PROPERTIES OF

THERMOPLASTIC STARCH/POLY (LACTIC ACID) BLENDS

PROPERTIES OF
THERMOPLASTIC STARCH/POLY (LACTIC ACID) BLENDS

By

YU QING BAI

A Thesis

Submitted to the School of Graduate Studies

In Partial Fulfillment of the Requirements

For the Degree

Master of Applied Science

McMaster University

MASTER OF APPLIED SCIENCE (2007) McMaster University

(Chemical Engineering) Hamilton, Ontario

TITLE: Properties of Thermoplastic Starch/Poly (lactic acid) Blends

AUTHOR: Yu Qing Bai

B. Eng. (Qingdao University of Science &Technology)

SUPERVISOR: Dr. Andrew Hrymak

Dr. Qiang Liu

NUMBER OF PAGES: xix; 152

Abstract

Properties of plasticized thermoplastic corn and pulse starches and their blends with poly (lactic acid) (PLA) were studied. Water and glycerol acted as plasticizer components for a ratio of starch/glycerol/water (wt/wt) fixed at 50/36/14 based on previous studies. PLA was used in blends to improve the properties of thermoplastic starch (TPS). Maleic anhydride (MA) was used as a coupling agent to increase the miscibility of PLA and TPS phases. Cloisite 30B, a type of organoclay, was added into the material system to improve the properties of blends. In order to enhance the hydrophobicity, alkyl ketene dimmer (AKD), used as a sizing agent, were introduced to material system. Both internal and surface sizing methods were applied.

Measurements of rheological and mechanical properties were performed on a Rosand capillary rheometer and Instron tensile testing machine. The thermal and morphological properties of blends were characterized using differential scanning calorimetry and scanning electron microscopy. The contact angles were measured using a goniometer equipped with a video camera and a computer with drop shape analysis software for calculating the contact angles.

The use of maleic anhydride as a coupling agent significantly improved the tensile strength and modulus of blends and the blend morphologies were more homogeneous. Improvements in tensile strength and modulus were achieved as Cloisite 30B nanoclay was used as a filler in TPS/PLAgMA blends. Some hydrophobicity was obtained for blends with Cloisite 30B. Blends of TPS/PLAgMA/clay showed shear-thinning behaviors at 150° C. .

ACKNOWLEDGEMENTS

I would like to express my most sincere thanks to:

Dr. Andrew Hrymak, my supervisor, his guidance and encouragement provided extremely helpful to this study.

Dr. Qing Liu, my co-supervisor, for his guidance and many helpful discussion and advices in this research project.

Ms. Elizabeth Takacs, lab manager of MMRI, for her training in experimental equipments and her assistance and discussion in experimental procedures.

Dr. Hyun-Jung Chung, postdoctoral fellow in Agriculture Agri-food Canada, for his training on DSC and discussions on DSC thermograms.

Jinling Liu, for her helpful discussion on thermal properties of polymer.

My wife, Li Hua Wang, and my son, Luke Bai, for their supports and encouragements.

The partially financial support from Agriculture and Agri-Food Canada for this research project is deeply appreciated

Table of Contents

PAGE

List of Figures

List of Tables

Nomenclature

AAC	aliphatic-aromatic copolyesters
AKD	alkyl ketene dimmer
ASA	alkenylsuccinic anhydride
ASTM	American Society for Testing and Materials
ATC	Acetyl triethy citrate
DIH	diisocyanatohexane
DSC	differential scanning calorimetry
HAS	high amylose cornstarch
HIPS	high-impact polystyrene
IPD	isoporone diisocyanate
LDPE	low-density polyethylene
MA	maleic anhydride
MDI	methylenediphenyl diisocyanate
MMT	montmorillonites
Mw	molecular weight
Na	natural sodium
NH	natural hectorite
NS	normal cornstarch
PBAT	poly (butylenes adipate terephthalate)
PBSA	polybutylene succinate adipate

PCL	polycaprolactone
PE	polyethylene
PEA	poly (ester amide)
PEG	poly (ethylene glycol)
PET	polyethylene terephthalate
PHAs	polyhydroxyalkanoates
PHB	Polyhydroxybutyrate
PHBV	poly (hydroxybutyrate-co-valerate)
PHH	polyhydroxyhexanoate
PHV	polyhydroxyvalerate
PLA	poly (lactic acid)
PLAgMA	poly (lactic acid) grafted maleic anhydride
n	power law index
PP	polypropylene
PPG	poly (propylene glycol)
PS	polystyrene
PVC	polyvinyl chloride
SEM	scanning electron microscope
$\dot{\gamma}$	shear rate, s^{-1}
η	shear viscosity, Pa.s
m	consistency index, $Pa.s^n$
ΔH_m	enthalpy of fusion, J/g

χ_c:	crystallinity, %
T_c	crystallization temperature, °C
TDI	toluene diisocyanate
T_g	glass transition temperature, °C
T_m	melting temperature, °C
TPS	thermoplastic starch
WS	waxy cornstarch
wt	weight percentage, %
WVTR	water vapor transmission rate, $g/m^2/day$

CHAPTER 1

INTRODUCTION

1.1 Background

In recent years, the environmental problem of solid waste disposal has become an important issue due to the huge amount of non-biodegradable waste stored in landfills. Most of today's synthetic polymers are produced from petrochemicals and are not biodegradable. These persistent polymers are a significant source of environmental pollution when they are dispersed in nature. Biopolymer materials derived from renewable resources have been studied by many researchers because of the material biodegradability. Nowadays, much interest has been focused on three major groups of biodegradable plastics: polylactide (PLA), polyhydroxybutyrate (PHB) and starch-based polymers.

Starch, a completely biodegradable polymer, is available in large quantities from renewable plant sources such as the seeds of cereal grains (corn, wheat and rice), tubers (potato), pulse (bean, pea and lentil) and the pith of tapioca palm (Swinkels, 1985). However, in practice, the applications of thermoplastic starch as a possible alternative to replace petroleum-based polymers are limited by its drawbacks of water sensitivity and poor mechanical properties.

Native starches can be blended with some plasticizers to form thermoplastic starches (TPS) under the influence of heat and shear in a batch mixer. The properties of TPS have been widely studied (Stepto, 2003; Funke et al, 1998; Soest et al, 1996). In order to improve the properties of TPS, some researchers attempted to blend TPS with some high performance biodegradable polymers such as polycaprolactone (PCL) (Averous et al, 2000), poly (lactic acid) (PLA) (Martin and Averous, 2001) and polyamide (Averous et al, 2000).

Poly (lactic acid (PLA) is a linear and biodegradable aliphatic polyester derived from renewable resources such as cornstarch and sugarcane. As a high performance synthetic biopolymer, PLA has been attractive for disposable and biodegradable plastic substitutes due to its better mechanical properties (Table 1.1). However, PLA is still more expensive than the petroleum-based synthetic plastics and the degradation rate is still slow as compared to the waste accumulation rate (Ray et al, 2003). To overcome these drawbacks, PLA can be blended with starch to increase biodegradability and reduce costs (the costs of starch and PLA were shown in Table 1.2). Nevertheless, some drawbacks of TPS/PLA blends still limit their usage in many applications.

This research work is focused on the improvement of properties of starch/PLA blends. In this thesis, two different source starches are applied. Various types of starches with different amylose content are plasticized by water and glycerol. Maleic anhydride (MA) is used as the coupling agent to increase the miscibility of PLA and starch. The effects of nanoclay on the properties are investigated. The morphological properties, rheological properties, mechanical properties, water absorption and barrier properties of mixture are evaluated.

Table 1.1 Physical and mechanical properties of poly (lactic acid) (PLA) (Martin and Averous, 2001)

	Density	T_m (°C)[b]	T_g (°C)[c]	Modulus (MPa)	Elongation at break (%)	Tensile stress at break (MPa)	Biodegradation mineralization (%)[d]	WVTR[e]
PLA[a]	1.25	152	58	2,050	9	/	100	172

[a] PLA Dow-Cargill (Nature works)
[b] T_m: Melting temperature from DSC measurements
[c] T_g: Glass transition from DSC measurements
[d] At 60days in controlled composting according to ASTM 5336
[e] WVTR: Water Vapor Transmission Rate at 25°C, unit: g/m^2/day

Table 1.2 Costs of starch and PLA (National Starch &Chemical, 2005)

	Content	Cost (CA$/kg)	Trademark	Manufacturer
HAS	70wt% amylose	2.74	Hylon VII	National Starch &Chemical
NS	23wt% amylose	0.60	MELOJEL	National Starch &Chemical
PLA	\	24.00	4042D	Cargill Dow LLC

HAS: high amylose cornstarch
NS: normal corn starch

1.2 Research Objectives

The objective of this project was to develop a new type of biodegradable packaging material using starch-based thermoplastics. The major works in this thesis were the improvement and enhancement of properties of corn starch/PLA blends based on the results of the previous work. The second objective is to investigate the properties of three types of pulse starches blended with PLA to improve the properties of their blends by using additives and optimizing the processing conditions. The overall work in this thesis is addressed as the following:

- Improve the miscibility of starch and PLA using interfacial modification methods by means of grafting maleic anhydride (MA) onto PLA.
- Enhance the mechanical properties of thermoplastic starch (TPS) and PLA grafted MA (PLAgMA) blends by employing nanoclay into the material system.
- Estimate the effects of nanoclay on the thermal, rheological, morphological and mechanical properties.
- Improve the hydrophobicity of TPS/PLAgMA blends using internal and surface sizing methods
- Investigate the properties of pulse (bean, pea and lentil) starches according to the same methods as cornstarches.

1.3 Outline of Thesis

The following chapters outline the framework of research in this thesis.

Chapter 1 has presented the brief introduction to the background and importance of this project; the objectives and the brief structure of this thesis. An introductory overview with the relevant background information is described in Chapter 2. In this chapter, previous work on starch-based polymers is summarized and some additives used to improve the properties of starch/PLA are introduced.

The experimental procedure is presented in Chapter 3. Designs of experiments, descriptions of apparatus, preparations of samples and conditions of processing are depicted in this chapter. The results and discussions are shown in Chapter 4. The experimental data are analyzed and the structures and properties of thermoplastic starch and PLA blends with nanoclay are presented in this chapter. The conclusions are shown in Chapter 5. Finally, some possible future work related to this project is presented in Chapter 6.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Biodegradable Polymer

"Biodegradable", as per the definition of American Society for Testing and Materials (ASTM), is "capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds or biomass in which the predominant mechanism is the enzymatic action of microorganisms" (ASTM D-5488-584d, ASTM Publications).

Biodegradable polymer is a polymer that can be decomposed to CO_2, H_2O, CH_4 and other low molecular-weight products under the influence of microorganisms in both aerobic and anaerobic conditions (Ratner et al, 1996). All residuals after decomposition should be nontoxic in environmental assessments and also should be incorporated into a natural cycle (Williams, 1987).

Table 2.1 Classification of biodegradable polymer (Ikada and Tsuji, 2000)

Natural polymers		Synthetic polymers	
Sub-classification	Examples	Sub-classification	Examples
1. Plant origin		1. Aliphatic polyesters	
1.1 Polysaccharides	Cellulose, Starch, Alginate	1.1 Glycol and dicarbonic acid polycondensates	Poly(ethylene succinate) Poly(butylene terephthalate)
2. Animal origin		1.2 Polylactides	Polyglycolide, Polylactides
2.1 Polysaccharides	Chitin (Chitosan), Hyaluronate	1.3 Polylactones	Poly(e-carpolactone)
		1.4 Miscellaneous	Poly(butylene terephthalate)
2.2 Proteins	Collagen (Gelatin), Albumin	2. Polyols	Poly(vinyl alcohol)
3. Microbe origin		3. Polycarbonates	Poly(ester carbonate)
3.1 Polyesters	Poly(ε-hydroxyalkanoate)		
3.2 Polysaccharides	Hyaluronate	4. Miscellaneous	Polyanhydrides, Poly(a-cyanoacrylate)s, Polyphosphazenes, Poly(orthoesters)

Biodegradable polymers are formed in nature during the growth cycles of all organisms or are synthesized from monomers under the controlled conditions. Depending on the sources of biodegradable polymers, polymers can be classified as natural or synthetic polymers as illustrated in Table 2.1. Of them, starch is a type of naturally synthetic polysaccharide.

2.1.1 Biodegradable Starch-based Polymers

Starch, a natural and biodegradable polymer, is composed primarily of amylose (poly-α-1, 4-D-glucopyranoside) and amylopectin (poly-α-1, 4-D-glucopyranoside and poly-α-1, 6-D-glucopyranoside). In addition to amylose and amylopectin, it also contains some minor components such as proteins, lipids, inorganic substances and nonstarch polysaccharides (Liu, 2005). However, the properties of starch are dominated by the major components of amylose and amylopectin.

Starch was first introduced into the plastic industry as filler to be blended with more expensive polymers for economic reasons due to its availability and low cost. In some cases, starch could also strengthen the mechanical modulus of a composite. As is well known, natural starch can be biodegraded in the water and soil. So more and more researchers became interested in its biodegradability and its use as a substitute for petroleum-based polymers. Starch has also been used more extensively to blend with thermoplastics, such as low-density polyethylene (LDPE) (Arvanitoyannis et al, 1998; St-Pierre et al, 1997; Rodriguez-Gonzalez et al, 2003), polypropylene (Liu et al, 2003;

Bagheri, 1999) and polystyrene (De Graaf and Janssen, 2001). However, these blends cannot be used as biodegradable plastics because of their nonbiodegradable synthetic-polymer components.

During the past decade, considerable effort has gone into totally biodegradable starch-based plastics. Dry starch in granule form exhibits poor flowability and processibility, but plasticized starch, called “thermoplastic starch (TPS)”, has good processibility, flexibility and stretchability similar to conventional polymer melts. Also TPS can be processed through traditional polymer-processing methods such as extrusion, injection and blow molding (Funke et al, 1998; Halley et al, 2001). Melted thermoplastic materials are obtained under the combined conditions of shearing, temperature and plasticization during extrusion and then the materials can be transformed by means of thermoforming and injection molding (Averous and Fringant, 2001).

