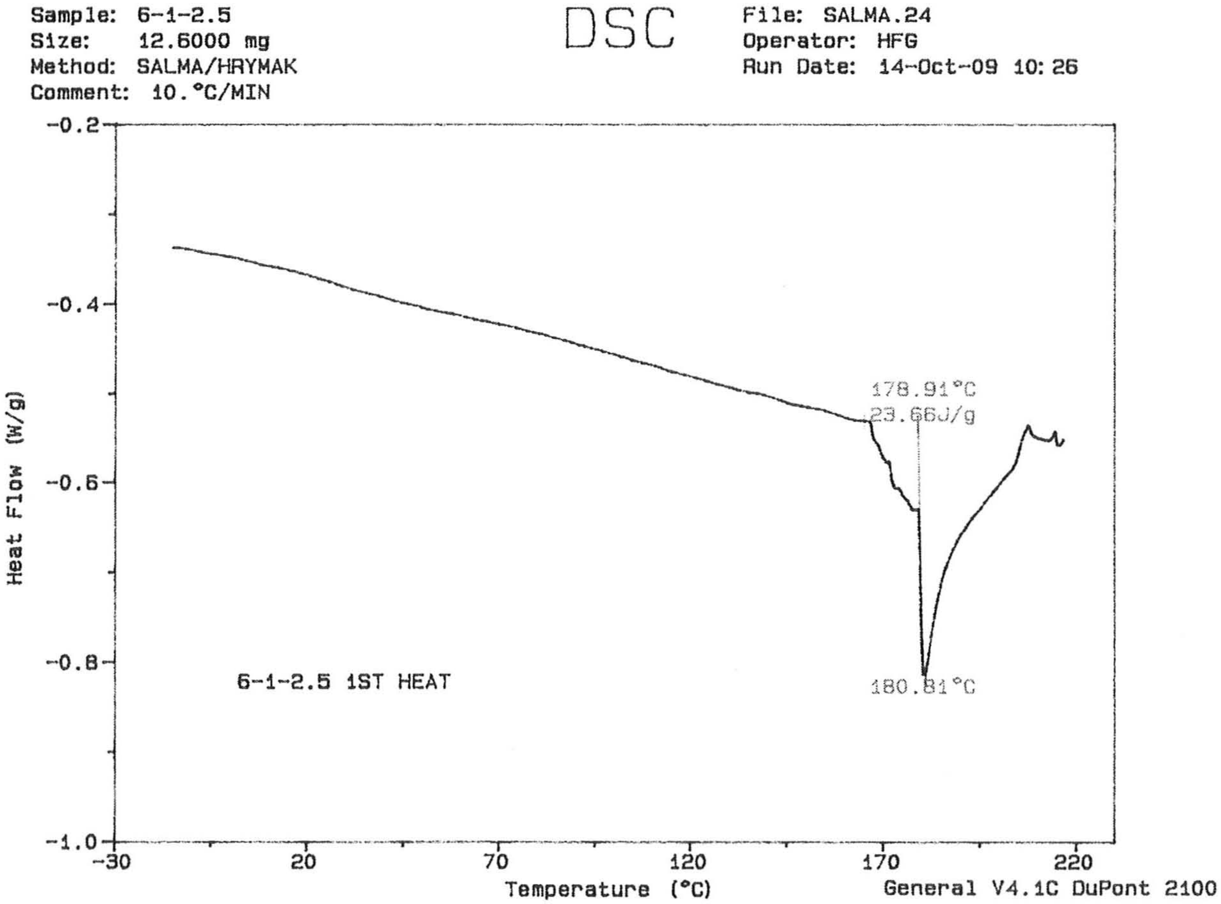


Figure A1 Melting transition of extruded TPS with 10.5% water and 26.3% glycerol, from the first DSC heat

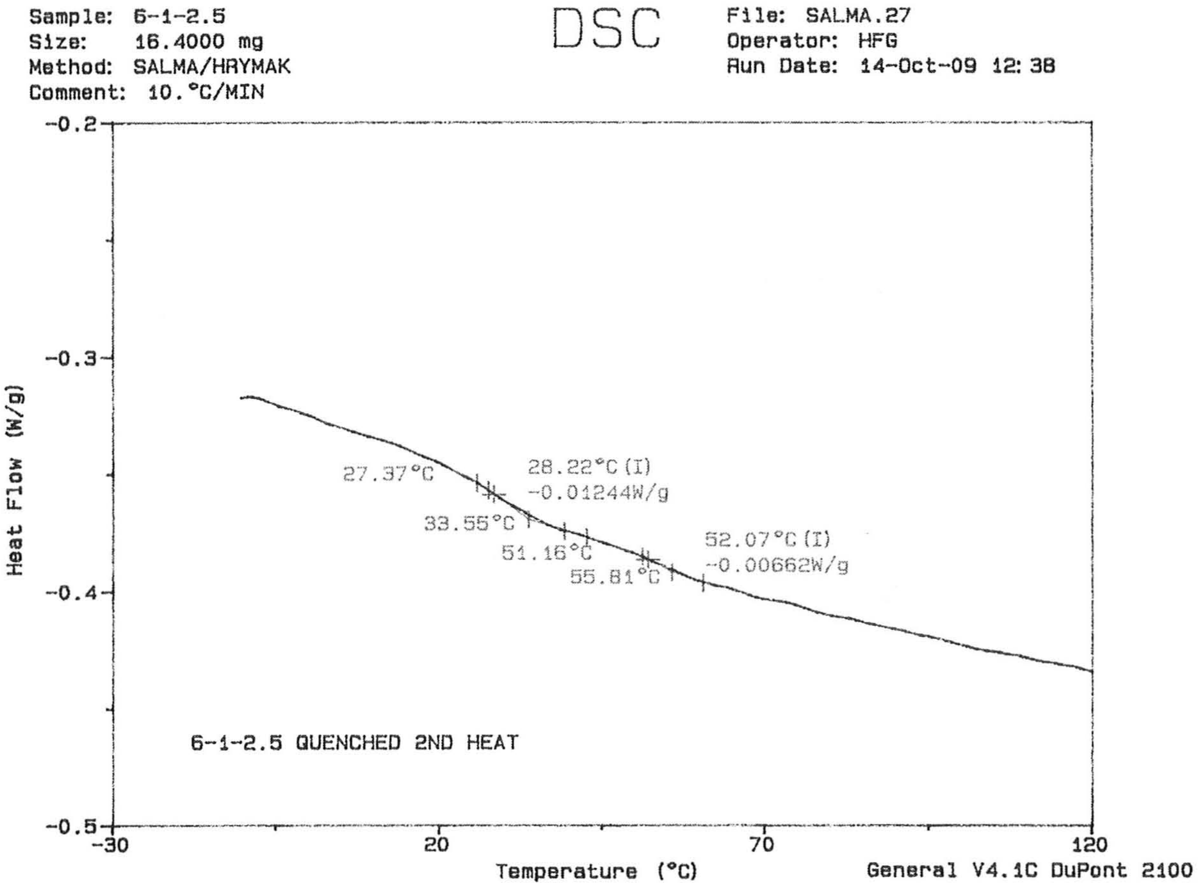
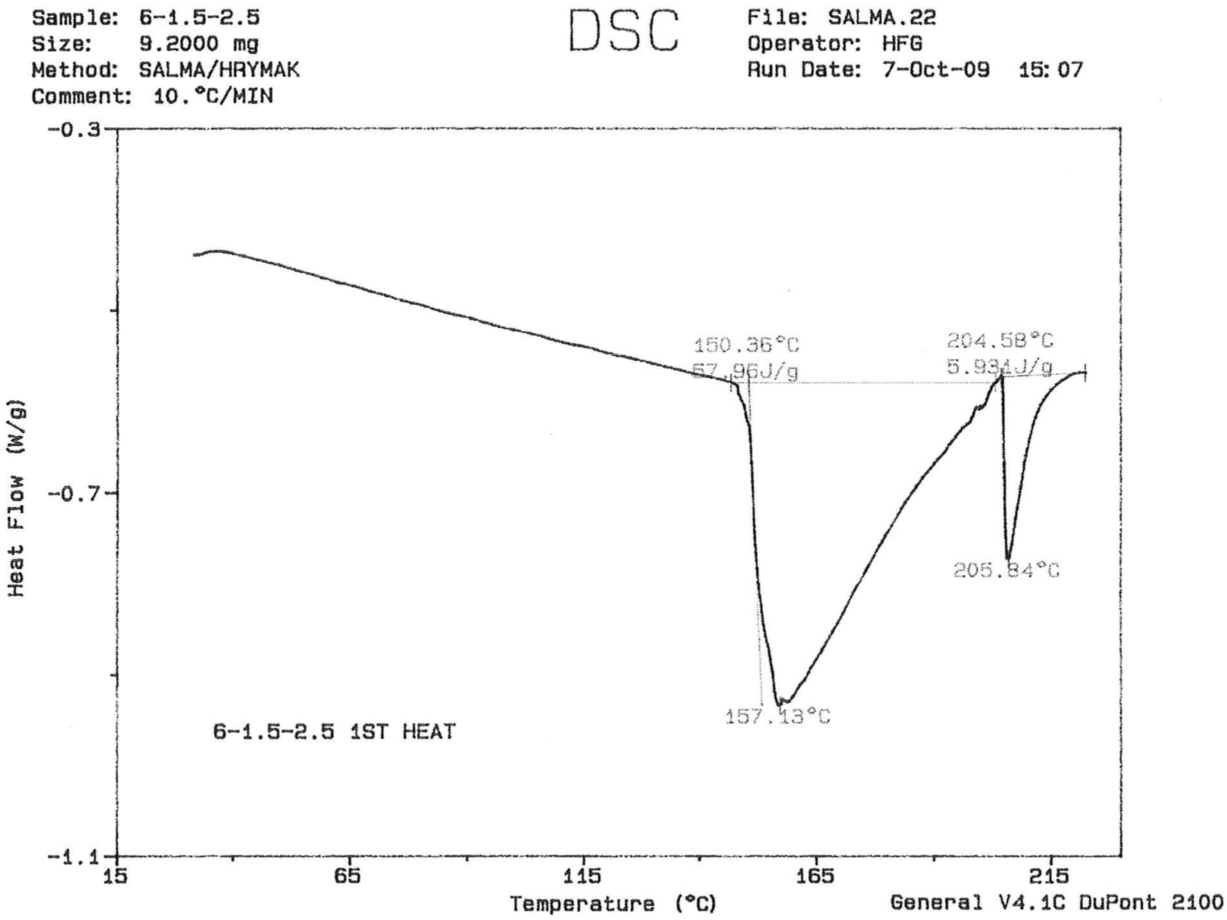


Figure A2 Glass transition of extruded TPS with 10.5% water and 26.3% glycerol, from the second DSC heat



Sample: 6-1.5-2.5
Size: 9.2000 mg
Method: SALMA/HRYMAK
Comment: 10.°C/MIN

File: SALMA.22
Operator: HFG
Run Date: 7-Oct-09 15:07

Figure A3 Melting transition of extruded TPS with 15% water and 25% glycerol, from the first DSC heat

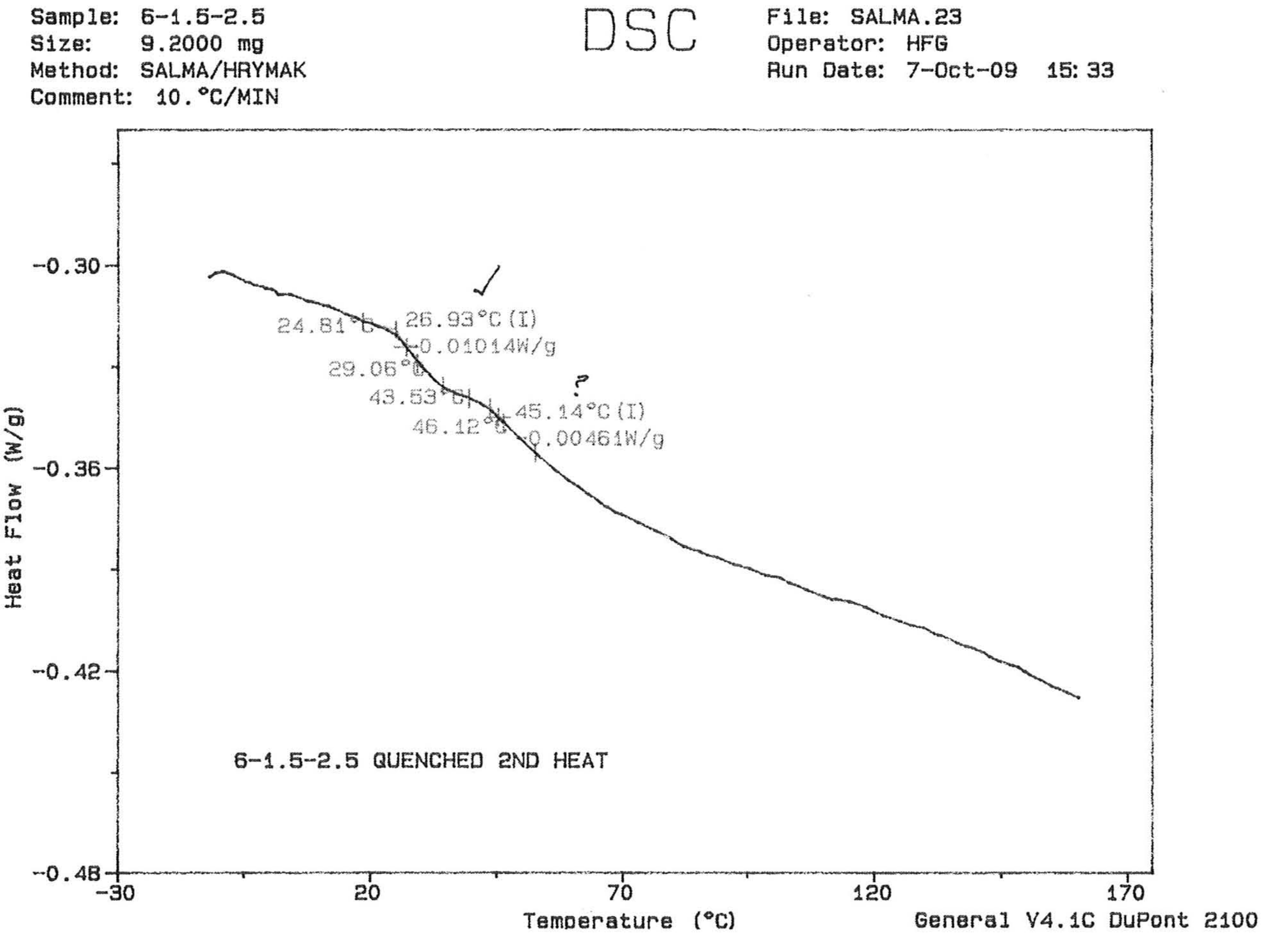


Figure A4 Glass transition of extruded TPS with 15% water and 25% glycerol, from the second DSC heat

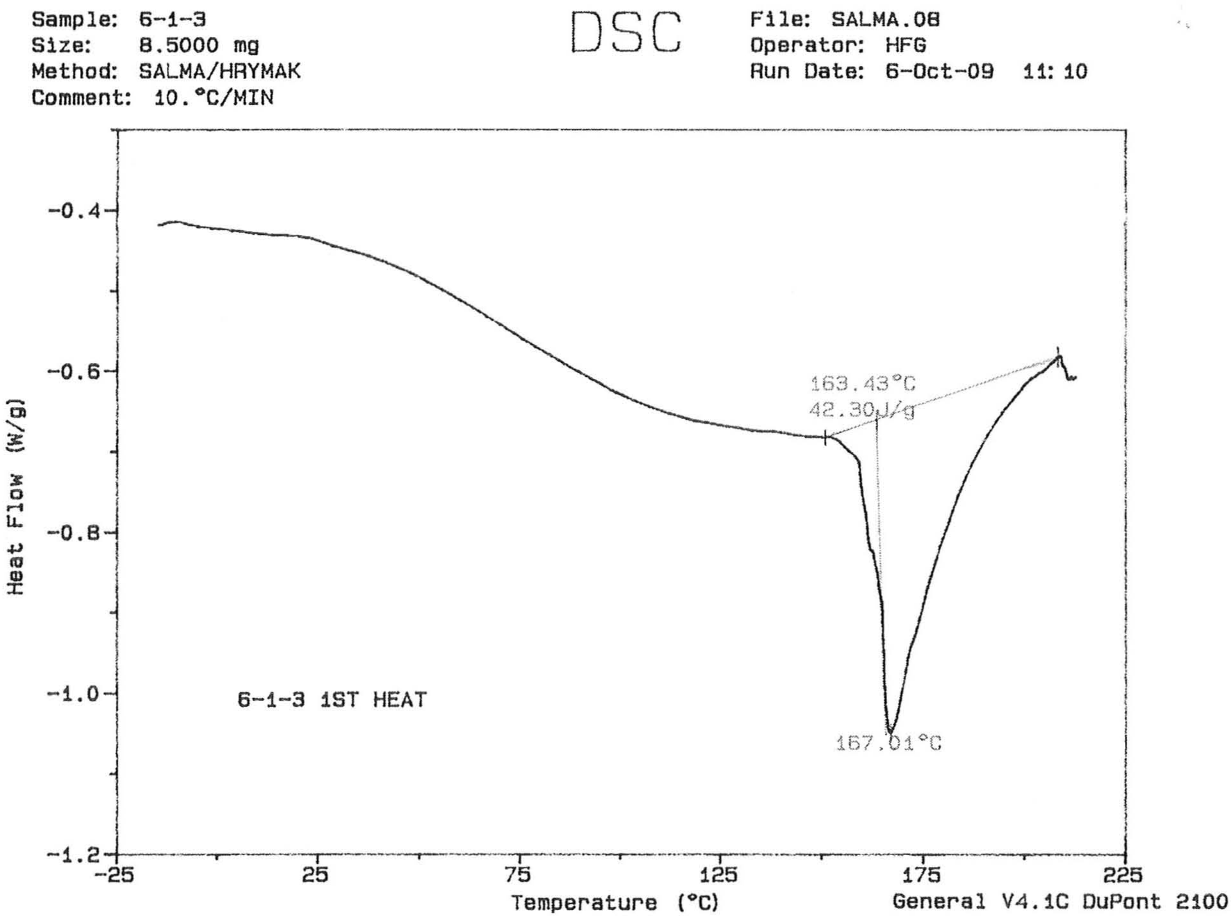


Figure A5 Melting transition of extruded TPS with 10% water and 30% glycerol, from the first DSC heat

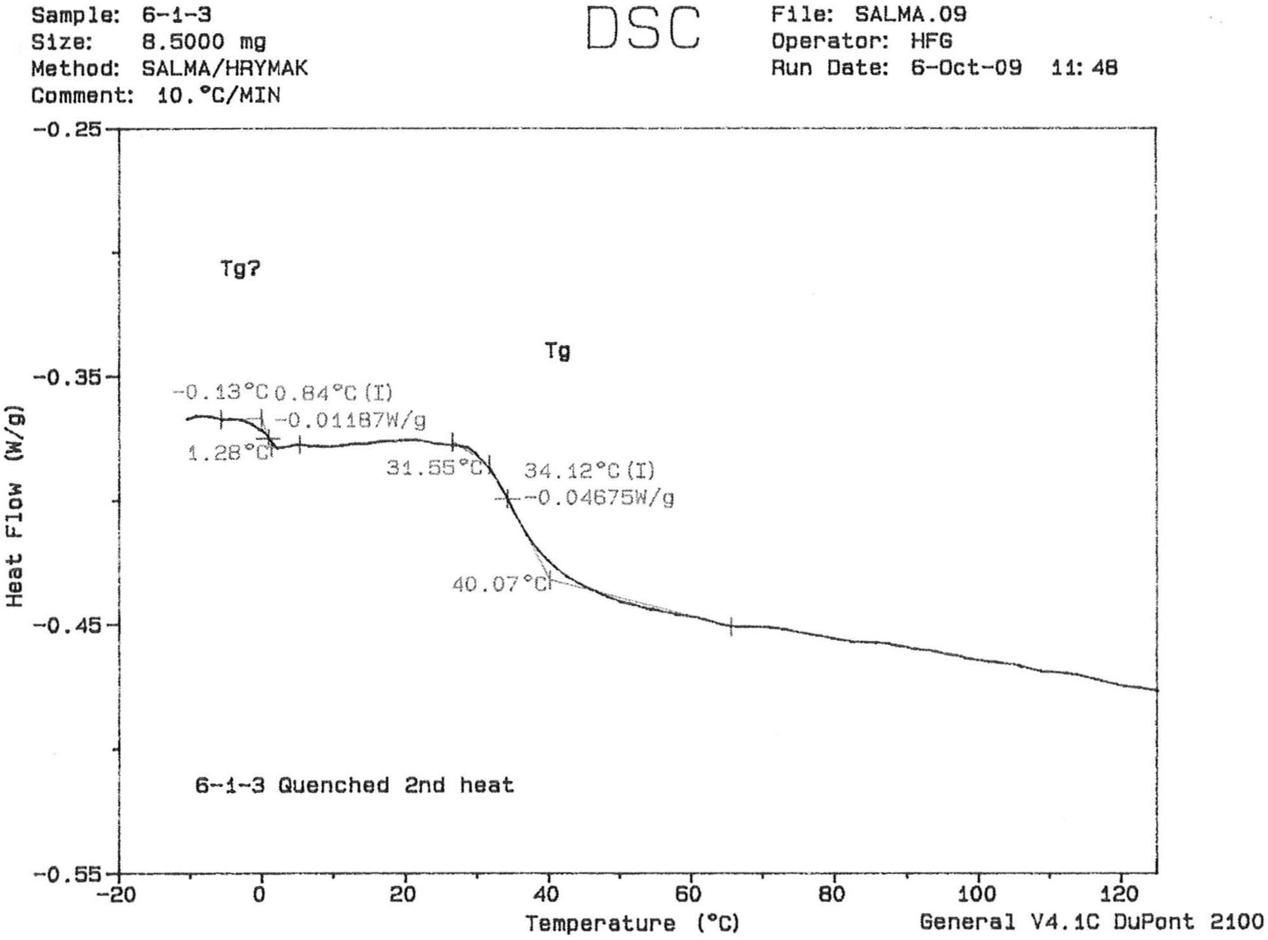


Figure A6 Glass transition of extruded TPS with 10% water and 30% glycerol, from the second DSC heat