Unfortunately, plasticized starch is highly hydrophilic and readily disintegrates on contact with water. The higher the starch content, the higher the hydrophilicity. To overcome these drawbacks and maintain their biodegradability, one strategy is to blend TPS with the other biodegradable polymers with higher property performance, as the starch has free hydroxyl groups that readily undergo reactions such as acetylation, esterification and etherification. The polymers used in the blend of TPS are usually aliphatic polyesters such as polycaprolactone (PCL) (Averous et al, 2000), poly (lactic acid) (PLA) (Martin and Averous, 2001), poly (hydroxybutyrate-co-valerate) (PHBV)

(Kotnis et al, 1995), poly (ester amide) (PEA) (Martin et al, 2001 and Averous et al, 2000). In some cases, an aromatic polyester like poly (butylenes adipate terephthalate) (PBAT) (Martin et al, 2001; Averous and Fringant, 2001) can also be used for property improvement.

Applications of thermoplastic starch include film (such as shopping bags) over wrap, and mulch film. Foam loose fill packaging and injection molded foam products, such as take-away containers, are also applications. Foamed polystyrene has been identified as a target product to be substituted by starch-based foam (Cinelli et al, 2006)

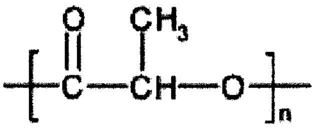
2.1.2 Biodegradable Polyesters

Polyesters play a predominant role as biodegradable plastics due to their potentially hydrolysable ester bonds. The polyester family can be classified in two groups based on their molecular structures: aliphatic (linear) polyesters like PLA and aromatic (aromatic rings) polyester like polybutylene adipate/terephthalate (PBAT).

Another important classification of biodegradable polyester is based on the origin. Naturally produced polyesters like PHA are actually synthesized by microbes, with the polymer accumulating in the cells of microbes in the growing period. Synthetic polyesters are polymerized from monomers under certain conditions similar to synthetic aliphatic polyesters synthesised from diols and dicarboxylic acids via condensation polymerisation. Both PCL and PBS are synthetic aliphatic polyesters.

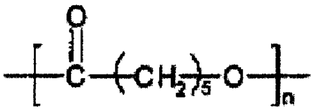
Polyester also can be divided into two types – renewable polyester and nonrenewable polyester. In the biodegradable polyester family developed commercially, some polyesters are renewable such as poly (lactic acid) (PLA), polyhydroxyalkanoates (PHAs), polyhydroxybutyrate (PHB), polyhydroxyvalerate (PHV), and polyhydroxyhexanoate (PHH); and some are nonrenewable like aliphatic-aromatic copolyesters (AAC), polybutylene adipate/terephthalate (PBAT), polybutylene succinate (PBS), polycaprolactone (PCL), polybutylene succinate adipate (PBSA) etc.

Averous (2004) classified biodegradable polyesters in two groups: agro-resources based polyester and petroleum-based polyester. PLA and PHAs are examples of two agro-resources based polyesters; PCL and PEA belong to the group of petroleum-based polyesters. The chemical structures of typical polyesters are shown in Figure 2.1.



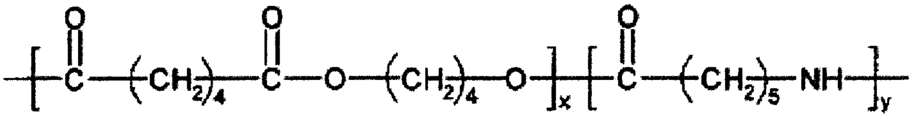
$$\left[-\overset{\overset{O}{\|}}{C}-\overset{\overset{CH_3}{|}}{CH}-O- \right]_n$$

Poly (lactic acid) (PLA)



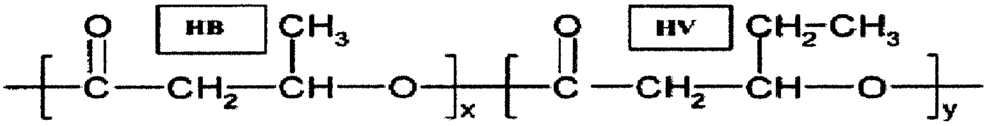
$$\left[-\overset{\overset{O}{\|}}{C}-(CH_2)_5-O- \right]_n$$

Poly caprolactone (PCL)



$$\left[-\overset{\overset{O}{\|}}{C}-(CH_2)_4-\overset{\overset{O}{\|}}{C}-O-(CH_2)_4-O- \right]_x\left[-\overset{\overset{O}{\|}}{C}-(CH_2)_5-NH- \right]_y$$

Polyesteramide (PEA)



$$\left[-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{CH_3}{|}}{CH}-O- \right]_x\left[-\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{CH_2-CH_3}{|}}{CH}-O- \right]_y$$

Polyhydroxyakanoate: Poly(hydroxybutyrate-co-hydroxyvalerate (PHBV)

Fig 2.1 Chemical structures of typical biodegradable polyesters (Averous, 2004)

Poly (lactic acid) (PLA)

Poly (lactic acid) (PLA) is a linear aliphatic polyester, produced two ways: catalytic ring opening of the lactide group and poly-condensation of naturally produced lactic acid. PLA is a high performance biodegradable polyester. Wang et al (2001) reported that PLA is a crystallized polymer with crystallization temperature (T_c) of 100°C and a glass transition temperature (T_g) of 62°C. The DSC testing results indicate that the melting temperature is located at 175°C. PLA becomes unstable and decomposes when the processing temperature exceeds 220°C. The thermal properties of PLA (Cargill LLC) were investigated by Martin and Averous (2001). The glass transition temperature was reported to be 58 °C and the melting temperature was 152°C. No crystallinity transition is observed. The glass transition temperature (T_g) highly depends on the ratio of two isomers (L-lactic acid and D-lactic acid). PLA derived from L-lactic acid has a high melting point and high crystallinity. PLA is almost a fully amorphous polymer when the L-lactic acid content is lower than 80% (Sinclair, 1996).

PLA exhibits higher tensile strength (68.4 MPa) and modulus (2050 MPa) below T_g, but the elongation is no more than 9.4%. However, plasticized PLA shows good flexibility. The elongation of PLA plasticized by polyethylene glycol ($M_w = 400$) can reach 160% (Martin and Averous, 2001).

Application developments for PLA have generated increasing attention in the past few years. For conventional plastic packaging, flexible film and rigid containers are the largest market for plastic resin consumption. PLA is becoming a growing alternative as a food packaging material in film and container. Auras et al (2003, 2005) studied the physical, mechanical, barrier and compatibility properties of PLA and its blends with 40% recycled content from industrial trimming process (for the purpose of lowering the cost) and pointed out that PLA and its blends exhibited the similar performance to polystyrene (PS) and polyethylene terephthalate (PET) for making container for fresh food packaging. As an alternative to HIPS, PVC and cellulosics, PLA is being used in some high-clarity packaging applications such as candy wrap, optically enhanced films, and shrink labels (Mehta et al, 2005)

Table 2.2 Comparisons of physical and mechanical properties of PLA and some conventional polymers*

	Density g /cm^3	T_m (°C)	T_g (°C)	Modulus (MPa)	Elongation at break (%)	Tensile strength (MPa)	Applications
PLA^a	1.25	152^b	58^c	2,050	9	53	Food contact container: tray and planter boxes
LDPE	0.92	110	-100	393	400	11.7	Films
PP	0.905	160	-5	1500	140	34.9	Packaging, durable goods, auto parts, automotive parts
PS	1.05	\	105	3000	6.9	43.9	Packaging, foam sheet, molded parts

^{a}PLA Dow-Cargill (Nature works)

$^b T_m$: Melting temperature from DSC measurements

$^c T_g$: Glass transition from DSC measurements

*: Reference: Martin and Averous, 2001 and Matweb online

Table 2.3 Barrier performances of clear resins (Mehta et al 2005)

Polymer	WVTR[a]	Permeation[b]	
		Oxygen	CO2
PLA	21	40	183
HIPS[c]	10	300-400	NA
Nylon 6	23	3	NA
PET	1	3-6	15-25
PP	0.7	150	NA
PVC	2	5-20	20-50

[a] g-mil/100 in. 2-day

[b] cc-mil/100in. 2-day-atm

[c] High-impact polystyrene

Polyhydroxyalkanoates (PHAs)

PHAs, aliphatic polyesters, were the first biodegradable polyesters to be used in plastics. PHAs can be produced naturally via microbial process on sugar-based media. PHB and PHV are members of the PHA family of polymers.

Aliphatic polymers such as PHAs, and more specially homopolymers and copolymers have been proven to be readily biodegradable (Sudesh et al, 2000). The applications of PHAs are blow and injection-molded bottles and plastic films. However, unlike petroleum-based polymers, the high production cost of PHAs limit their usage.

Polycaprolactone (PCL)

Polycaprolactone (PCL) can be made by the ring-opening polymerization of caprolactone (Albertsson and Varma, 2002). PCL is semicrystalline polyester with a degree of crystallinity of 50%, a low melting point between 58 to 60°C, and a low density of 1.145 g/cm^3 (Ajili and Ebrahimi, 2007). Injection-molded samples show a modulus of 400 MPa and yield stress of 15 MPa (Bastioli et al, 1995). PCL is easy to process by injection molding, film blowing and extrusion.

The applications of PCL are suited for the use of food-contact form trays, loose fill and film bag. But the high cost still limits the wide use for the biodegradation polymer applications for a long time. Cost barriers have been overcome by blending the PCL with the cheaper materials such as cornstarch (Averous et al, 2000).

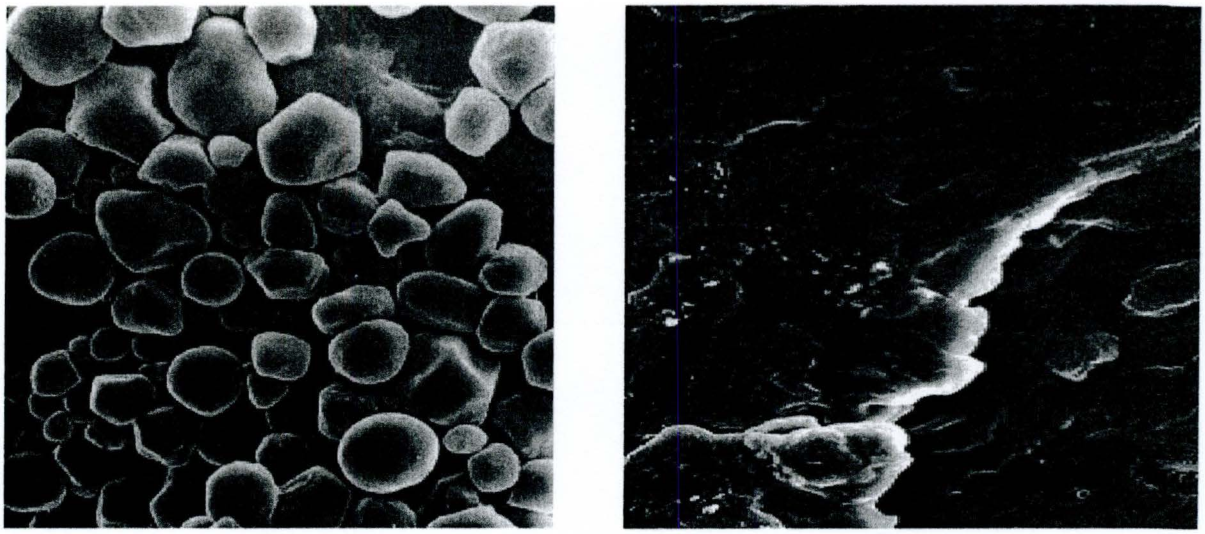
2.2 Thermoplastic Starch/Poly (lactic acid) Blends

2.2.1 Structure and Properties of Thermoplastic Starch

Native starch can be processed into a thermoplastic material in the presence of some plasticizers under the influence of heat and shear. During the process of plasticization, the granules are swelled and disrupted (as illustrated in figure 2.2). Extensive heating in excess water causes swelling and then rupture of starch granules, loss of crystallinity and release of soluble molecules from the granules.

When starch granules are in the presence of water and higher temperatures, gelatinization will take place. Yu et al (2006) proposed two steps in the process of starch gelatinization: firstly, starch swells and amylose and amylopectin leaches from starch granules; secondly, partially hydrated starch crystallites tend to melt at a higher temperature. Their testing results also indicated that shear viscosity is increased in the gelatinization process.

Mechanical properties have been studied by many researchers (Martin and Averous, 2001; Huang, 2005). The mechanical properties of TPS have strong relationships to the starch content and the type and level of plasticizer. The tensile strength and the modulus decrease and elongation increases with starch content decreasing (Martin and Averous, 2001). Huang (2005) reported that the content of amylose in the starch also affects the mechanical properties of TPS. The tensile strength and modulus of TPS with higher amylose content are higher than that of TPS with lower amylose content. But the elongation at the break increases with amylose content decreasing. The effects of plasticizer on the mechanical properties will be discussed in chapter 2.2.3.1.



A B

Figure 2.2 SEM images: (a) native starch; (b) thermoplastic starch (Yu et al, 1996)

2.2.2 Structures and Properties of Thermoplastic Starch and PLA Blends

TPS has some drawbacks, such as water sensitivity and poor mechanical properties, to limit its industrial applications. One of the solutions to overcome these disadvantages is to blend TPS with some hydrophobic polymers with high performance. PLA is one candidate for these biodegradable polymers

Ke and Sun (2000) studied the thermal transition behaviors of PLA and starch/PLA blends by differential scanning calorimetry (DSC). The results indicated that the thermal behaviors of starch/PLA blends are the similar to that of pure PLA. Huang (2005) investigated the thermal properties of three types of thermoplastic cornstarch/PLA blends in presence of plasticizers of water/glycerol, and the results indicated that the blends contained high amylose cornstarch, normal cornstarch or waxy cornstarch have very similar thermal transition behaviors. All results demonstrated that the thermal transitions of starch/PLA or TPS/PLA blends are mainly from the PLA, not the starch. In some cases, the type and level of plasticizer could also change the thermal transition temperature. (Martin and Averous, 2001).