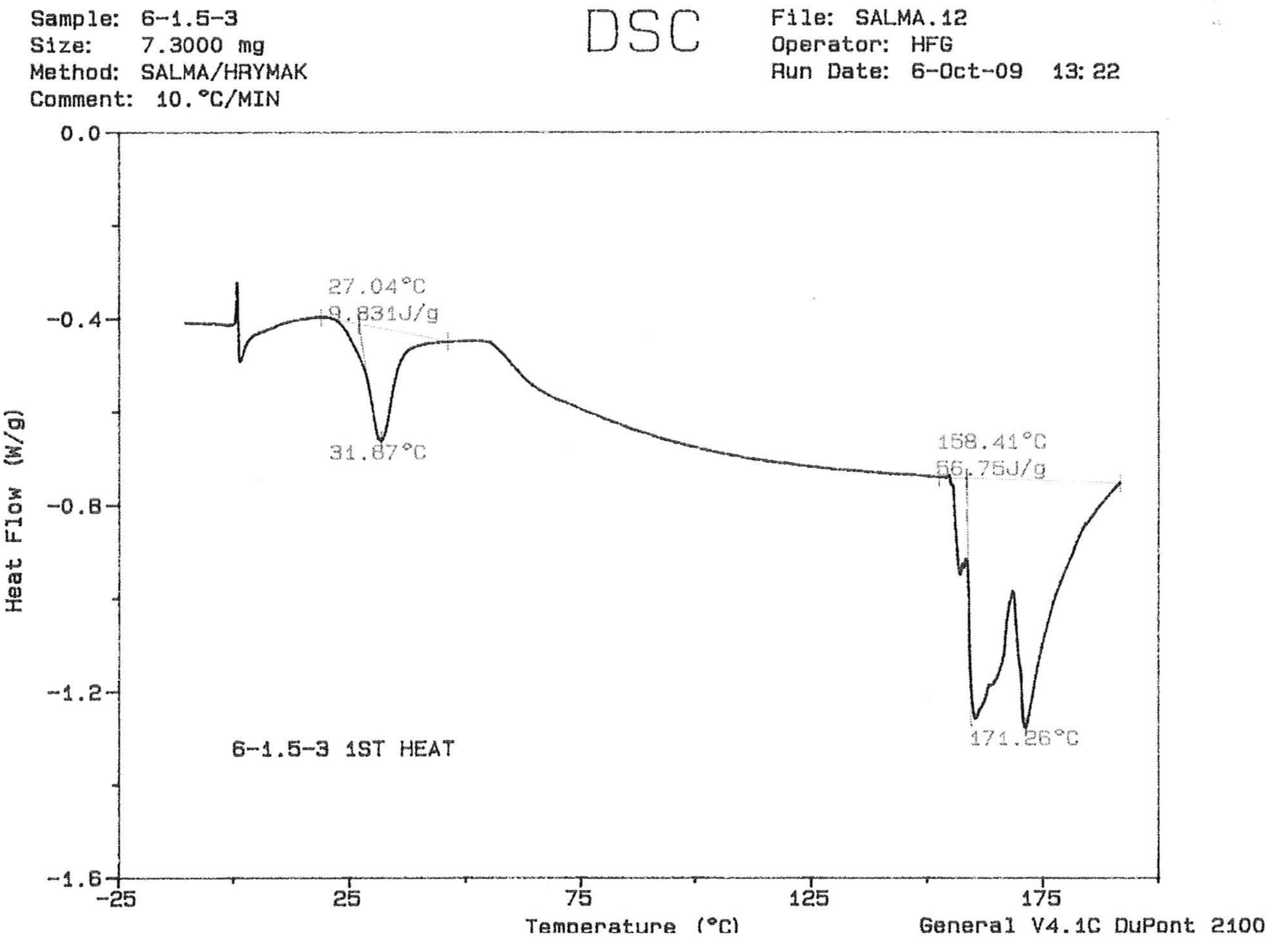


Figure A7 Melting transition of extruded TPS with 14.3% water and 28.6% glycerol, from the first DSC heat

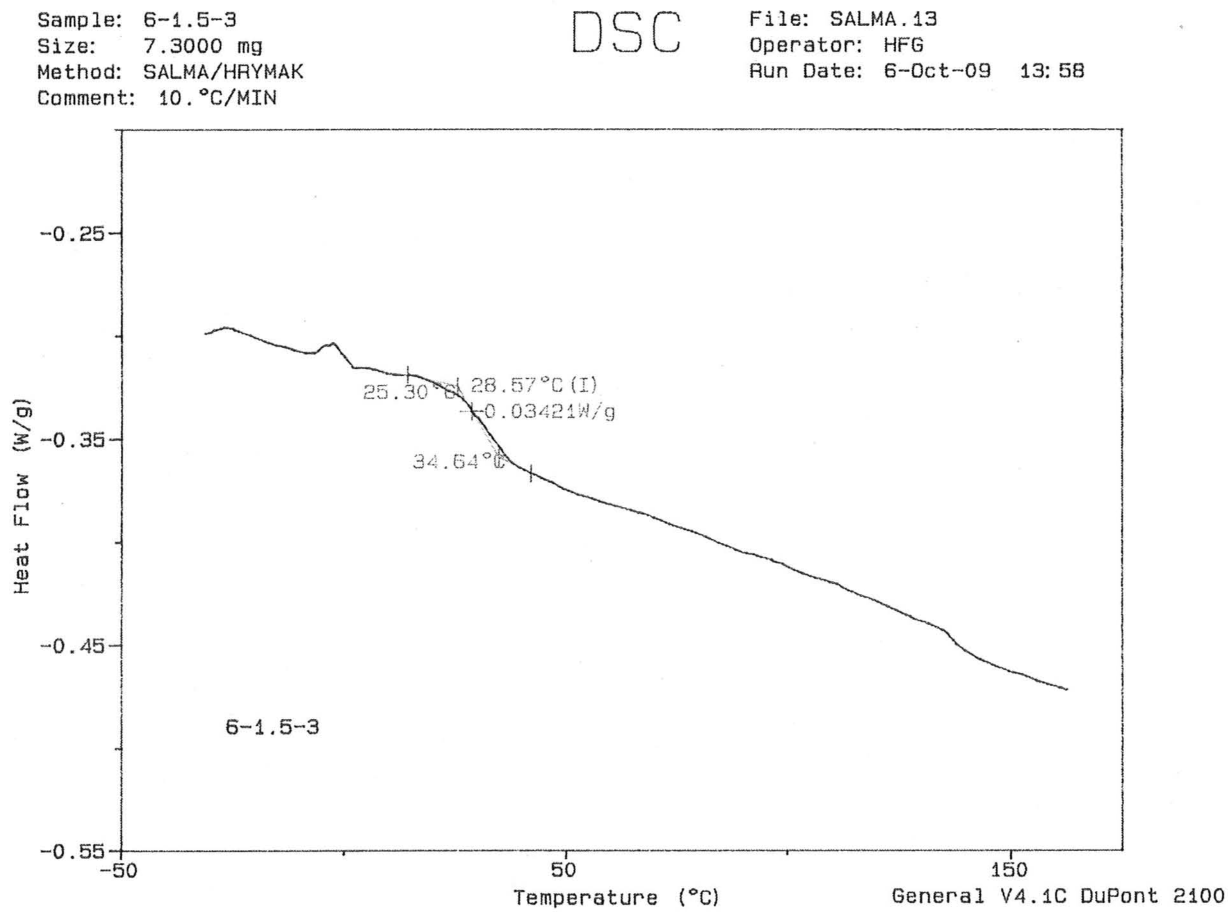


Figure A8 Glass transition of extruded TPS with 14.3% water and 28.6% glycerol, from the second DSC heat

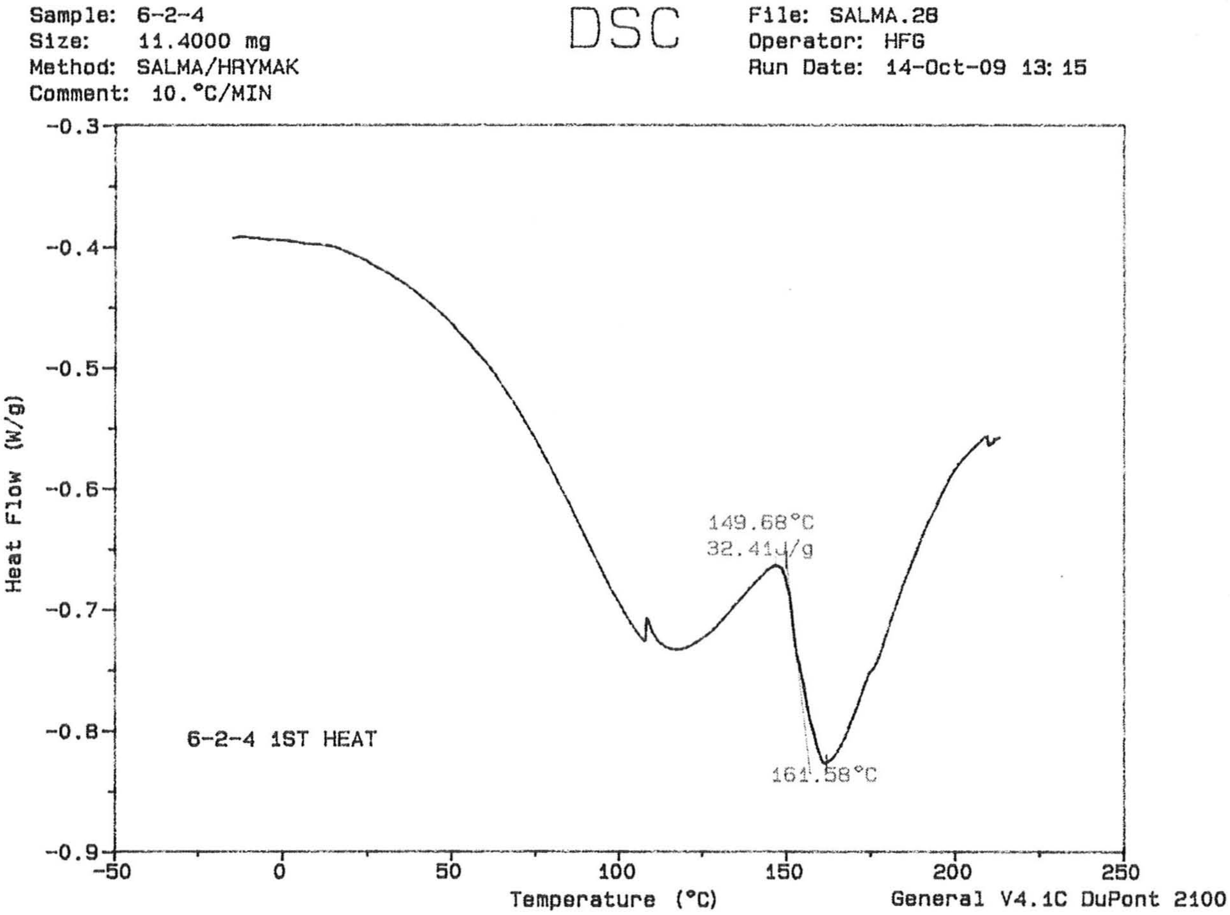


Figure A9 Melting transition of extruded TPS with 14.3% water and 28.6% glycerol, from the first DSC heat