For blends of PLA/starch, the starch content has a dramatic effect on the mechanical properties (Table 2.4). Tensile strength and elongation of the blends decrease as the concentration of starch increases. However, for blends of PLA and starch gelatinized with water/glycerol, the mechanical properties are enhanced and toughness is improved comparing to the blends of PLA/pure starch, since the gelatinization of starch improves the interfacial adhesion between starch and PLA (Park and Im, 2000).

Table 2.4 Mechanical properties of cornstarch and PLA blends (Ke and Sun, 2000)

Blend of Starch/PLA	Tensile Strength (MPa)	Modulus (GPa)	Elongation (%)
0/100	61.0	1.20	6.33
20/80	42.4	1.61	2.90
50/50	32.4	1.63	2.15
70/30	18.9	1.83	1.10

2.2.3 Improvements on Properties of Starch and PLA Blends

Compared to TPS, the mechanical properties and hydrophobicity of TPS/PLA blends are significantly improved; however, the drawbacks of TPS/PLA blends are still obvious especially as the starch content increases beyond 60%. The flexibility, processibility, hydrophobicity, water sensitivity and barrier properties of the blends need to be enhanced further so as to be a suitable packaging material.

2.2.3.1 Plasticizer

Plasticizer, one of the most important classes of plastic additives, can give plastics flexibility, processibility, stretchability and durability because it can reduce the intermolecular force and increase the intermolecular mobility. A good plasticizer should be chemically compatible with the polymer to yield a stable and homogeneous mixture. It also should be nontoxic for the food contact packaging materials. Blends of starch/PLA are usually brittle, having an elongation range of 2 –5% (Ke and Sun, 2001). A plasticizer should be used to improve the elongation and reduce the glass transition temperature of amorphous domains and the melting point of crystalline phase (Loudin et al, 1997).

Acetyl triethy citrate (ATC) is a small citrate ester and commonly used as plasticizer for many polymers. Labrecque et al (1997) reported citrate esters were readily miscible with PLA and effectively improved the elongation. Zhang and Sun (2004) used ATC as plasticizer, which markedly improved the elongation of starch/PLA blends when loading level of ATC was above 8%. But ATC weakens the mechanical behaviors of the blends. Yu et al (1998) reported that the glycerin is a fine plasticizer for starch. Ke and Sun (2001) used glycerol and sorbitol as plasticizers in the starch/PLA material system and reported that glycerol does not improve the elongation of the blend until the concentration exceeds 25% and sorbitol has no effect on flexibility of the blend. Poly (ethylene glycol) (PEG) and poly (propylene glycol) (PPG) are polyethers with low molecular weight and are used widely as plasticizers. PEG has not only a good miscibility with PLA but also it can enhance the flexibility of PLA (Sheth et al, 1997). But PEG and PPG slightly improve the flexibility of the starch/PLA blend than ATC (Ke and Sun, 2001).

Wool and Sun (2005) deem that water and glycerol are the most commonly used plasticizers and water is probably the most important component to change the properties of TPS. Ke and Sun (2001) reported blends containing glycerol have a uniform and smooth morphology and glycerol has a better plasticization effect for starch than other plasticizers. Many researchers have used water and glycerol as plasticizers for starch (Huang, 2005; Sarazin et al, 2005; Averous and Fringant, 2001; Yu et al, 1996)

2.2.3.2 Coupling agents

Blends with immiscible polymers show poor properties due to the low capability of interdiffusion among molecules. Interfacial adhesion plays a vital role in mechanical properties of polymer blends. Normally, blends with high interfacial adhesion are expected to be obtained since higher interfacial adhesion can produce higher mechanical properties (Wool and Sun, 2005). A common way to improve the compatibility and interfacial adhesion between two immiscible polymers is to apply reactive coupling agents into the material system. Coupling agents containing reactive functional groups should be able to react with each polymer in the blends.

Starch and PLA are thermodynamically immiscible due to the higher interfacial tension at the interphase between PLA and starch (Wang et al, 2001). Starch is polyol containing many hydroxyl groups, but PLA is a polyester containing both hydroxyl and carboxylic acid end groups. Potential coupling agents should be chemicals with functional groups, such as –NCO, -COOH and $-NH_2$, which are able to react with both starch and PLA.

Methylenediphenyl diisocyanate (MDI) can improve dramatically the tensile strength from 36.0 MPa to 66.7 MPa as the level of MDI increases from 0 to 5% (Wang et al, 2001). In addition, toluene diisocyanate (TDI), isoporone diisocyanate (IPD), diethylene triamine and 1,6- diisocyanatohexane (DIH) can also enhance the interfacial adhesion and mechanical properties of starch and PLA blend (Jun, 2000). Considering toxicity, these chemicals are not suitable to be additives for food contact packaging materials.

Maleic anhydride (MA) is considered as an effective coupling agent for starch and PLA. The functional group of anhydride can highly react with hydroxyls from starch to form ester linkages in presence of an initiator of Luperox 101 (Vaidya and Bhattarchaya, 1994). Schematically, the reaction is shown in the figure 2.3. Zhang and Sun (2004) reported that a PLA/starch (55/45) composite with 1.0% MA and 10 wt % L101 (MA basis) had a tensile strength of 52.4 MPa and 4.1% elongation, close to neat PLA.

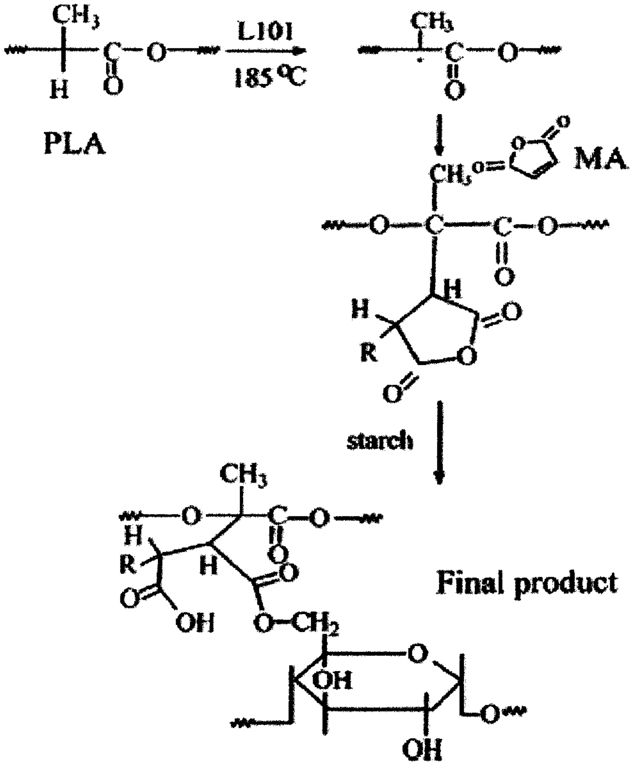


Figure 2.3 Proposed chemical reactions among PLA, starch, MA, and initiator L101 (Zhang and Sun, 2004)

2.2.3.3 Nanocomposite

Polymer/layered silicate nanocomposites have attracted great interest in recent years because these nanocomposites often exhibit remarkable improvements in the material properties, such as modulus, tensile strength and barrier properties, compared with virgin polymer. Normally, three types of nanocomposites could be achieved thermodynamically by melt compounding (shown as figure 2.4) and an exfoliate structure is expected (Alexandre and Dubois, 2000). Exfoliation occurs when the layered clays are substantially expanded and no longer parallel (figure 2.4 c)

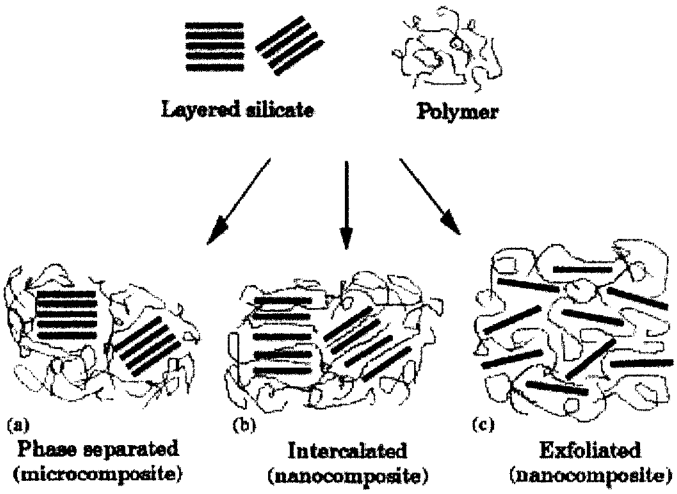


Figure 2.4 Scheme of different types of composite arising from the interaction of layered silicates and polymers: (a) phase separated microcomposite; (b) intercalated nanocomposite and (c) exfoliated nanocomposite. (Alexandre and Dubois, 2000)

Intercalated and exfoliated composites are considered as nanocomposites and the barrier properties of blends are improved when the ultimate structures of nanocomposites are achieved (McGlashan and Halley, 2003; Velzen, 2005).

Thermoplastic starch (TPS) reinforced by clay has been investigated by some researchers. The clays used in these research works are natural and modified clays. Natural sodium montmorillonite (Na-MMT), a kind of hydrophilic clay, readily forms a nanocomposite with TPS (Chen and Evans, 2005). The tensile strength of TPS increased from 2.6 to 3.32 MPa with the presence of 5-wt% Na-MMT (Park et al, 2003). However, unlike Na-MMT, kaolinite is a kind of non-swelling clay and should form a separated phase with starch in the hybrid. The modulus of TPS-Kaolinite composites is lower than that of TPS-Na-MMT composite (Chen and Evans, 2005). Natural hectorite, also a swelling clay, is partially exfoliated with TPS. The modulus of TPS/NH blend is higher than that of TPS/Kaolinite, but lower than that of TPS/Na-MMT. The treated hectorite, obtained via modifying natural hectorite with 2 methyl, 2 hydrogenated tallow quaternary ammonium chloride, is organophilic ammonium-treated clay and the clay particles cannot disperse well in the TPS. So the TPS -treated hectorite blend exhibits low tensile properties and barrier properties (Chen and Evans, 2005).

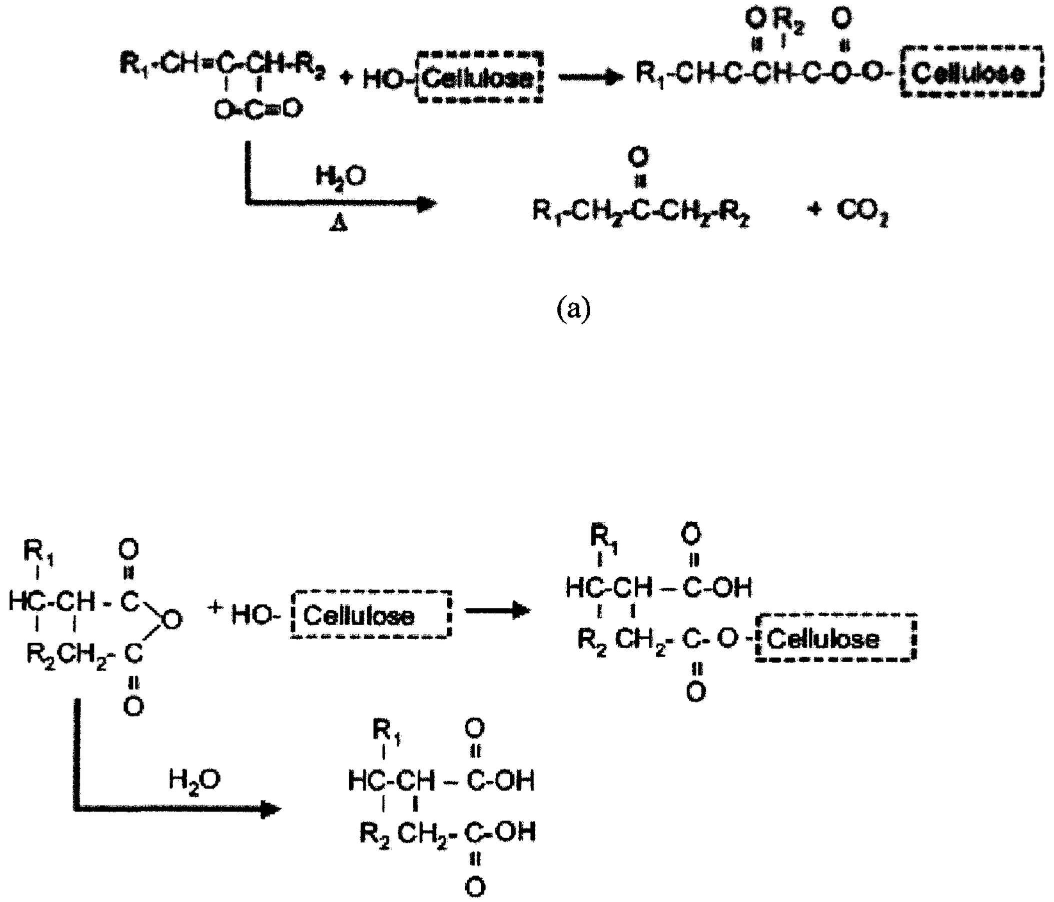
In order to improve the mechanical and barrier properties of TPS/PLA blends, nanoclay is added as one of the components. Cloisite 30B, a product of Southern Clay Co. (USA), is a type of treated-MMT with ammonium cations of methyl tallow bis (2-hydroxyethyl). Pluta et al (2006) pointed out that the blend of PLA/Cloisite 30B can form the structure of nanocomposite. The effects of Cloisite 30B on the properties of TPS/PLA will be investigated in this thesis.