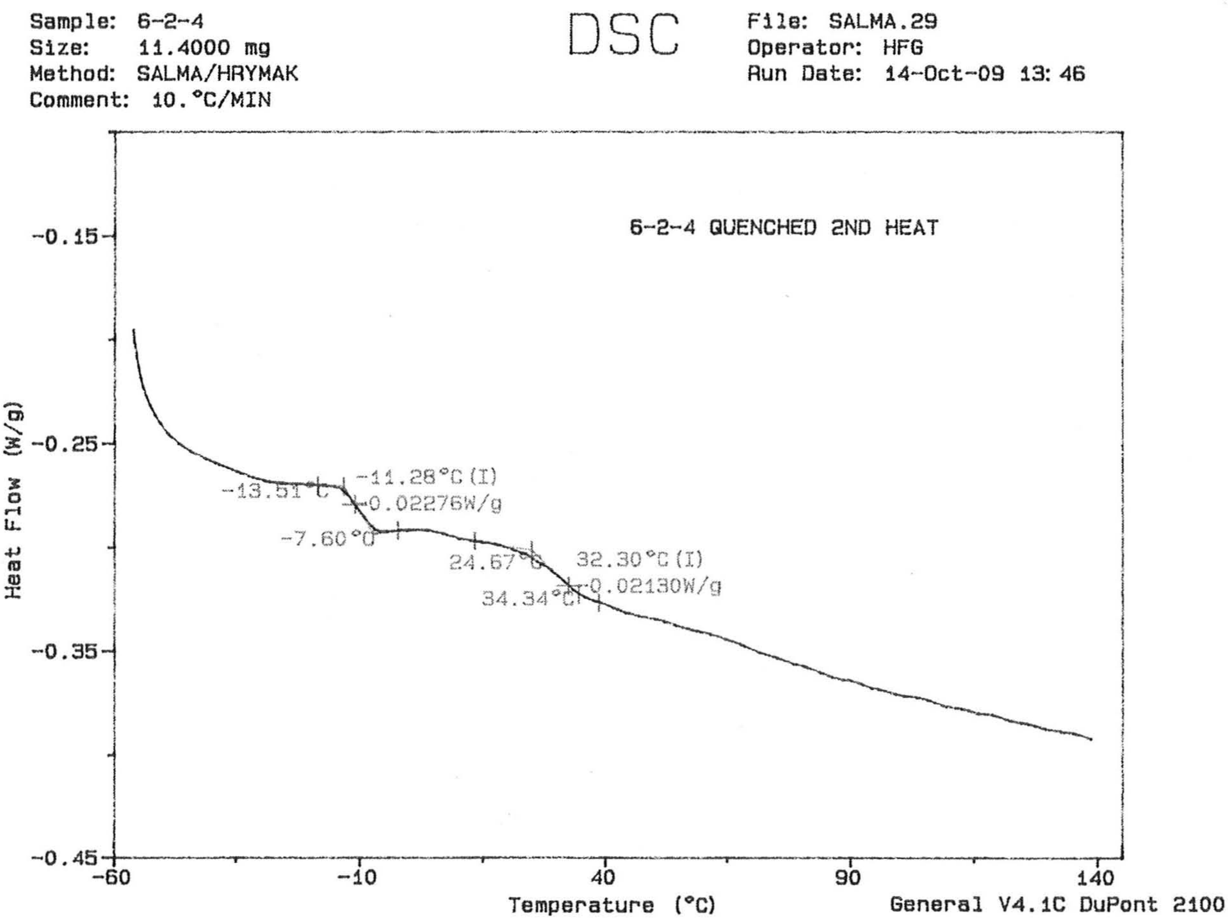


Figure A8 Glass transition of extruded TPS with 16.6% water and 33.4% glycerol, from the second DSC heat

Appendix B

Water uptake properties of TPS blends

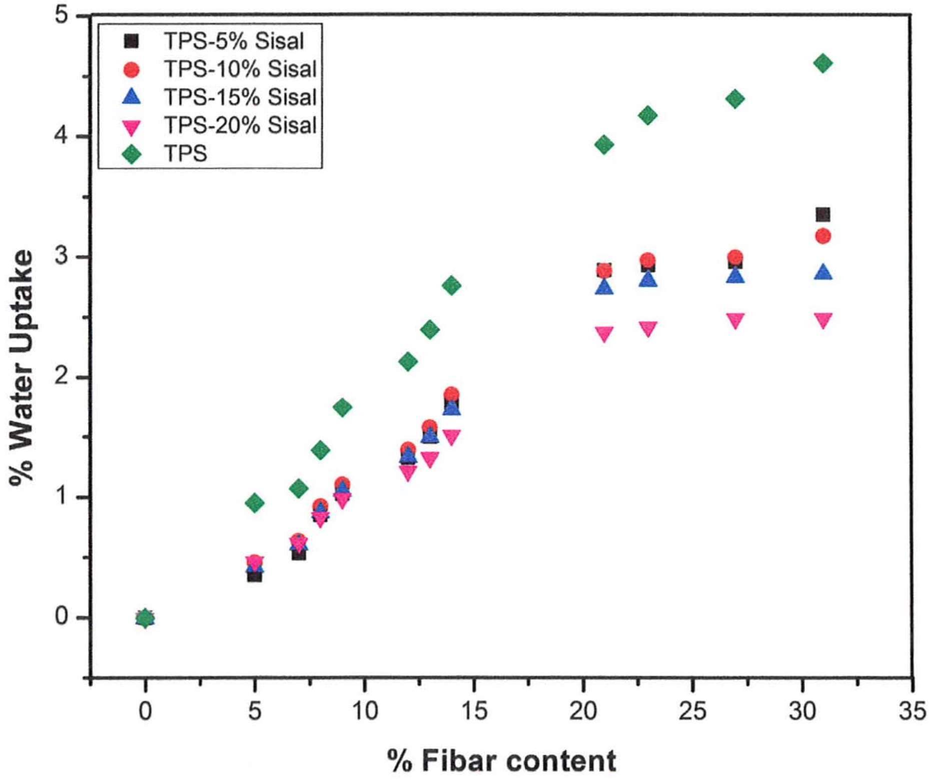


Figure B 1 Water uptake of TPS, and TPS reinforced with sisal fiber with 2 % paraffin wax at 75% RH

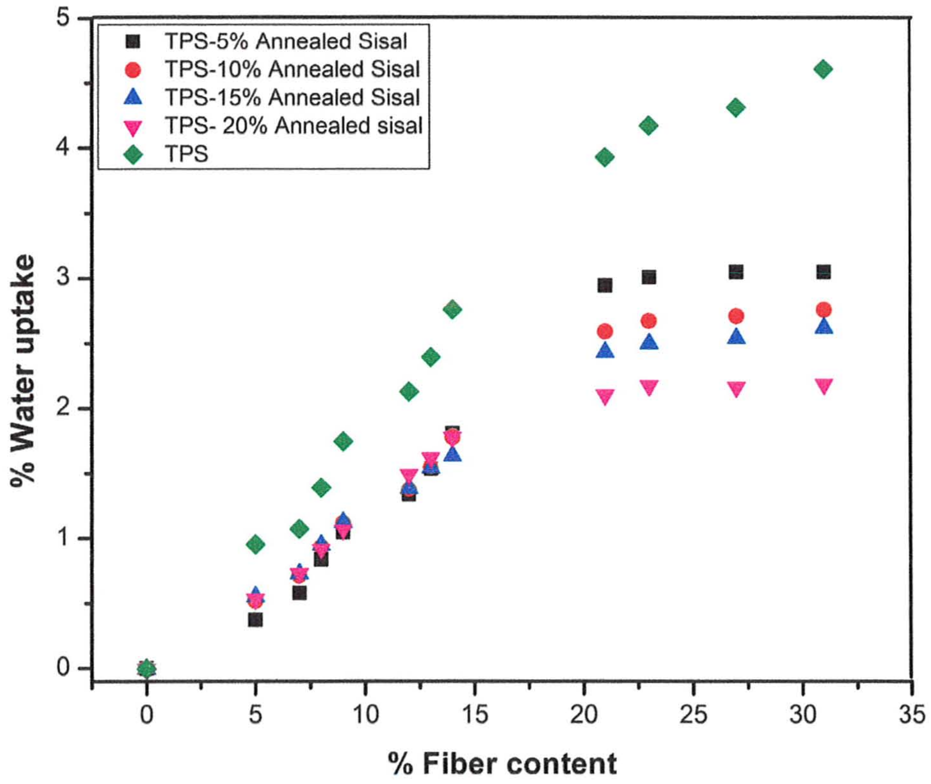


Figure B 2 Water uptake of TPS, and TPS reinforced with annealed sisal fiber with 2 % paraffin wax at 75% RH

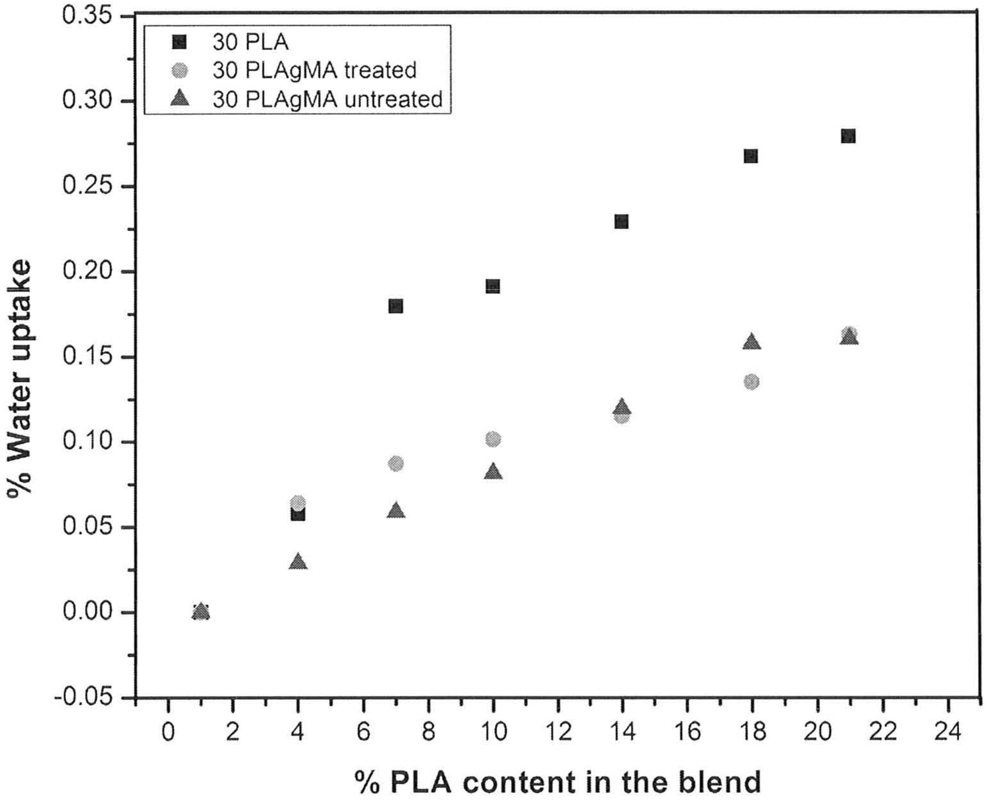


Figure B 3 Water uptake of TPS, and TPS/PLA blend with 2 % paraffin wax at 75% RH