2.2.3.4 Surface Modification and Sizing Agents

The hydrophobicity of TPS/PLA blend is improved significantly compared with TPS due to the hydrophobic PLA. But blends still exhibit the higher level of water absorption (Ke et al, 2003) because of the dominant effect of hydrophilic starch. The key of hydrophobicity enhancement for TPS/PLA blend is achieving more hydrophobicity for starch.

Starch exhibits hydrophilicity because of numerous of polar hydroxyl groups on the molecular chain. Decreasing the amount of hydroxyl groups or changing the structure of hydroxyl group are considered as potential methods to hydrophobize starch. The reaction of silicones with starch, which leads to starch-O-silicone linkages, has been reported (Ueda et al, 1987). Functional silicones bearing pendant amino groups have also been used to hydrophobize starch (Smith, 1985). Brook et al (1997) investigated silicone-modified starch and indicated that it shows very good hydrophobicity.

In the paper industry, sizing agents are usually added to the paper stock to achieve a degree of hydrophobicity (Ravnjak et al, 2007). The key factor for developing sizing properties in paper is the reaction between sizing agent and hydroxyl groups in the cellulose. Alkylketene dimer (AKD) and alkenylsuccinic anhydride (ASA) are widely used as sizing agents in paper industry (Zimmerman and Hercules, 1995). Schematically, reactions AKD and ASA with hydroxyl groups on cellulosic fibre are illustrated in figure 2.5.



(a)

(b)

Figure 2.5 Reactions of (a) Alkylketene dimer (AKD) and (b) alkenylsuccinican hydride (ASA) with hydroxyl groups and water (Zhang et al, 2007)

Like cellulose, the molecular structure of starch also contains numerous hydroxyl groups. The potential reactions could be similar to the cellulose. In this thesis, the effects of AKD on the hydrophobicity are investigated.

CHAPTER 3

EXPERIMENTAL PROCEDURES

3.1 Experimental Materials

Five types of starches were used in this research work. All starches are food grade and contain approximately 11% moisture. The summary of their some characteristics, provided by the manufactures is presented in the Table 3.1.

Table 3.1 Material properties of native starches used in the study

Starch	Manufacturer	Source	Trade Name	Amylose Content
HAS[a]	National Starch &Chemical Company	Corn	HYLON VII	70%
Normal Starch	National Starch &Chemical Company	Corn	MELOJEL	23%
Pea Starch	/	Pea	/	39%
Bean Starch	/	Mung	/	40%
Lentil Starch	/	Lentil	/	38%

[a]HAS: High Amylose Starch

Poly (lactic acid) pellets (4042D) were purchased from Cargill Dow LLC (Minnetonka, MN). Glycerol with boiling point of 182°C and 99+% purity were provided by Sigma-Aldrich Canada LTD. Maleic anhydride (99% purity) was also obtained from Sigma-Aldrich. Nanoclay, Cloisite 30B, was purchased from Southern Clay Products Inc. (USA). Luperox 101 (2, 5- bis (tert-butylperoxy)–2, 5-dimethyl-hexane) was supplied by Sigma-Aldrich Canada LTD.

3.2 Preparation of Experimental Samples

3.2.1 Thermoplastic Starch (TPS)

All types of starch were dried in a vacuum oven at 80°C for 24 hours prior to processing. Dried starches were premixed with glycerol and water in a standard kitchen-use blender at room temperature. The basic formula of starch/glycerol/water was set at 50/36/14 (wt/wt/wt) to provide reasonably good morphological and mechanical properties (Huneault and Li, 2006). The mixture of starch, glycerol and water was kept at room temperature for 5 minutes before being loaded into a Haake Rheomix 3000 Batch Mixer with roller rotors for blending. The blending conditions were 120°C at 45 rpm for 4 minutes (Huang, 2005). The mixture was cooled to room temperature and then ground into powder using a granulator. In order to prevent thermal degradation of PLA, the water must be removed from the blends prior to blending with PLAgMA. The water removal was performed in a vacuum oven at 60°C for 24 hours. The samples were sealed in the plastic bags after water removal

3.2.2 Poly (lactic acid) Grafted Maleic Anhydride (PLAgMA)

Maleic Anhydride (MA) chips were ground into powder and then premixed with PLA and Luperox 101 (L101) in an aluminum tray by hand in order to be uniformly wetted by L101 liquid. The blending ratio of PLA/MA/L101 was 100/2/0.25 (wt/wt/wt) (Huneault and Li, 2006). The mixture was loaded into Haake Rheomix 3000 Batch Mixer for blending under the conditions of 180°C, 45 rpm and 4 minutes. The mixture was cooled into room temperature and then ground into powder. The powder was stored in a sealed plastic bag.

3.2.3 TPS and PLAgMA Blends

Water free TPS and PLAgMA were premixed in a tray by hand and then loaded into Haake Rheomix 3000 Batch Mixer for blending. The conditions were 150°C at 45 rpm for 6 minutes. The mixture was cooled into room temperature and then ground into powder. The powder was sealed in a plastic bag with zipper.

3.2.4 TPS and PLAgMA Blends with Nanoclay

Cloisite 30B was dried at 100°C in a vacuum oven for 8 hours prior to processing. All components (TPS, PLAgMA and Cloisite 30B powders) were premixed in a tray according to various ratios (shown in Table 3.2). These composites were prepared in Haake Rheomix 3000 Batch Mixer under 150°C at 45 rpm for 6 minutes. For some special formulae (shown in Table 3.2) the blending times were 4 minutes. The mixtures were ground into powders and sealed in plastic bags after cooling to room temperature.

Table 3.2 Compositions and blending conditions of thermoplastic starch/PLAgMA blends

No	Starch type	TPS/PLAgMA ratio, wt/wt	Clay content, wt%	Haake Mixer	
				Temperature, C	Time, min
1	H.A.S	100/0	0	120	4
2	H.A.S	70/30	0	150	6
3	H.A.S	70/30	1	150	6
4	H.A.S	70/30	2	150	4
5	H.A.S	70/30	2	150	6
6	H.A.S	70/30	3	150	6
7	H.A.S	70/30	5	150	6
8	H.A.S	70/30	8	150	6
9	N. S.	100/0	0	120	4
10	N. S.	70/30	0	150	6
11	N. S.	70/30	2	150	6
12	N. S.	70/30	3	150	6
13	N. S.	70/30	5	150	6
14	Pea	100/0	0	120	4
15	Pea	70/30	0	150	6
16	Pea	70/30	2	150	6
17	Pea	70/30	3	150	6
18	Pea	70/30	5	150	6
19	Lentil	100/0	0	120	4
20	Lentil	70/30	0	150	6
21	Lentil	70/30	2	150	6
22	Lentil	70/30	3	150	6
23	Lentil	70/30	5	150	6
24	Bean	100/0	0	120	4
25	Bean	70/30	0	150	6
26	Bean	70/30	5	150	6

Note: ratio of starch/glycerol/water: 50/36/14 (wt/wt); roller speed of Haake mixer: 45 RPM

3.2.5 Surface Sizing and Internal Sizing Procedures

3.2.5.1 Surface Sizing

A mixture of 0.1 g AKD and 125 ml heptane was put into a glass jar sealed with a lip for stirring with a glass rod by hand and then agitated on a magnetic plate stirrer with a stir bar for 3 hours (Shen et al, 2000). Selected samples prepared using lab-scaled hot press machine at 150°C were dipped in the AKD-Heptane solution for 10 seconds. Heptane in the sized samples was allowed to evaporate in a fume cupboard for 20 min prior to drying them in an oven under the temperature of 105°C for 1 hour. Dried samples were stored and sealed in the plastic bags for 24 hours prior to contact angle testing.

3.2.5.2 Internal Sizing

Sizing agent AKD and water were premixed in a cup and then blended with dried starch and glycerol in the blender. The blend ratios were shown in the Table 3.3. The mixture was kept for 5 min at room temperature and then loaded in to the Haake Rheomix 3000 batch mixer for blending. The conditions were 120°C at 45 rpm for 4 minutes. The mixture was cooled naturally into the room temperature and then ground into powder. The water in the powders was removed in a vacuum oven at 60°C for 24 hours. The water free TPS were blended with PLAgMA and nanoclay for 6 min at 150° C and 45 RPM in Haake mixer. The naturally cooled mixture were ground into powder again and then sealed in a plastic bag. This procedure was so-called internal sizing.

Table 3.3 Experiments of AKD internal sizing on HAS/PLAgMA/nanoclay (5% clay content) blends

No.	Experimental Code	Starch/AKD wt/wt	Starch/plasticizer wt/wt	Glycerol/water wt/wt	TPS/PLAgMA wt/wt
1	TP-HAS-AKD1	100/0.05	50/50	36/14	70/30
2	TP-HAS-AKD2	100/0.075	50/50	36/14	70/30
3	TP-HAS-AKD3	100/0.1	50/50	36/14	70/30

Blending conditions on Haake Mixer:
TPS: 120°C/4min/45RPM;
TPS/PLAgMA/Clay: 150°C/6min/45RPM

3.3 Characterization Measurements for TPS and PLAgMA Blends with Nanoclay

3.3.1 Rheological Property

Shear viscosity at various shear rates for each sample shown in table 3.2 was measured at 150°C using Rosand Precision Advanced Capillary Rheometer (Bohlin Instruments, UK). Two dies were used in the twin bores- long die and zero-length die. The L/D of the long die is 16/1. Both Bagley correction and Rabinowitsch correction were applied (Vlachopoulos, 2003). The extruded fibers were considered as post-extrusion molded samples and cut into 100 mm in length for tensile property testing.

3.3.2 Differential Scanning Calorimetry

Differential scanning calorimetry experiments were performed using a 2920 Modulated DSC equipped with a refrigerated cooling system (RCS) (TA Instruments, USA). Samples used for DSC measurements were sealed in aluminum hermetic pans and the weight for each sample was around 10mg. The hermetically sealed aluminum pan was put into the cell together with a reference hermetic pan and cooled to 5°C. After being equilibrated at 5°C, the sample was heated from 5°C to 180°C at a thermal scan rate of 10°C/min, and then cooled to -30°C at the same rate of 10°C/min and equilibrated at -30°C. This process was so-called the first thermal scan. After equilibration at -30°C, the sample was heated again from -30°C to 200°C at the rate of 10°C/min. The curve of second thermal scan was monitored. A nitrogen flow (150ml/min) was applied throughout the thermal scan and helium gas was used during cooling.

The software of a TA Universal Analysis 2000 unit was used to analyze the second thermal scan curves. Melting temperature T_m and crystallization temperature T_c were read from the peak values of respective endotherms and exotherms. When multiple endothermic peaks occurred, the peak temperature of the main endotherm was considered as T_m.

3.3.3 Tensile Testing

The fibers extruded through the Rosand Capillary Rheometer during Rheological testing were cut to 100 mm in length. All prepared fibers were preconditioned at 25°C with a relative humidity of 50% for 48 hrs to relax internal stresses prior to mechanical testing (Zhang and Sun, 2004).

The tensile tests were performed on an Instron tensile testing machine (Series IX Automated Material Testing System) according to ASTM D882-02 at room temperature with a crosshead rate of 5 mm/min and a 50 mm gauge length. Five specimens were replicated to test each sample.

3.3.4 Scanning Electron Microscope

The morphological characterization of the selected samples was assessed using Philips Scanning Electron Microscope (Philips Scientific and Industrial Equipment, The Netherlands) with an accelerating voltage of 20V. In order to observe the morphology of samples prepared with different blending times on the Haake Rheomixer test specimens were selected from the samples with the different blending time. In addition, the samples with various nanoclay contents were chosen for observation. All specimens were sputter-coated with gold prior to observation.

3.3.5 Contact Angle Measurement

The selected samples were prepared using a lab-scale hot press machine. The particles of TPS/PLAgMA/nanoclay blends were loaded in a circular mold with diameter of 25 mm and thickness of 2 mm at 170°C and held for 5 minutes and then cooled to around 60°C before removal from the mold. The prepared samples were sealed in the plastic bags for 24 hrs before contact angle testing.

The volume of the water droplet can be obtained precisely by means of a syringe fitted with a needle used to form the drop. The contact angle formed between the water droplet placed on the surface of material and the kinetics of spreading is related to the hydrophobicity of materials. The initial angle for hydrophobic material is larger than that for hydrophilic material. Contact angles were measured using a goniometer equipped with a Sanyo camera and a computer with drop shape analysis software (FTA200, Version 2.0) designed for calculating the value of contact angles from the shape of attached water droplet.

Chapter 4

Results and Discussion

4.1 Structure and Properties of Thermoplastic Cornstarch and PLAgMA Blends with Nanoclay

4.1.1 Thermal Properties

In the study of polymers and their applications, it is important to understand the concepts of the glass transition temperature (T_g) and melting temperature (T_m). T_g is the temperature at which the amorphous phase of the polymer is converted between rubbery and glassy states. T_g constitutes the most important mechanical property for all polymers. T_m is the temperature at which the state changes from solid to melt. For a semi-crystalline material, the crystalline phase will disappear when T_m is reached by heating. The melting temperature, T_m is an important factor for determination of polymer blending conditions.

Thermoplastic high amylose cornstarch and normal cornstarch were blended with PLA grafted maleic anhydride (PLAgMA) at various nanoclay (Cloisite 30B) compositions and the thermal behavior of these blends were evaluated using DSC. The effects of thermal history of samples were eliminated by the first thermal scan. The thermal properties determined from the second thermal scan are summarized in Table 4.1.

Table 4.1 DSC characteristics of thermoplastic cornstarch/PLAgMA/nanoclay blends

Starch Type	Blends	Ratio of Blends wt/wt	Clay content wt%	T_g (˚C)	T_c (˚C)	Crystallization enthalpy, J/g	T_m (˚C)	Melting enthalpy J/g
HAS	HAS-TPS/PLAgMA	100/0	0%	\	\	\	\	\
	HAS-TPS/PLAgMA	70/30	0%	58.7	113.7	10.57	151.7	11.18
	HAS-TPS/PLAgMA	70/30	1%	58.9	108.7	10.04	152.3	11.16
	HAS-TPS/PLAgMA	70/30	2%	58.9	110.7	10.41	152.4	10.54
	HAS-TPS/PLAgMA	70/30	3%	57.8	107.1	10.31	150.6	9.57
	HAS-TPS/PLAgMA	70/30	5%	58.6	111.4	9.99	152.1	8.69
	HAS-TPS/PLAgMA	0/100	0%	57.6	130.4	8.68	151.9	7.76
	HAS-TPS/PLA	70/30	0%	59.6	120.2	8.63	148.4	8.48
NS	NS-TPS/PLAgMA	70/30	0%	59.7	115.0	11.10	153.5	9.31
	NS-TPS/PLAgMA	70/30	5%	58.4	114.3	9.08	152.8	8.92

All DSC data were read from the second thermal scan in DSC thermograms. T_g, T_c and T_m are glass transition temperature, crystallization temperature and melting temperature, respectively.

High amylose cornstarch was blended with water and glycerol (water/glycerol = 14/36 wt/wt) at 120°C to form thermoplastic starch (HAS-TPS) in the Haake Rheomixer 3000. The thermal behavior evaluated by DSC indicated that no thermal transition was detected in the second thermal scan. The mixture of HAS-TPS after water removal was analyzed by DSC and no transition was observed (as shown in Figure 4.1). These results indicated that the water concentration of 14% had little or no effect on the thermal behaviors of HAS-TPS. Averous and Boquillon (2004) noted that the heat capacity change of plasticized starch during glass transition is too low to be determined by DSC.

The DSC thermogram of PLAgMA showed a glass transition temperature of 57.6°C, a crystallization temperature of 130.4°C and a melting temperature of 151.9°C. Huang (2005) reported that the pure PLA showed a glass transition at 58.4°C, a crystallization exotherm at 125.3°C and a melting endotherm at 153.3°C. Compared to PLA, the PLA grafted maleic anhydride (PLAgMA) had a lower T_g and T_m, and higher T_c. Because PLA underwent the graft reaction with maleic anhydride, the proportion of short chains decreased and the crystallization temperature shifted to a high value and the molecular mobility was restricted by PLAgMA, thereby decreasing crystallinity.

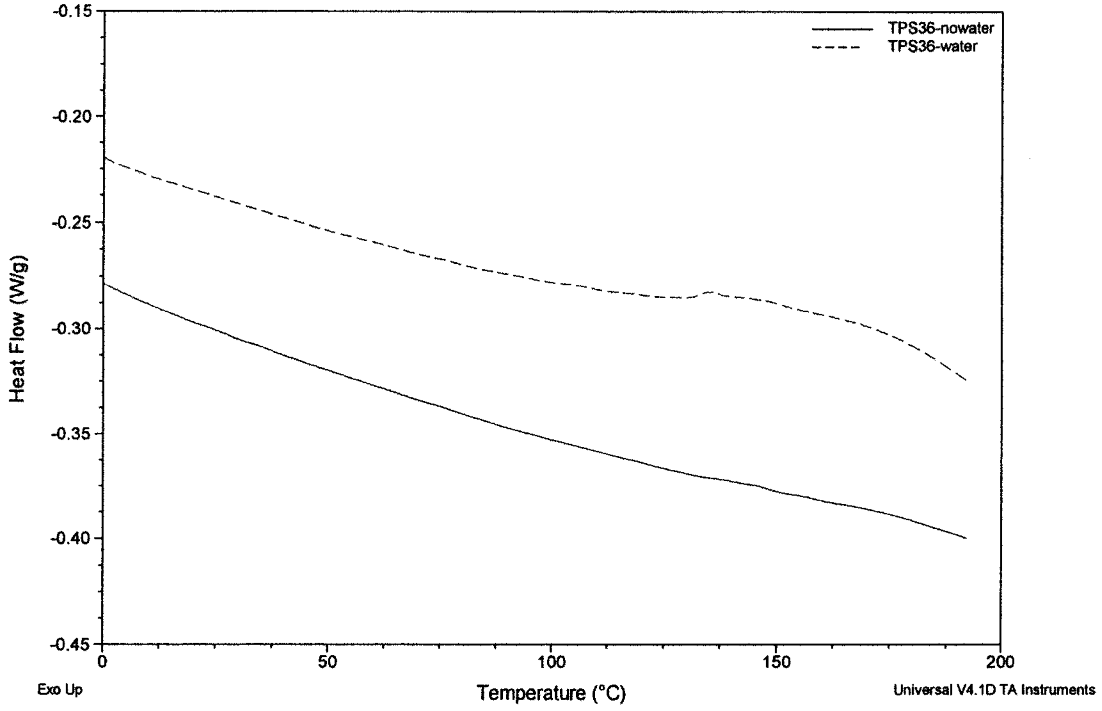


Figure 4.1 DSC thermograms of thermoplastic high amylose cornstarch and water free thermoplastic high amylose cornstarch (water removal prior to testing) in a second thermal scan. Starch/water/glycerol ratio (wt/wt): 50/14/36

The DSC thermogram of HAS-TPS in the second thermal scans showed no T_g, T_c or T_m peaks but that of the HAS-TPS/PLAgMA blends presented peak values of T_g, T_c and T_m (shown in Figure 4.2). Compared to the DSC thermogram of PLAgMA, HAS-TPS/PLAgMA blends exhibit a similar thermal transition behavior (see Figures 4.2 and 4.3), indicating that the thermal transition results of HAS-TPS/PLAgMA are mainly from PLAgMA, not from starch. These results are consistent with Wool and Sun (2005). However, there are double melting peaks in the DSC thermograms of TPS/ PLAgMA blends but only one melting peak appeared in that of pure PLAgMA. Similar to the melting peaks reported in plasticized starch/PLA blends by Wang et al (2003), these double melting peaks are caused by the plasticizer effect as well as a nucleation effect (Jang et al, 2007). The component of starch in blends acts as a nucleating agent to improve the kinetics of PLA crystallization, but does not affect the crystallization behavior of PLA (Ke and Sun, 2003c).

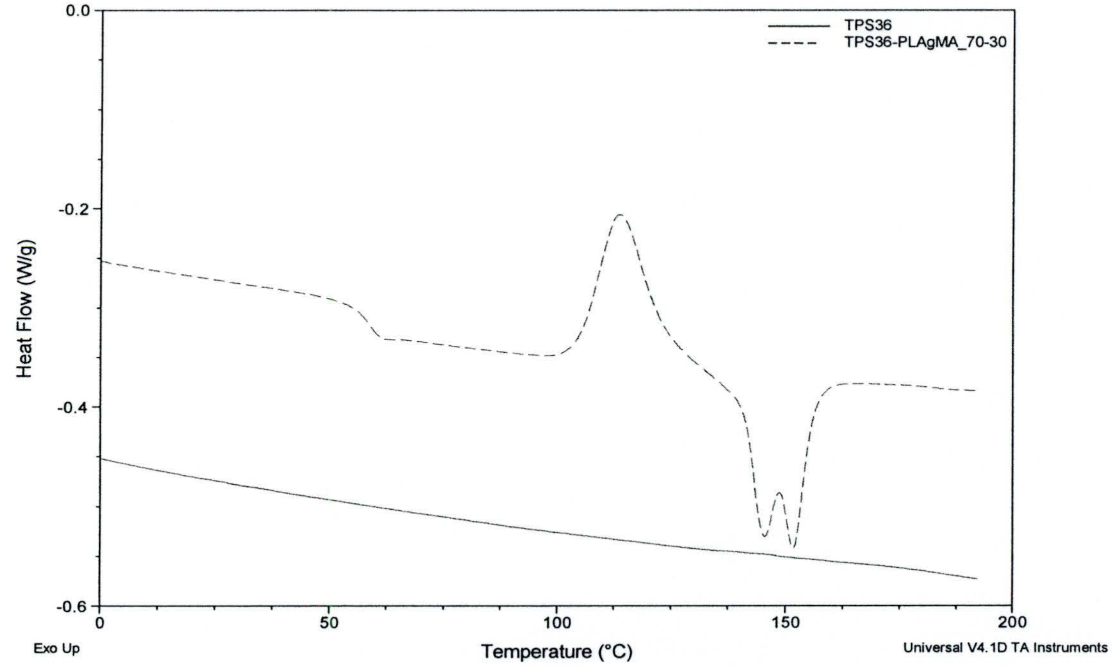


Figure 4.2 DSC thermograms of thermoplastic high amylose cornstarch and thermoplastic cornstarch /PLAgMA blend in a second thermal scan. Starch/water/ glycerol ratio (wt/wt): 50/14/36; TPS36/PLAgMA ratio (wt/wt): 70/30

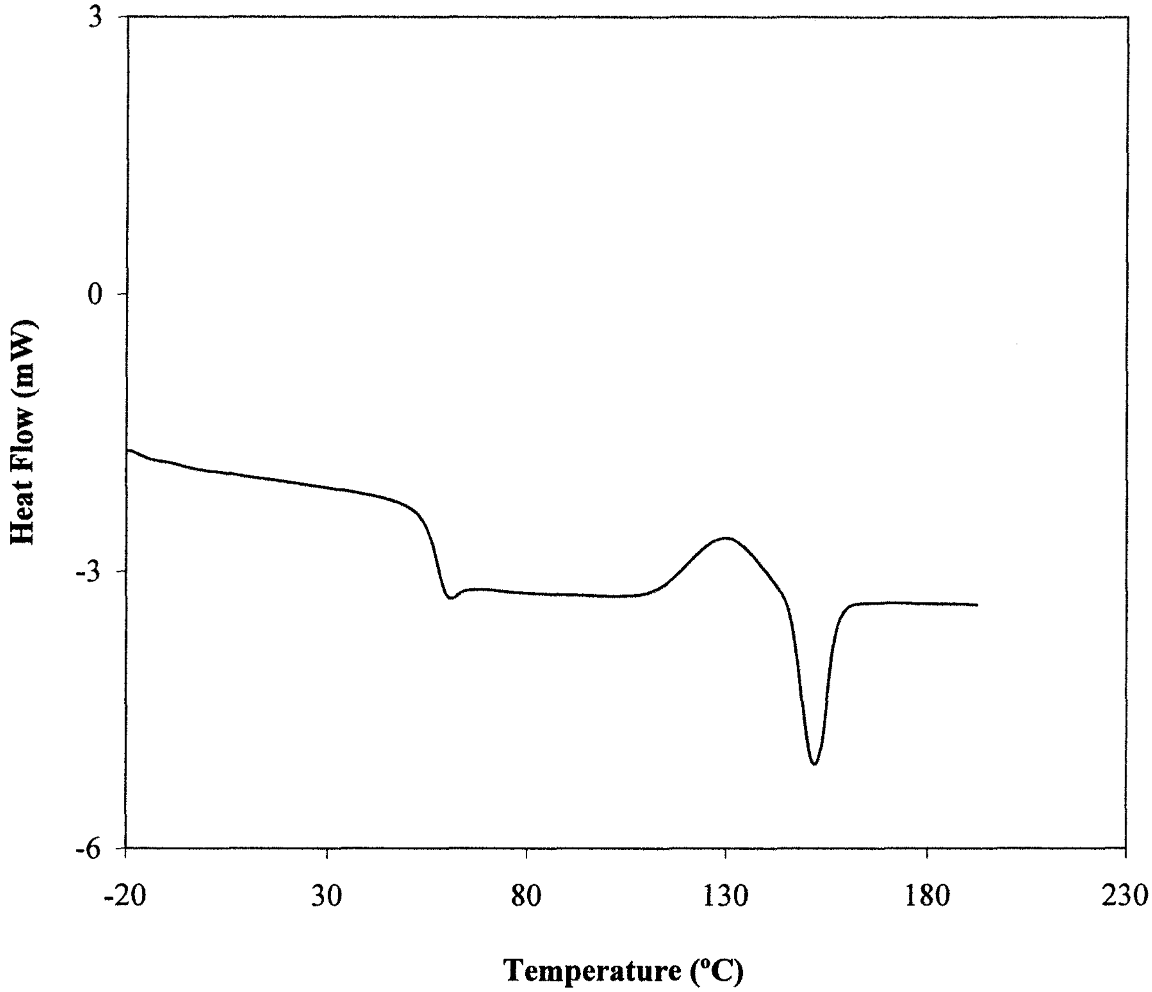


Figure 4.3 DSC thermograms of PLA grafted maleic anhydride in a second thermal scan. PLA/MA /L101 ratio (wt/wt): 100/2/0.25

The effects of blending time (in a Haake Rheomix 3000) on the thermal properties of thermoplastic high amylose cornstarch (HAS-TPS)/PLAgMA/nanoclay blends were studied. The DSC thermograms are shown in Figure 4.4 and the thermal characteristics are presented in Table 4.2. Compared with these parameters, the differences are very slight, indicating that the blending times of 4, 6 and 8 minutes (at 150°C) have no significant effect on the thermal properties of the blends.