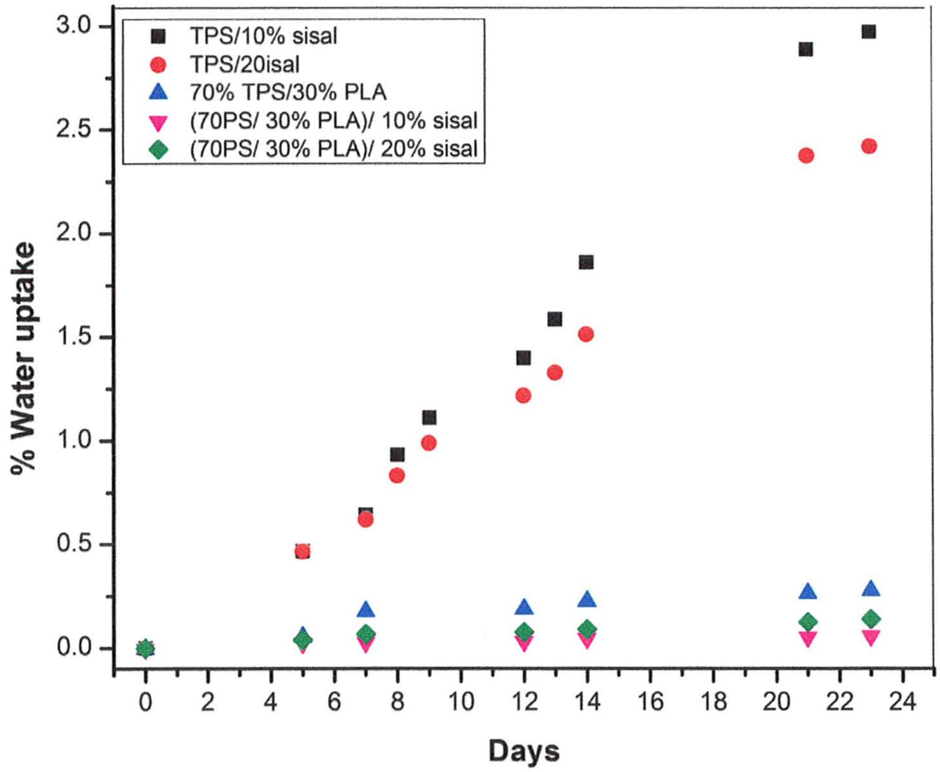


Figure B 4 Water uptake of TPS, and TPS/PLA, and TPS reinforced with sisal with 2 % paraffin wax at 75% RH

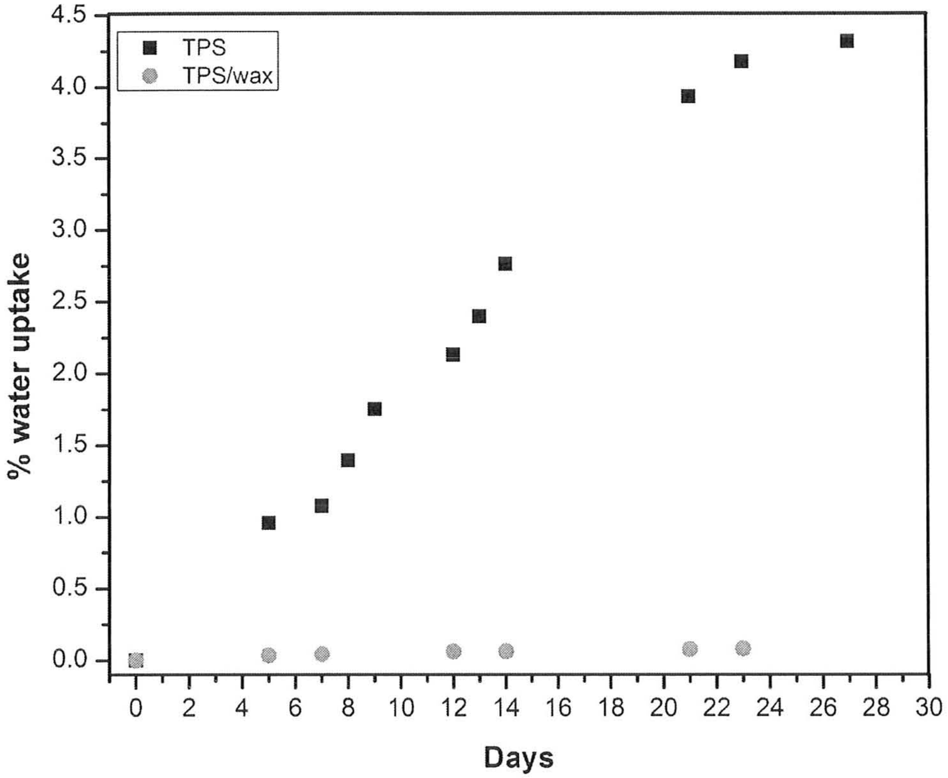


Figure B 5 Water uptake of TPS, and TPS blended with 2 % paraffin wax at 75% RH

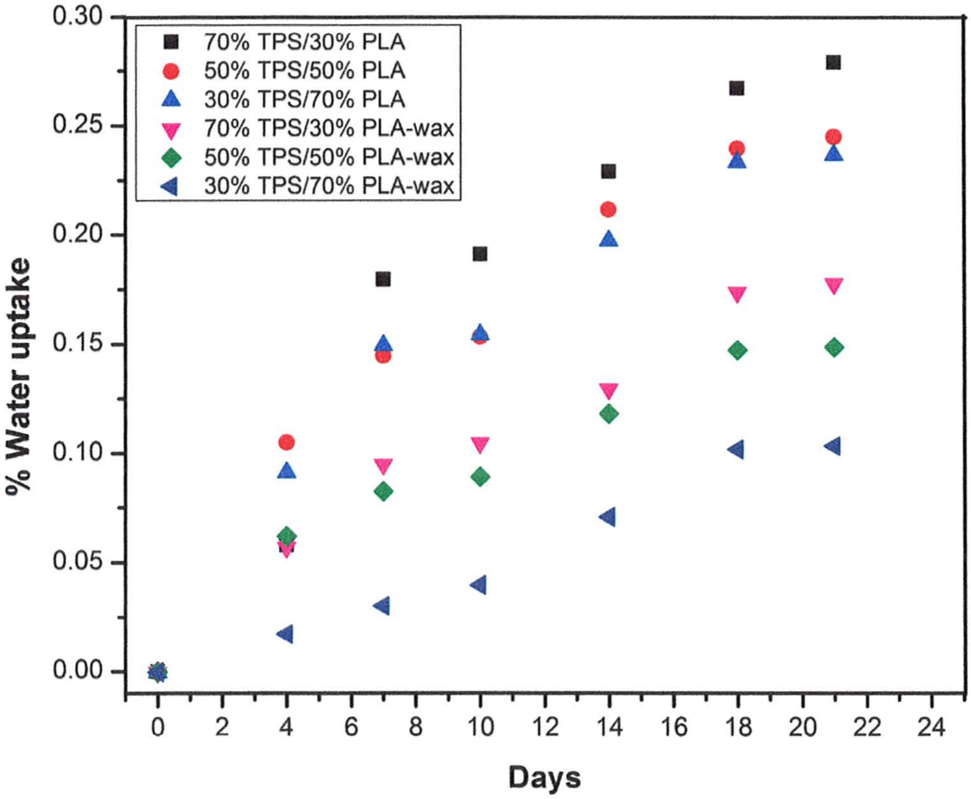


Figure B 6 Water uptake of TPS/PLA, and TPS/PLA blend with 2 % paraffin wax at 75% RH

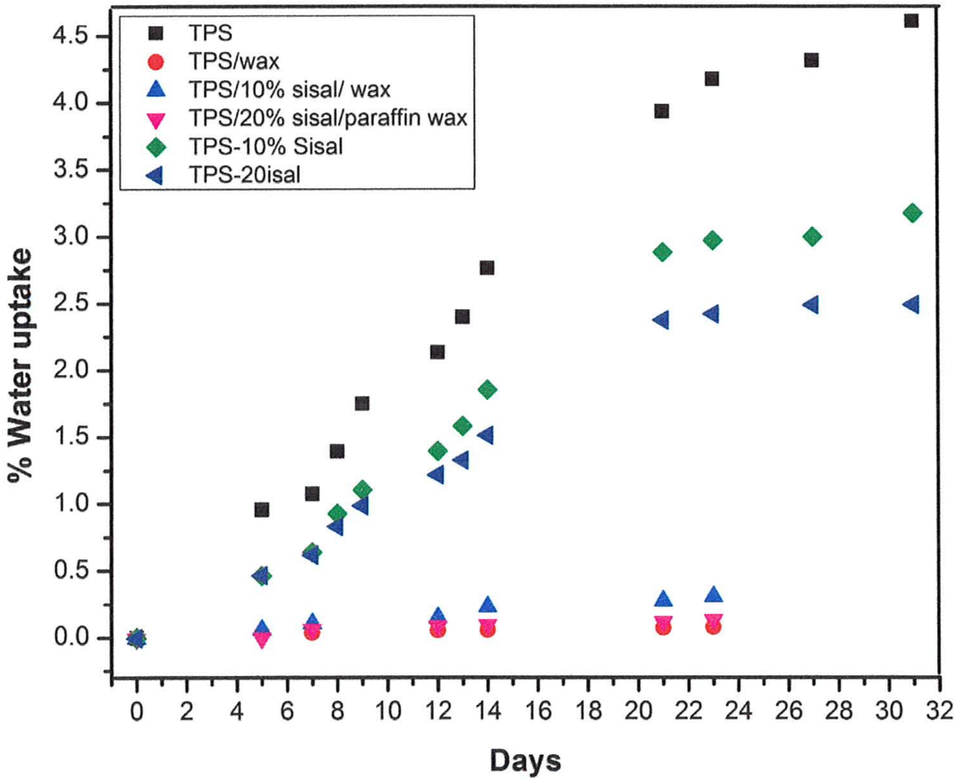


Figure B 7 Comparison between the water uptake of TPS/sisal composites, and their blends with 2 % paraffin wax at 75% RH

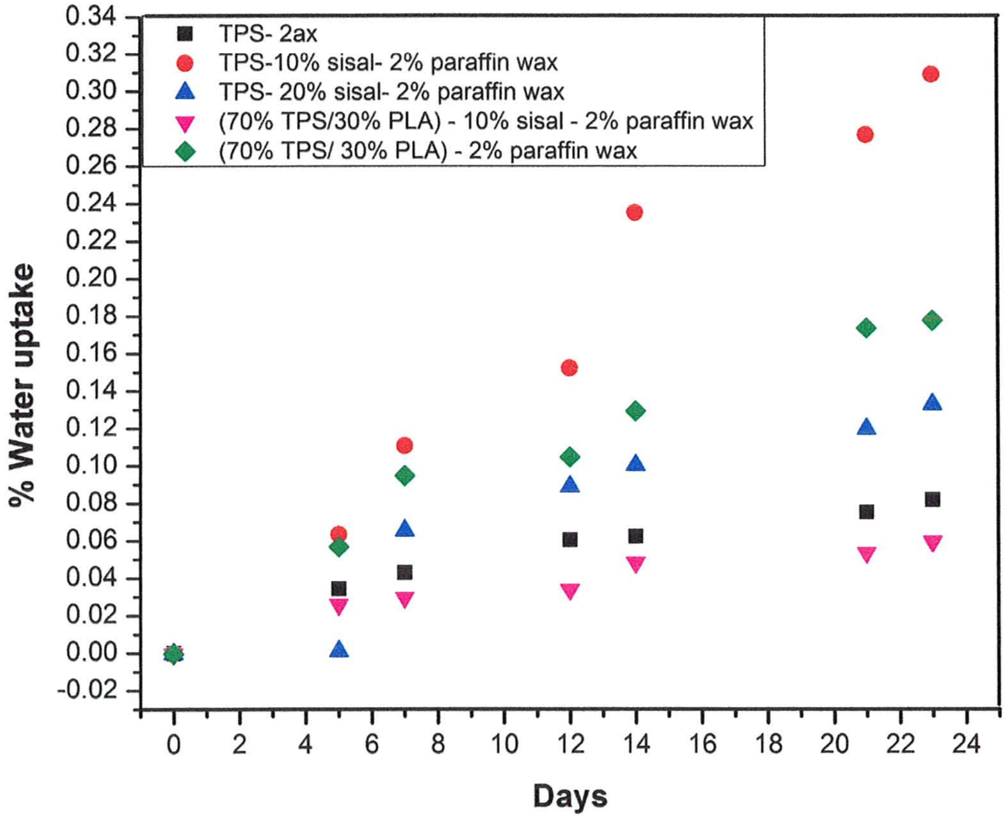


Figure B 8 Comparison between the water uptake of TPS blends, and their blends with 2 % paraffin wax at 75% RH

Appendix C

Water vapour transition properties of TPS blends

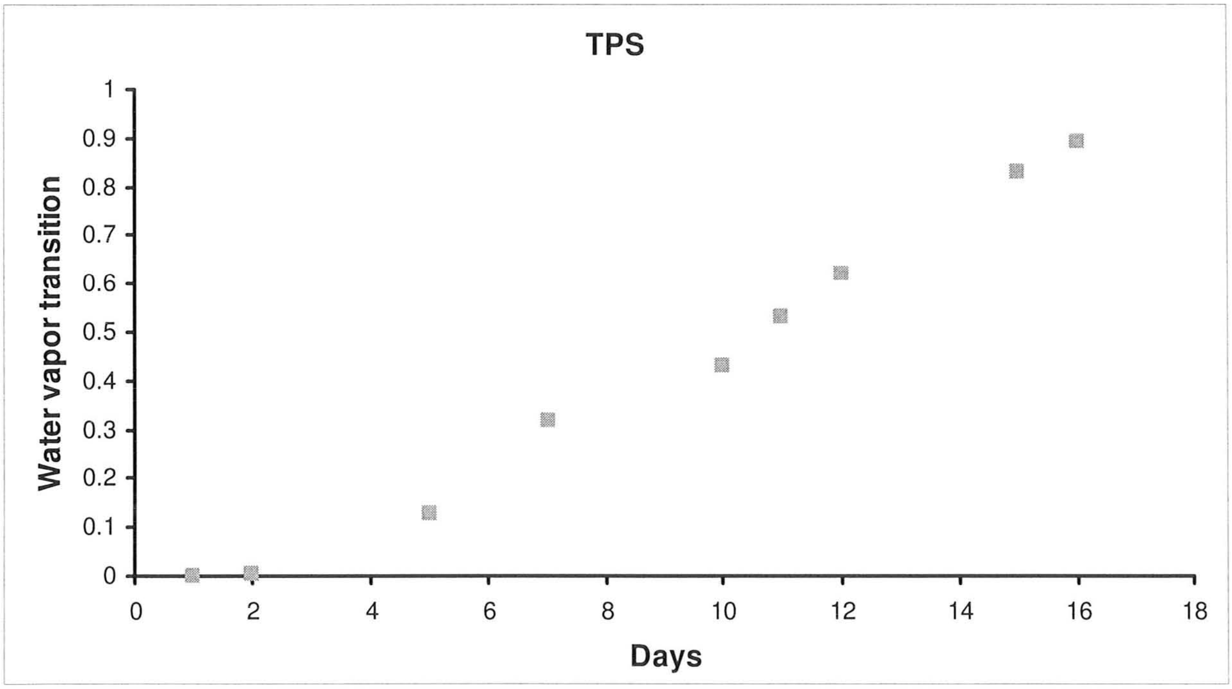


Figure C 1 Water vapor transition of TPS at room temperature from a cylender test container (cup mouth diameter, 1.5 cm)

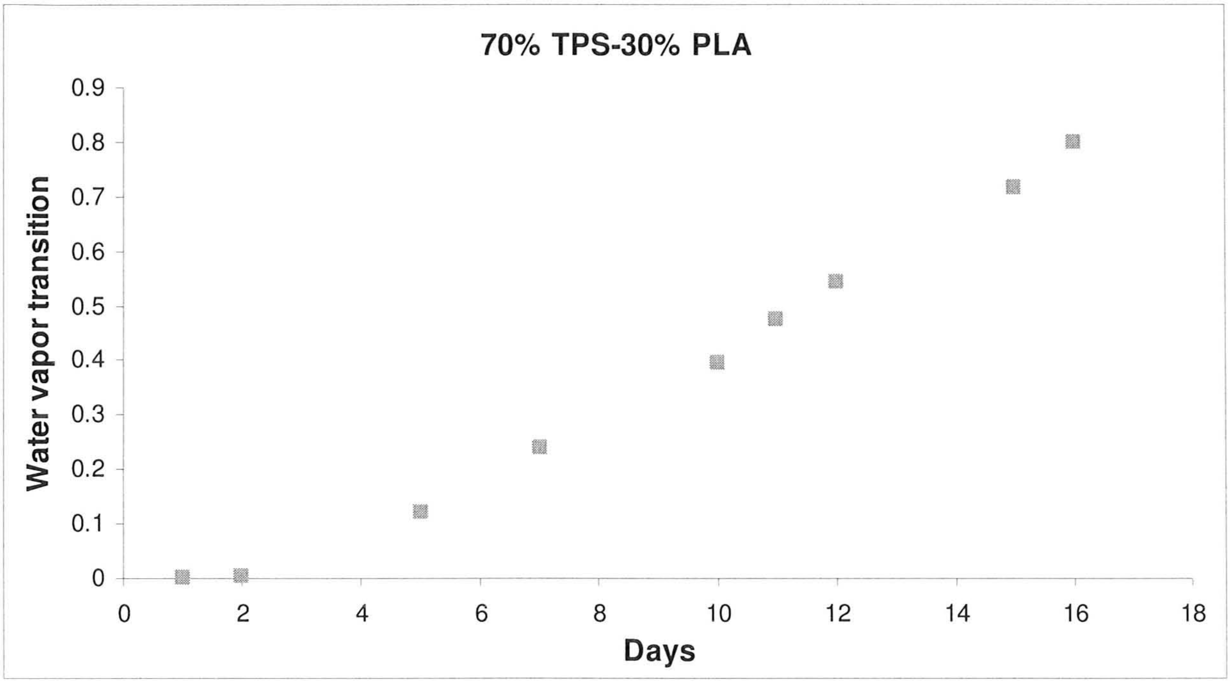


Figure C 2 Water vapor transition of TPS/PLA blend at room temperature from a cylinder test container (cup mouth diameter, 1.5 cm)

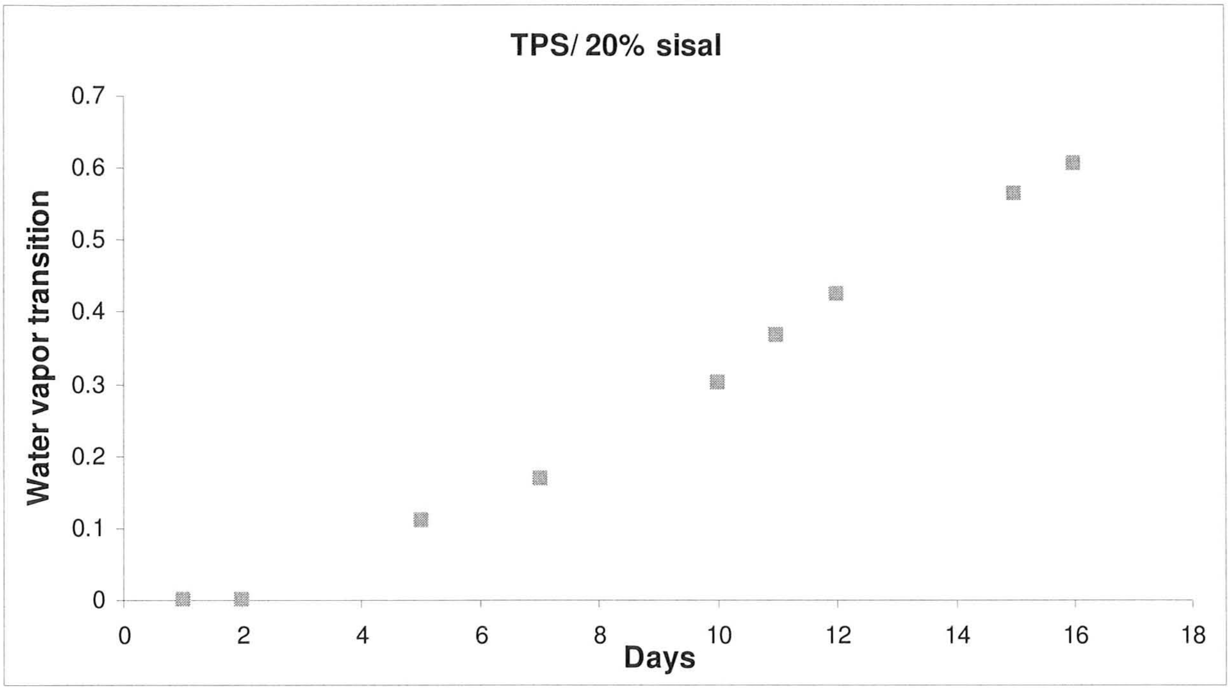


Figure C 3 Water vapor transition of TPS reinforced with 20% sisal fiber at room temperature from a cylinder test container (cup mouth diameter, 1.5 cm)

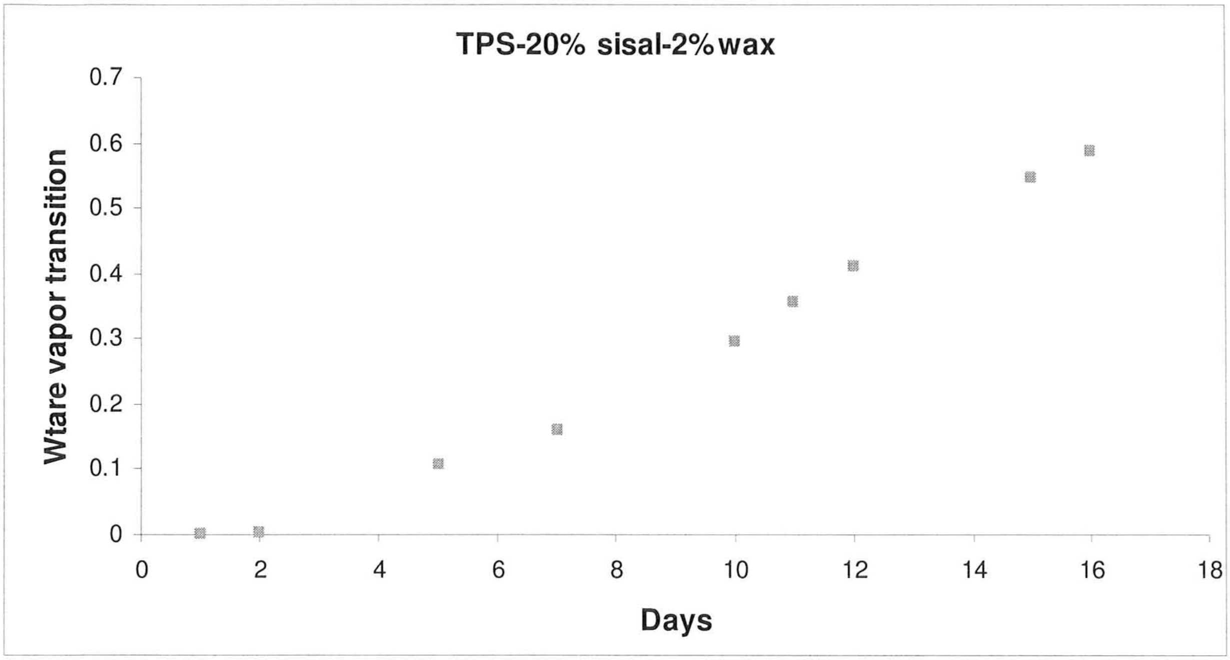


Figure C 4 Water vapor transition of TPS reinforced with 20% sisal fiber blended with 2% paraffin wax at room temperature from a cylinder test container (cup mouth diameter, 1.5 cm)