The thermal properties of thermoplastic high amylose cornstarch/PLAgMA blends at various nanoclay (Cloisite 30B) compositions were evaluated by DSC. As per the previous discussion, the DSC information of TPS/PLAgMA mainly comes from PLAgMA. Therefore, the crystallinity of the blends can then be calculated using the following equation (Fischer et al, 1972):

$$\chi_c = \frac{\Delta \mathrm{H}_m}{\Delta \mathrm{H}_m^0} \times 100\% \qquad \text{Eq. (4-1)}$$

Where, $\Delta \mathrm{H}_m$: the enthalpy of fusion of PLA component in the blend, J/g

$\Delta \mathrm{H}_m^0$: the enthalpy of fusion of PLA crystal of infinite size, 93.7J/g (Fisher et al, 1972)

χ_c: the crystallinity of blends, %

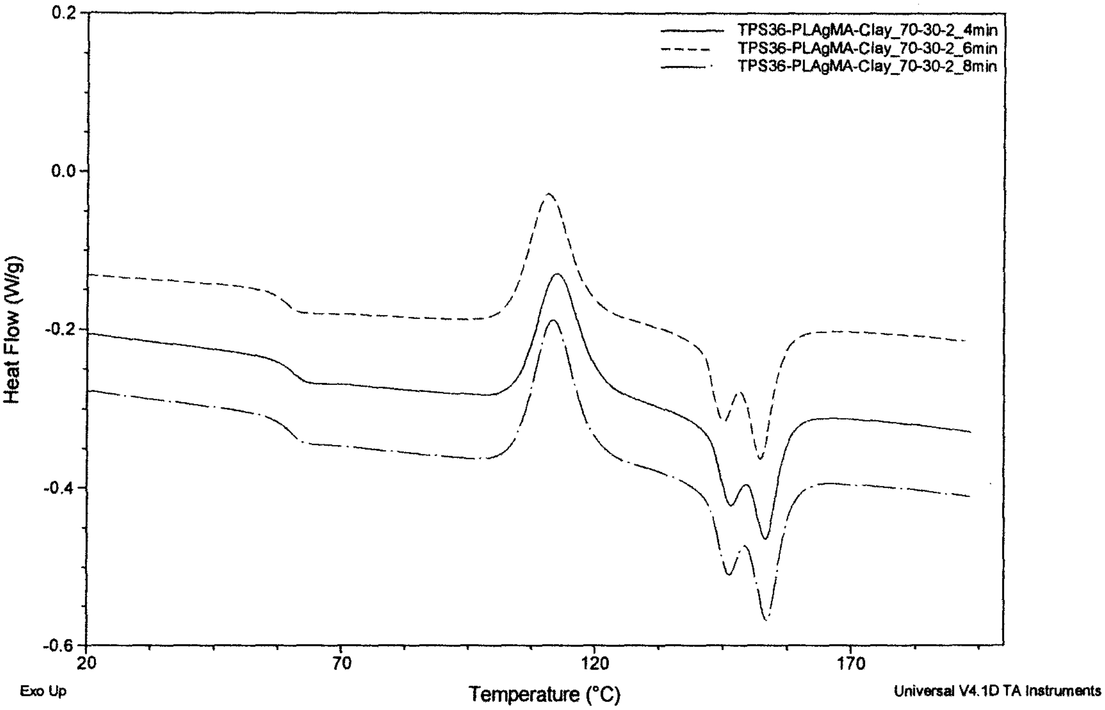


Figure 4.4 DSC thermograms of thermoplastic high amylose cornstarch/PLAgMA/ nanoclay blends in a second thermal scan. HAS-TPS/PLAgMA/Cloisite 30B ratio (wt/wt): 70/30/2; blending time on Haake Rheomix 3000: 4min, 6min and 8min, respectively

Table 4.2 DSC characteristics of HAS-TPS/PLAgMA/nanoclay blends at the different blending time

Blends	Ratios wt/wt	Blending time (min)	T_g °C	T_c °C	Crystallization enthalpy J/g	T_m °C	Melting enthalpy J/g
HASTPS/PLAgMA/30B-4	70/30/2	4	60.4	112.3	9.49	153.3	9.05
HASTPS/PLAgMA/30B-6	70/30/2	6	58.9	110.7	10.14	152.4	10.54
HASTPS/PLAgMA/30B-8	70/30/2	8	60.3	111.7	10.5	153.6	10.7

Table 4.3 DSC characteristics and calculation results of crystallinity of HAS-TPS/ PLAgMA/nanoclay blends

Blends	Ratio of blend wt/wt	30B content wt%	T_g °C	T_c °C	ΔH_c J/g	T_m °C	ΔH_m J/g	χ_c %
HASTPS/PLAgMA	70/30	0	58.7	113.7	10.57	151.7	11.18	11.93
HASTPS/PLAgMA	70/30	1	58.9	108.7	10.04	152.3	9.66	10.31
HASTPS/PLAgMA	70/30	2	58.9	110.7	10.41	152.4	10.54	11.25
HASTPS/PLAgMA	70/30	3	57.8	107.1	10.31	150.6	9.57	10.21
HASTPS/PLAgMA	70/30	5	58.6	111.4	9.99	152.1	8.69	9.27

Comparing the crystallinity in Table 4.3, the addition of clays did not have a significant effect on χ_c. It is difficult to strictly discuss the influence of clays on the crystallization behavior from the DSC results. For the plasticized starch/PLAgMA/clay blends, the glycerol plasticizer in TPS will migrate into the PLAgMA matrix and promote the crystallization of PLAgMA. Further studies indicated that clay can accelerate the crystallization by acting as a nucleating agent, but it cannot significantly affect the final attained crystallinity (Shibata et al, 2006).

For a starch content less than 40 wt%, the crystallinity of PLA in PLA/starch blend is increased compared to that of pure PLA but the crystallinity of PLA decreased with increasing starch content (Ke and Sun, 2003c). However, as the starch content increases and exceeds 40%, the mobility of the PLA molecule may be restricted by starch and the crystal growth rate is decreased. That may be attributed to the contents of amylose and amylopectin. The higher content of branch amylopectin may exhibit more restriction to the mobility of PLA molecule due to the entanglement of amylopectin with PLA molecule. DSC thermograms for blends with different amylose compositions are shown in Figure 4.5 and the DSC characteristics are shown in Table 4.4.

The difference between normal cornstarch (NS) and high amylose cornstarch (HAS) is the content of amylose in the starch. The amylose content of NS used in this research is 23 wt% and that of HAS is 70 wt%. In comparing the blends of HAS-TPS/PLAgMA with NS-TPS/ PLAgMA, one observes that the ΔH_m of blend with HAS is higher than that of one with NS. This may be due to the amylopectin restriction of PLA molecule mobility, which may be more than that due to amylose. For blends containing nanoclay (Cloisite 30B), the influence of each component is much more complicated. Clay acts as a nucleating agent to increase the crystallinity of PLA; however, the higher content of amylopectin limits the mobility of PLA. The crystallinity of PLA was balanced by the effects of both opposite factors.

Table 4.4 DSC characteristics of thermoplastics cornstarch/PLAgMA/Clay

Blends	Amylose content in starch (wt%)	Ratio of blend wt/wt	Clay content wt%	T_g °C	T_c °C	ΔH_c J/g	T_m °C	ΔH_m J/g
HASTPS/PLAgMA	70	70/30	0	58.66	113.7	10.60	151.7	11.2
NSTPS/PLAgMA	23	70/30	0	59.73	115.0	11.10	153.5	9.31
HASTPS/PLAgMA/clay	70	70/30	5	58.63	111.4	9.99	152.1	8.69
NSTPS/PLAgMA/clay	23	70/30	5	58.39	114.3	9.08	152.8	8.93

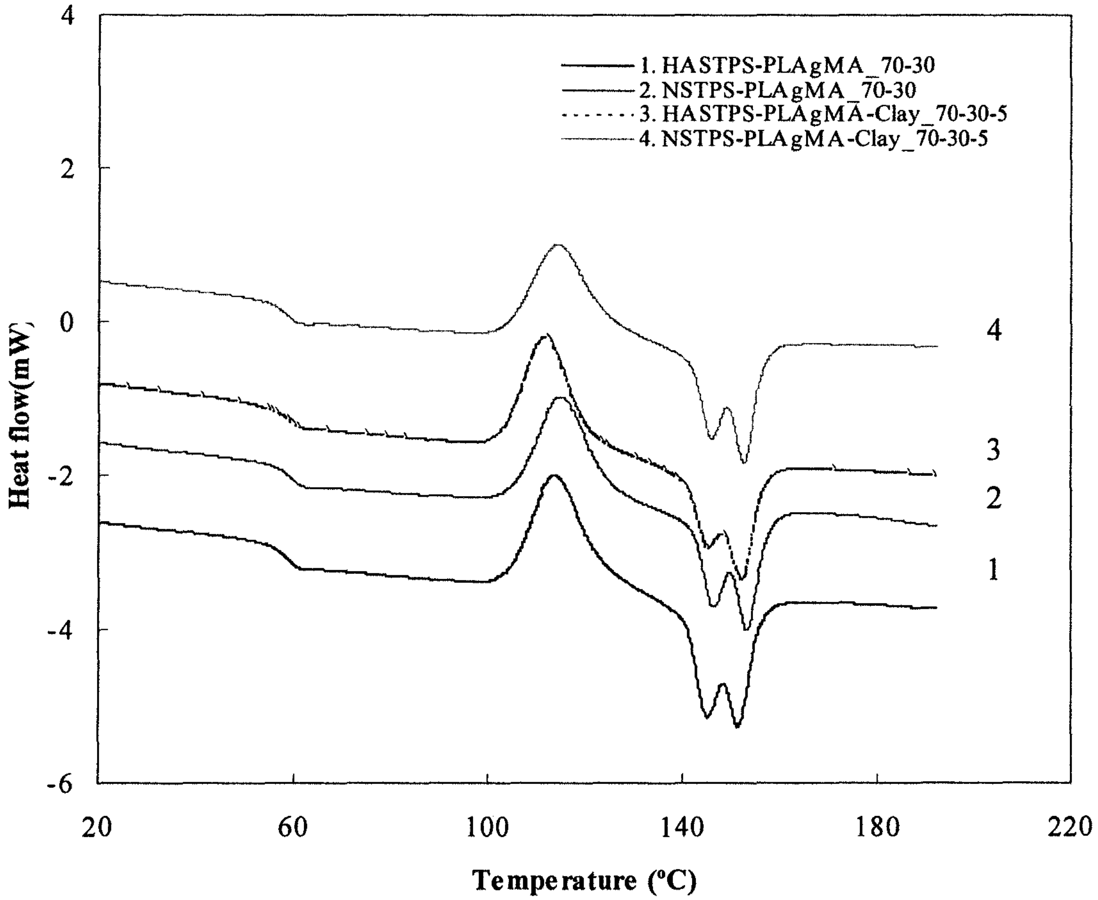


Figure 4.5 DSC thermograms of two types of thermoplastic cornstarch/PLAgMA blends and their blends with Cloisite 30B in a second thermal scan. Both thermoplastic cornstarch/PLAgMA ratio (wt/wt): 70/30; TPS/PLAgMA/Cloisite 30B ratio (wt/wt): 70/30/2

4.1.2 Rheological Properties

Rheological properties of thermoplastic starches and PLAgMA blends with nanoclay were studied on a Rosand Precision Advanced Capillary Rheometer. The effects of additives such as water, maleic anhydride and nanoclay on the rheological properties of thermal plastic cornstarch were investigated.

These thermoplastic starch blends exhibit a shear-thinning behavior. The relationship between shear rate and shear viscosity may be fitted by the power law at the temperature of 150° C. The power-law equation can be expressed as:

$$\eta = m\dot{\gamma}^{n-1} \qquad \text{Eq. (4-2)}$$

Where, η : shear viscosity, Pa.s

m : consistency index, Pa.s^{n}

$\dot{\gamma}$: shear rate, s^{-1}

n : power law index

The model parameters for high amylose cornstarch blends are shown in Table 4.5-4.7.

The gelatinization of starch depends on the content of water as one plasticizer component blended with starch in the Haake Rheomixer 3000 at a temperature of 120° C. The effect of water removal on the rheological properties of TPS is shown in Figure 4.6 and the power-law parameters are presented in Table 4.5. The results indicated that the blend containing water (HASTPS-PLAgMA_70-30-water) exhibited lower shear viscosity at the same shear rate than the blend without water (HASTPS-PLAgMA_ 70–30-nowater) did. The water, together with glycerol, acts as a plasticizer in blends and the concentration of plasticizers is decreased after water removal. Thus, the shear viscosity increases as plasticizer decreases. That is why the blend of HASTPS-PLAgMA_ 70–30 without water exhibits the higher shear viscosity at the same shear rate than that of HASTPS-PLAgMA_ 70–30 with water does.

Maleic anhydride acts as a compatibilizer in the starch/PLA blends to increase the compatibility of starch and PLA. The chemical reactions among starch, PLA and initiator Luperox 101 are illustrated in Figure 2.3. In the case of plasticized cornstarch and PLA blend, the effects of MA on the rheological properties were investigated (as shown in Figure 4.7 and Table 4.5). The shear viscosity of HASTPS/PLAgMA is significantly lower than that of HASTPS/PLA, which is consistent with Huneault and Li (2007).

Table 4.5 Power-law parameters for blends of thermoplastic high amylose cornstarch

Blends	Consistency index, m, Pa.s^n	Power law index, n	R^2
HASTPS-PLAgMA_70-30-water	2562.7	0.2507	0.9878
HASTPS-PLAgMA_70-30-nowater	3336.1	0.2927	0.9938
HASTPS-PLA_70-30-nowater	5347.7	0.5006	0.9895

Temperature: 150° C

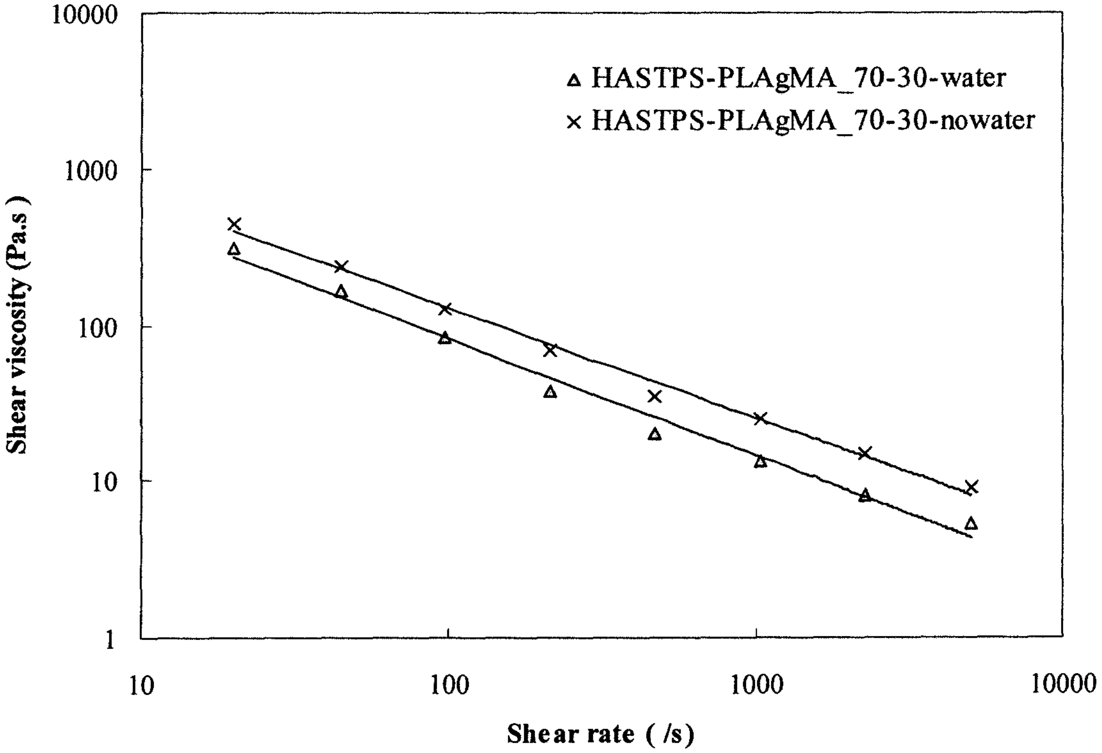


Figure 4.6 Rheological properties of thermoplastic high amylose cornstarch/PLAgMA (70/30) blends with water and water removal (starch/glycerol/water ratio: 50/36/14 wt/wt) (Temperature: 150° C)

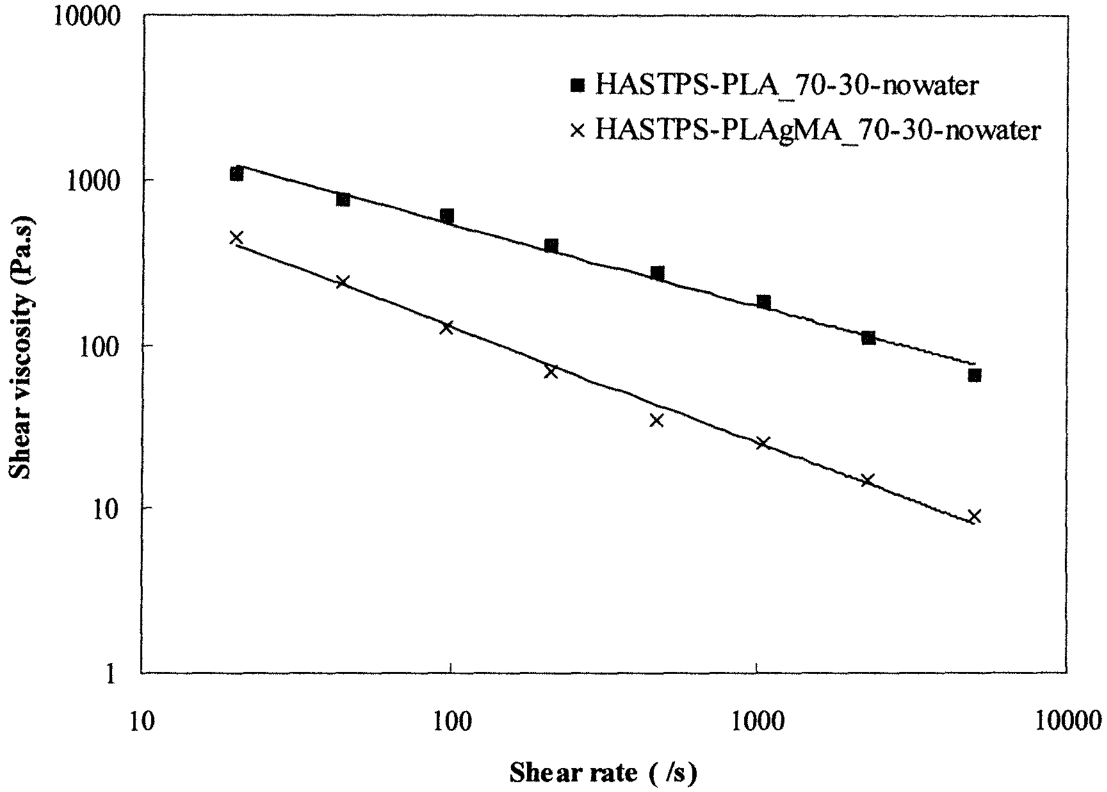


Figure 4.7 Rheological properties of water free HASTPS/PLA (70/30 wt/wt) blend and HASTPS/ PLAgMA blend (70/30 wt/wt). Ratio of PLA/MA/L101 (wt/wt): 100/2/0.25) (Temperature: 150° C)

Normally, the peroxide initiated graft-reaction increases the viscosity of polymers, for example, polyethylene grafted by MA (PEgMA). But the reactions of MA and L101 with plasticized starch/PLA are not simple as described in Figure 2.3. MA is highly reactive with hydroxyl in the presence of initiator (L101). The hydroxyl groups in glycerol could potentially react with MA. The residual water in the TPS phase may cause the opening of MA ring-cycle and thus reduce the reactivity of MA. Therefore, Huneault and Li (2007) proposed that the possible reasons for the viscosity decrease in the presence of MA and L101 were that the PLA chains first were broken by initiator and then free monomer can be grafted onto the reacted chain ends, as in the case of the polypropylene grafting reaction with MA (PPgMA), but this needs more evidence to be confirmed.

The effects of nanoclay on the rheological behaviors of thermoplastic cornstarch/ PLAgMA blends were studied on the dual capillary bore rheometer. The shear viscosity versus shear rate behaviour of the blends with two types of cornstarch is shown in Figure 4.8 and Figure 4.9. The power-law parameters, obtained by regression of the experimental data, are listed in Table 4.6 for blends of thermoplastic high amylose cornstarch/ PLAgMA/nanoclay and in Table 4.7 for blends of thermoplastic normal cornstarch/PLAgMA/ nanoclay.

Table 4.6 Power-law parameters for thermoplastic high amylose cornstarch/PLAgMA/ nanoclay blends

Blends	Content of Cloisite 30B (%)	Consistency index, m, Pa.s^n	Power law index, n	R^2
HASTPS-PLAgMA_70-30	0	9261	0.3199	0.9990
HASTPS-PLAgMA-30B_70-30-1	1	10507	0.3443	0.9980
HASTPS-PLAgMA-30B_70-30-2	2	16277	0.3202	0.9976
HASTPS-PLAgMA-30B_70-30-3	3	18433	0.3313	0.9997
HASTPS-PLAgMA-30B_70-30-5	5	19668	0.3509	0.9989
HASTPS-PLAgMA-30B_70-30-8	8	21425	0.3967	0.9974

Temperature: 150° C

Table 4.7 Power-law parameters for thermoplastic normal cornstarch/PLAgMA/nanoclay blends

Blends	Content of Cloisite 30B (%)	Consistency index, m, Pa.s^n	Power law index, n	R^2
NSTPS-PLAgMA_70-30	0	1001.2	0.4886	0.9717
NSTPS-PLAgMA-30B_70-30-2	2	3255.6	0.3979	0.9883
NSTPS-PLAgMA-30B_70-30-3	3	3384.6	0.4158	0.9902
NSTPS-PLAgMA-30B_70-30-5	5	5021.9	0.3823	0.9952

Temperature: 150° C

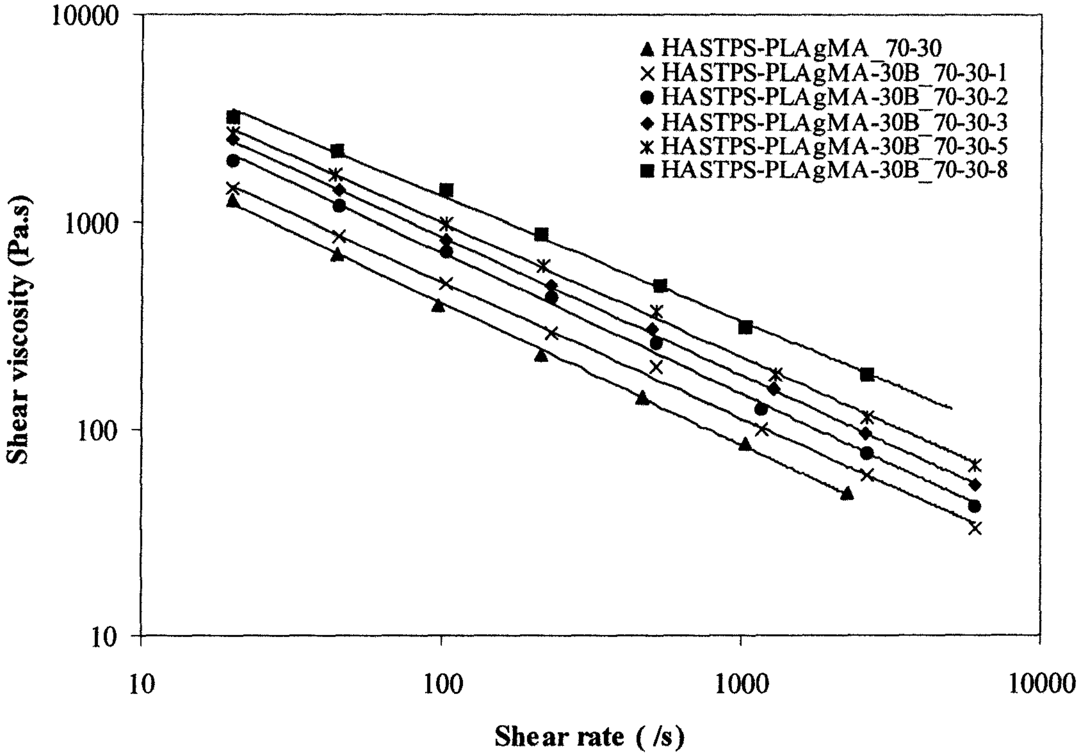


Figure 4.8 Rheological properties of thermoplastic high amylose cornstarch/PLAgMA blends with various contents of Cloisite 30B. (Contents of Cloisite 30B are 0%, 1%, 2%, 3%, 5% and 8%, respectively; Temperature of measurement: 150° C)

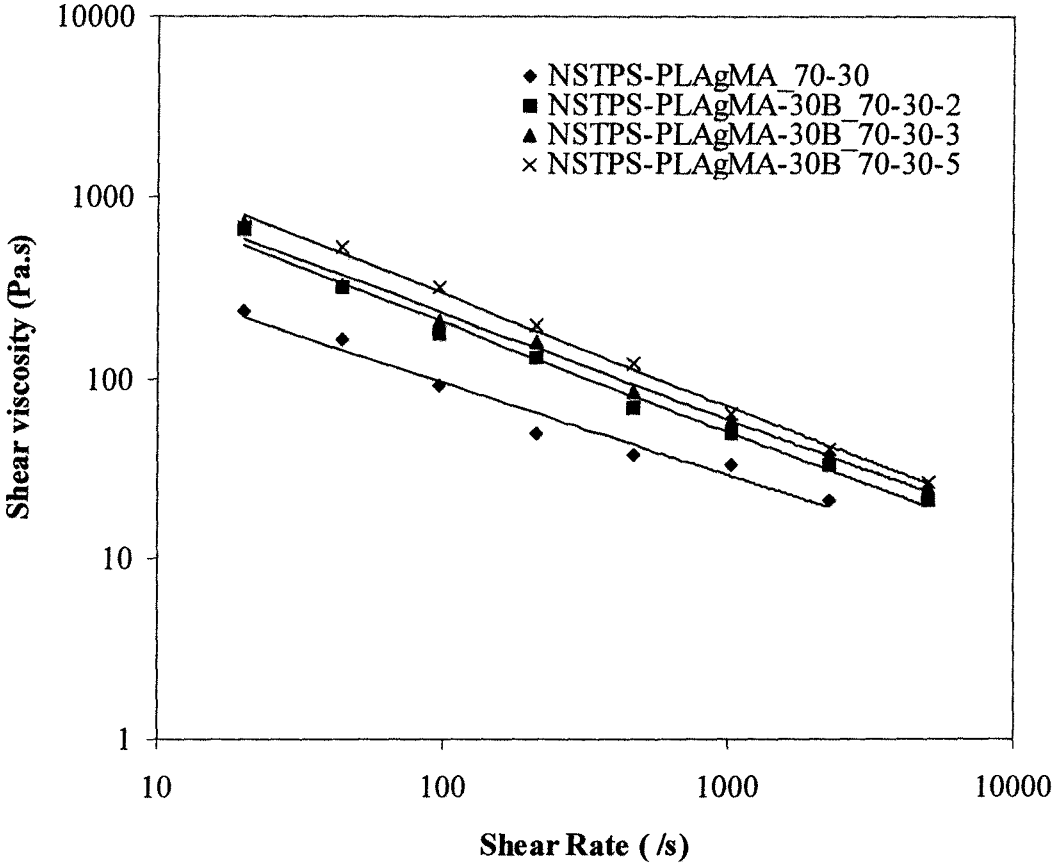


Figure 4.9 Rheological properties of thermoplastic normal cornstarch/PLAgMA blends with various contents of Cloisite 30B. (Contents of Cloisite 30B are 0%, 2%, 3% and 5%, respectively; Temperature of measurement: 150° C)

The addition of a small amount of nanoclay (Cloisite 30B) causes an increase in shear viscosity of both HASTPS/PLAgMA and NSTPS/PLAgMA. The shear viscosities of blends increase as the amount of nanoclay (Cloisite 30B) increases. For the HASTPS/PLAgMA, the shear viscosity can be expressed as $\eta = 9261\dot{\gamma}^{-0.6801}$. Similarly, the shear viscosity of NSTPS/PLAgMA blend can be described as $\eta = 1001.2\dot{\gamma}^{-0.5114}$. When these blends contain 5% nanoclay (Cloisite 30B), the shear viscosities can be described as $\eta = 19668\dot{\gamma}^{-0.6491}$ and $\eta = 5021.9\dot{\gamma}^{-0.6177}$ respectively, indicating that the content of nanoclay markedly increased the shear viscosities. Compared to the NSTPS/PLAgMA/Cloisite 30B blends, HASTPS/PLAgMA/ Cloisite 30B exhibits high shear viscosities (shown in Figure 4.10 and Figure 4.11). The difference may be attributed to the different amylose content and structure in starches. The linear amylose molecules have more hydrogen bonds, which increases the material viscosity (Huang, 2005).