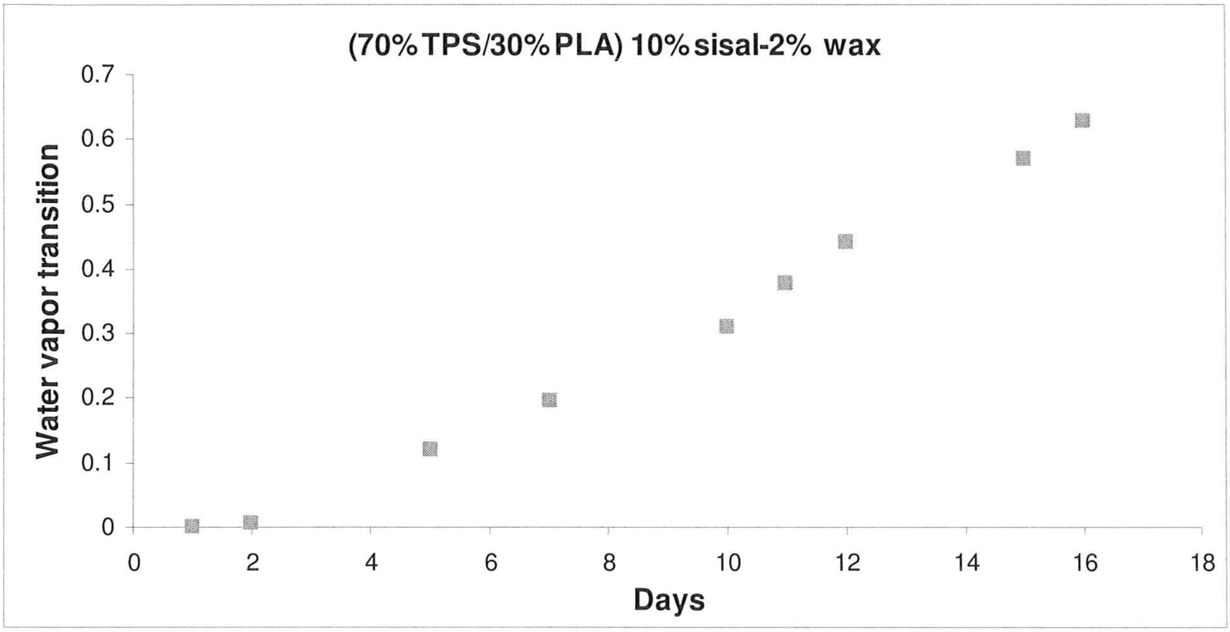


Figure C 5 Water vapor transition of TPS/PLA reinforced with 10% sisal fiber blended with 2% paraffin wax at room temperature from a cylinder test container (cup mouth diameter, 1.5 cm)

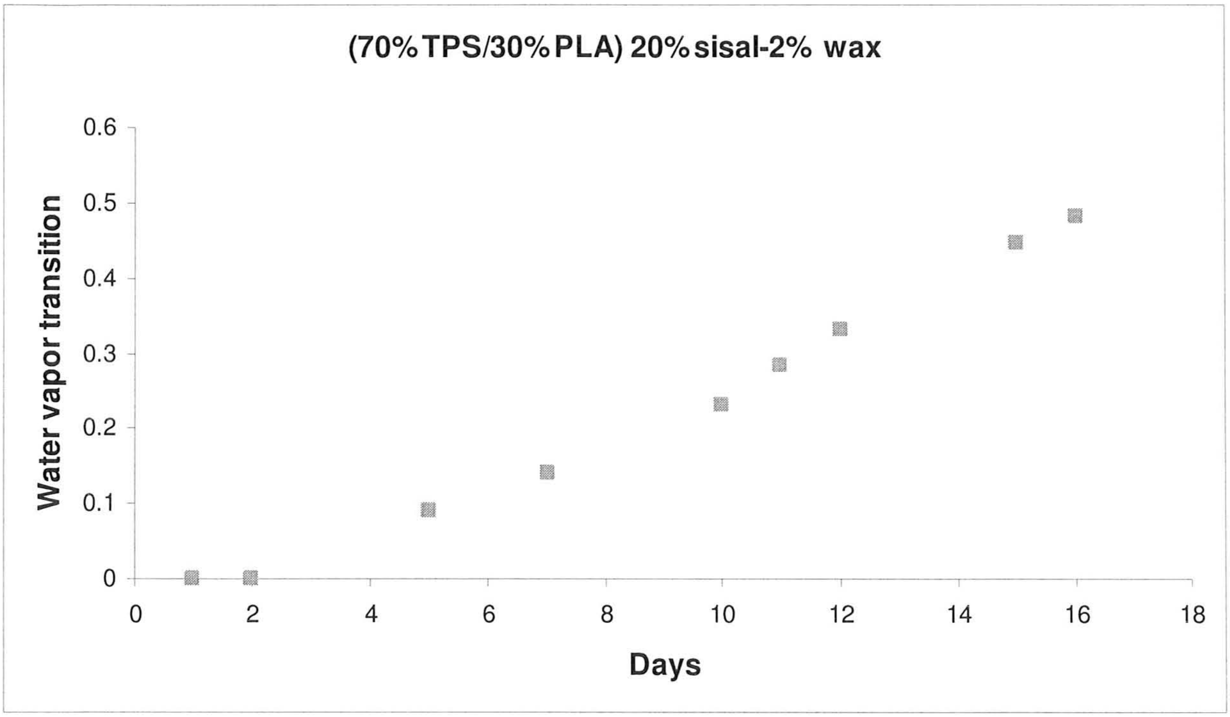


Figure C 6 Water vapor transition of TPS/PLA reinforced with 20% sisal fiber blended with 2% paraffin wax at room temperature from a cylinder test container (cup mouth diameter, 1.5 cm)

Appendix D

Comparison the mechanical properties of the blends with Solanyl

Solanyl biodegradable plastic is a bio-based, renewable plastic resins. Solanyl resins are mainly made out of potato starch. Solanyl as a commercial product available in the market is being used for short life, disposable products such as packaging, plant pots or disposable cutlery. To make a comparison between our final samples and a commercial product, Solanyl has been chosen as the reference and its mechanical and water resistance properties were compared with ours.

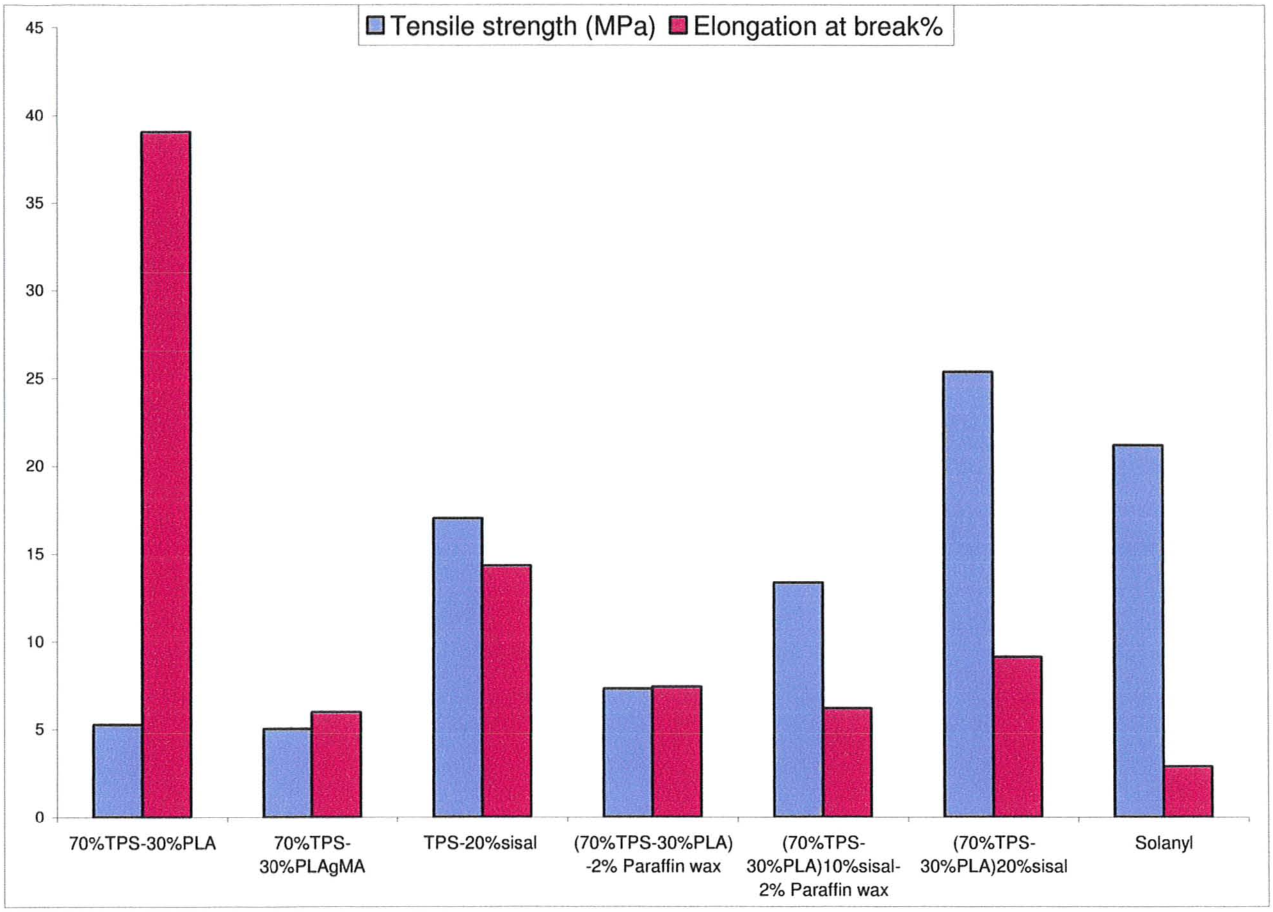


Figure D 1 A comparison between the tensile strength and elongation of Solanyl and of our TPS based samples

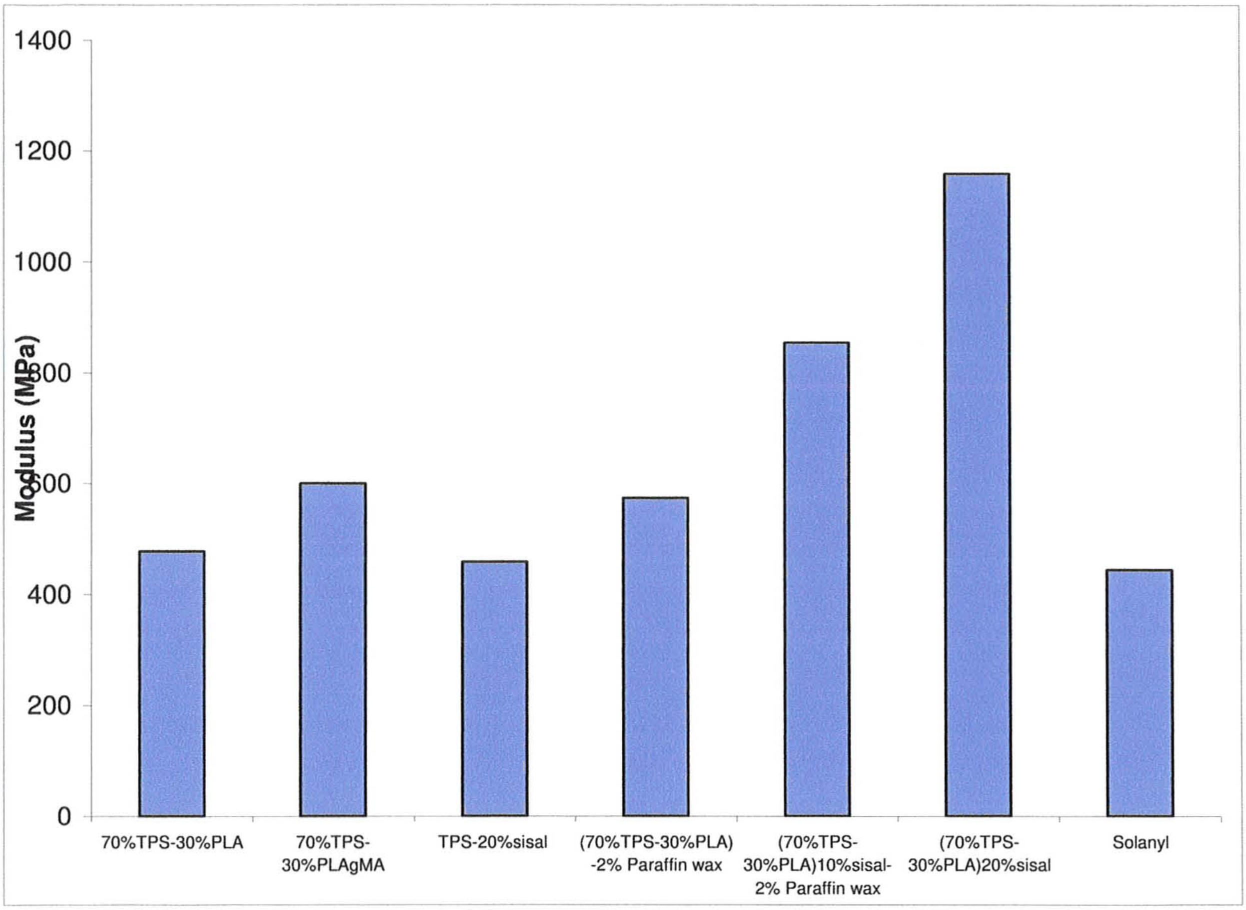


Figure D 2 Comparison between the Young's modulus of Solanyl and our TPS based samples

A comparison of the mechanical properties between our selected PS based samples and Solanyl materials, show that almost all the selected samples, in terms of elastic modulus, are even better than Solanyl products. In terms of tensile strength and elongation at break, we obtained some samples which are pretty close to the Solanyl products.

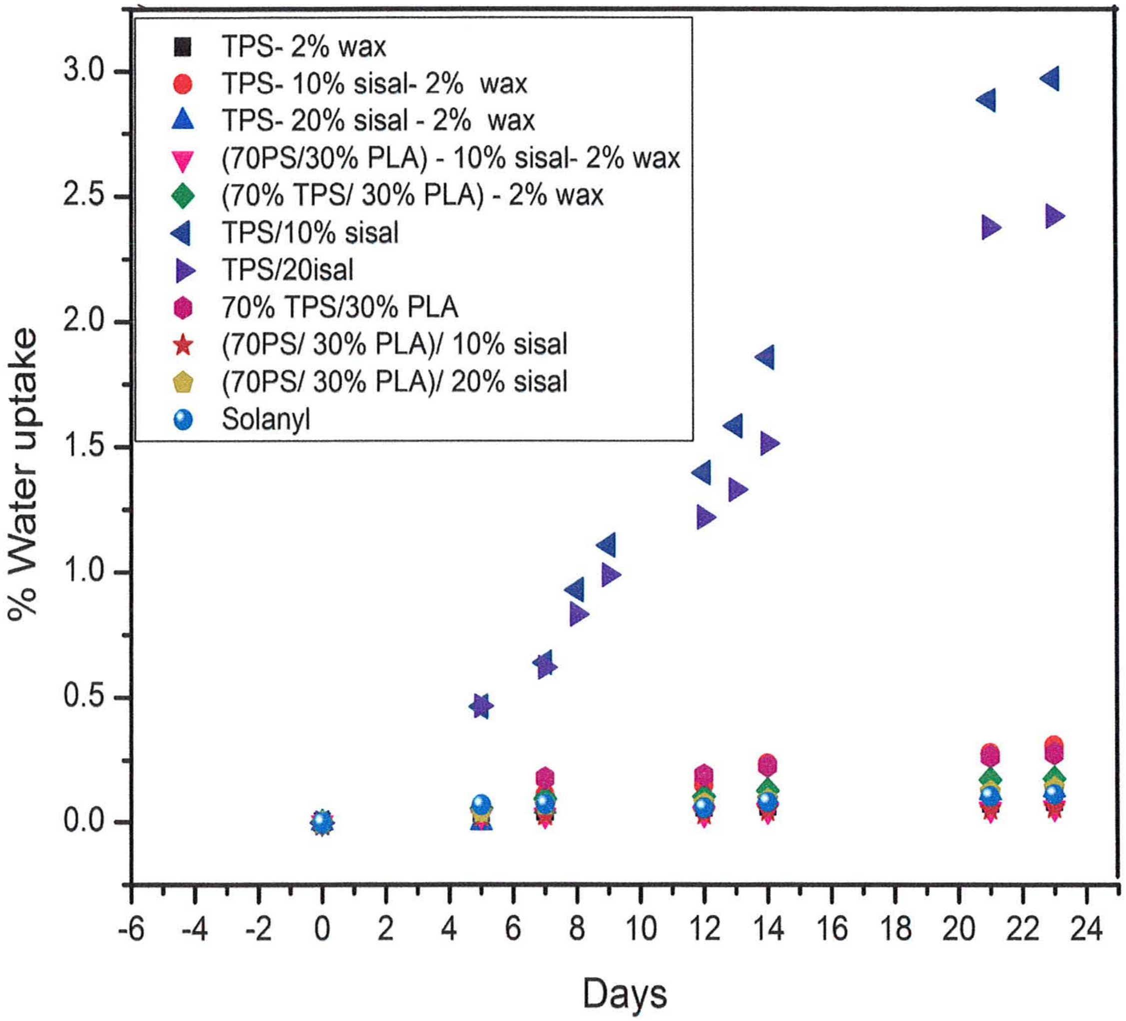


Figure D 3 Comparison between the water uptake of Solanyl and of our TPS based samples

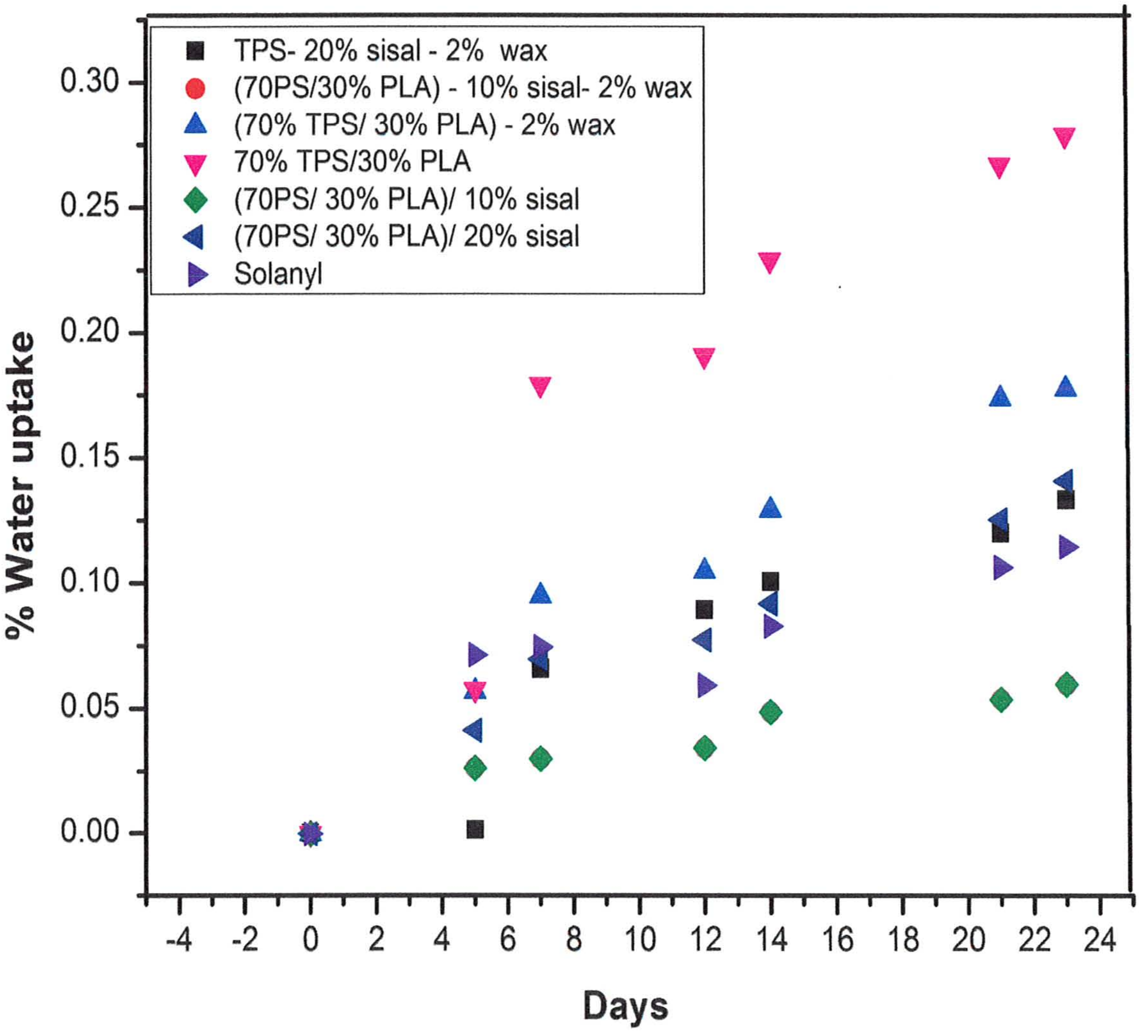


Figure D 4 Comparison between the water uptake of Solanyl and of our TPS based samples

Appendix E

Table E1 Physical and Mechanical properties of LDPE

Physical	**LDPE**
Density (g/cm^3)	0.92
Water uptake per 24 hrs (%)	≤0.01
Contact angle degree (°)	77
Mechanical	
Tensile Strength (MPa)	12.4-15.2
Elastic Modulus (MPa)	200-400
Elongation at Break (%)	600-650