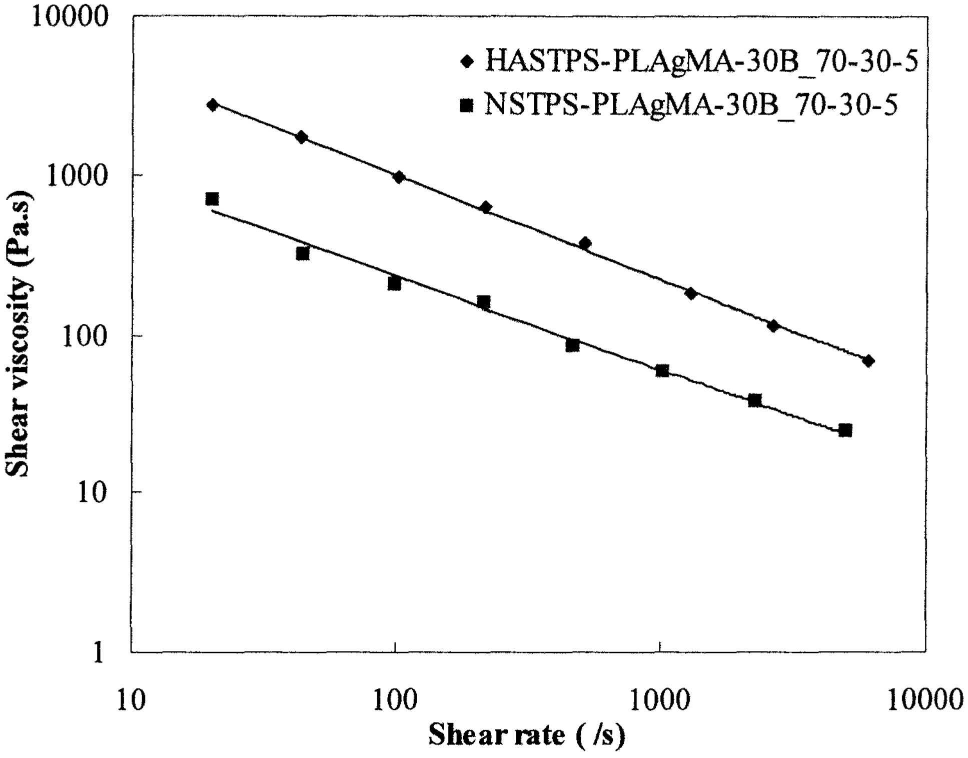


Figure 4.10 Comparison of rheological properties of TPS/PLAgMA/Cloisite 30B blends prepared by different type of cornstarch (Cloisite 30B content: 5%)

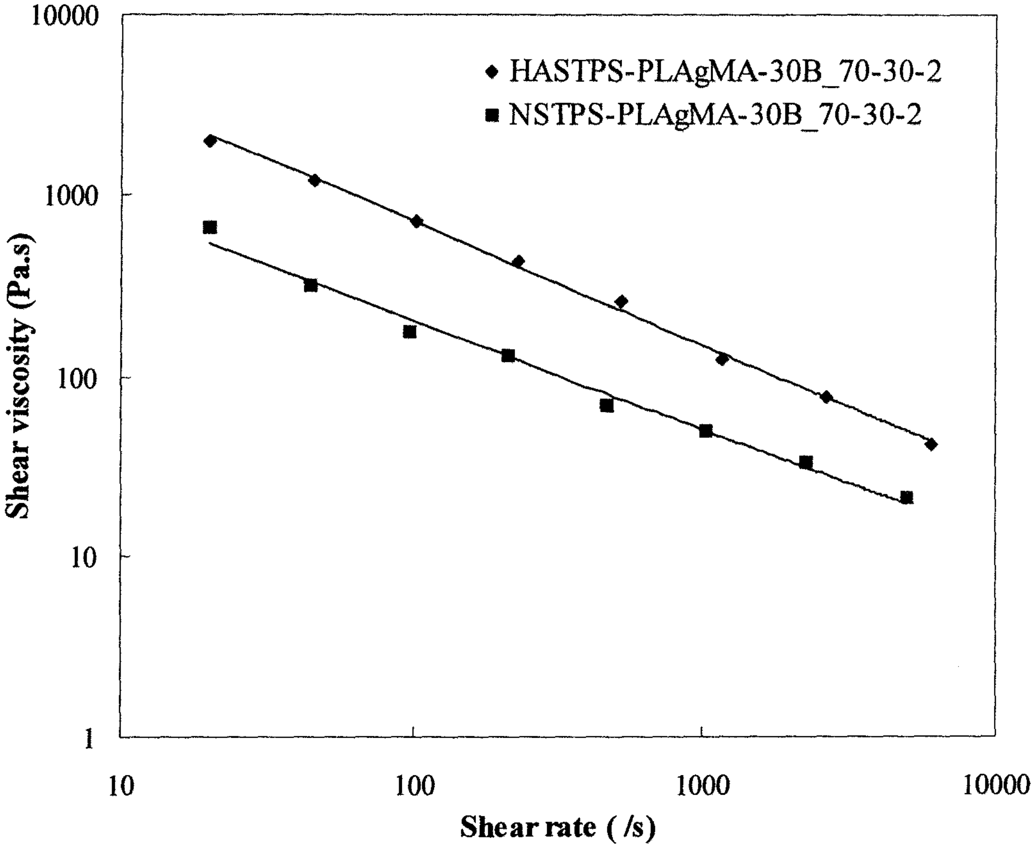


Figure 4.11 Comparison of rheological properties of TPS/PLAgMA/Cloisite 30B blends prepared by different type of cornstarch (Cloisite 30B content: 2%)

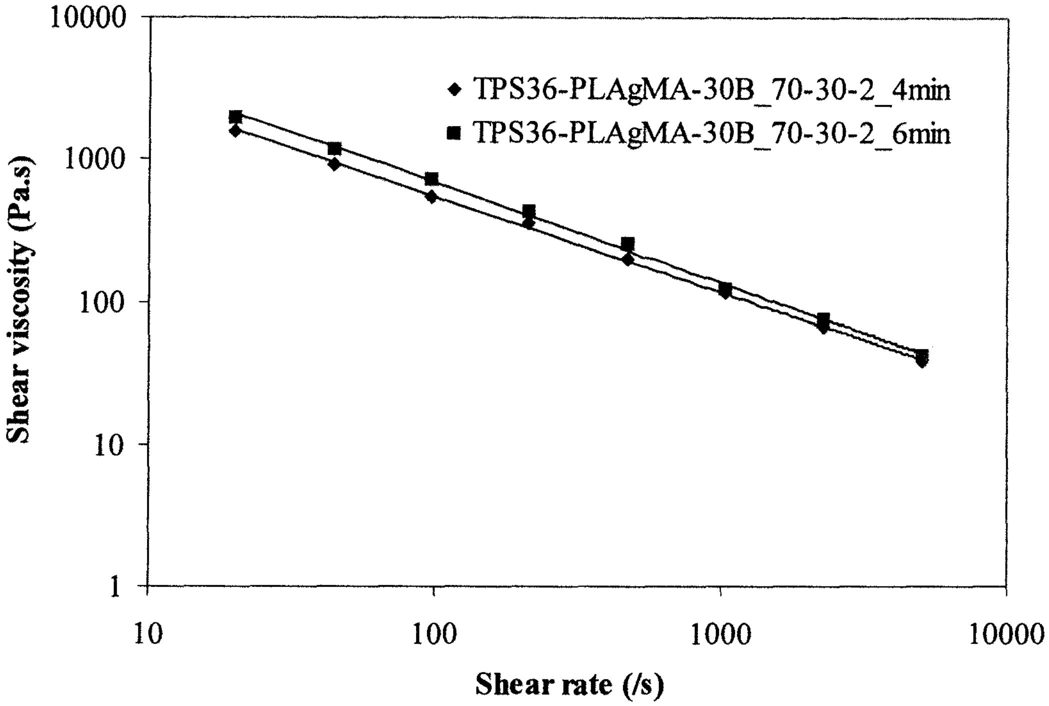


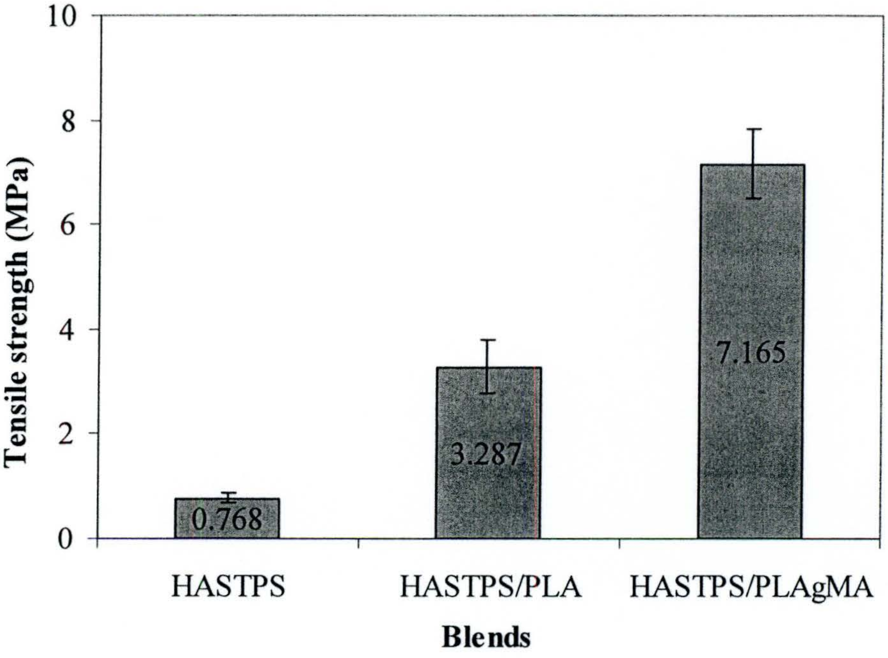
Figure 4.12 Comparison of rheological properties of TPS/PLAgMA/Cloisite 30B blends prepared under the different blending time on Haake batch rheomixer. Cloisite 30B content: 2%; Conditions on Haake: 150° C, 45RPM

A slight difference in rheological properties was found for the blends prepared under different blending times on Haake rheomixer as shown in Figure 4.12. The shear viscosities of HASPLAgMA-30B_4min and HASPLAgMA-30B_6min can be expressed as $\eta = 12013\dot{\gamma}^{-0.6703}$ and $\eta = 16277\dot{\gamma}^{-0.6798}$, respectively. The shear viscosity of the blend with 6 minutes of blending time was higher than that of blend with 4 minutes of blending time. This difference may be attributed to the morphological properties of the blend. The morphology of the 6-minute blend was more homogeneous than that of 4-minute blend. The morphological properties will be discussed in the section 4.1.4.

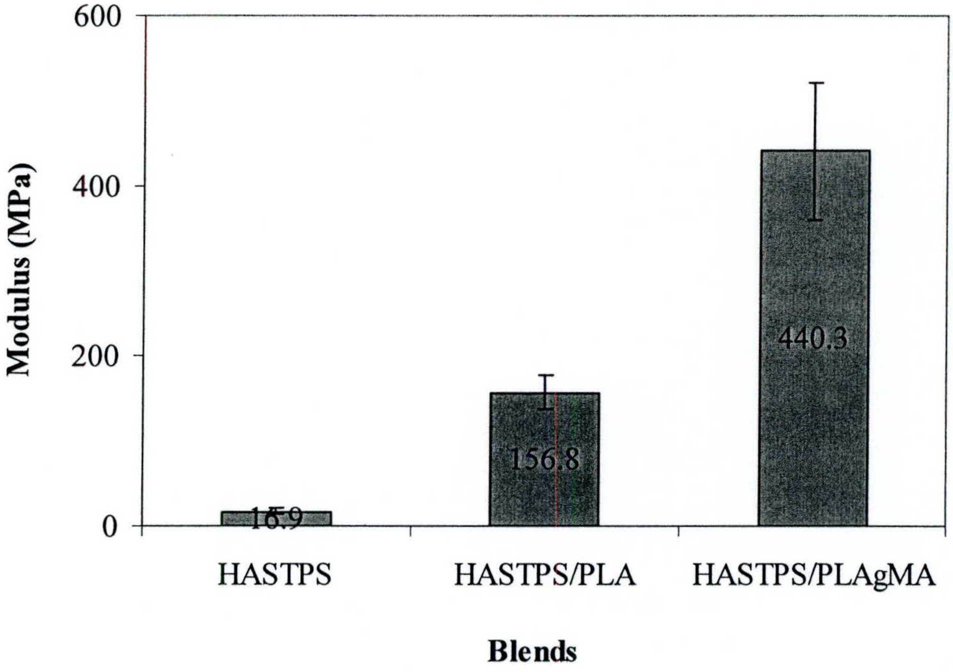
4.1.3 Mechanical Properties

Starch and PLA are immiscible, so maleic anhydride was used as a coupling agent to improve interfacial adhesion. The tensile stress-strain behaviors of HASTPS/PLA blended with MA were studied and the comparisons to the tensile properties of HASTPS and HASTPS/PLA are shown in Figure 4.13. The tensile strength and modulus of HASTPS/PLA were 3.287 MPa and 156.7 MPa respectively. After adding the MA coupling agent, the tensile strength and modulus were increased significantly: tensile strength increased to 7.165MPa and the modulus increased to 440.3 MPa. But the elongation of HASTPS/PLA was higher than that of HASTPS/PLAgMA. The water plasticizer was removed from HASTPS/PLAgMA. That is the possible reason why HASTPS/PLA exhibits the higher elongation at the break than HASTPS/PLAgMA does.

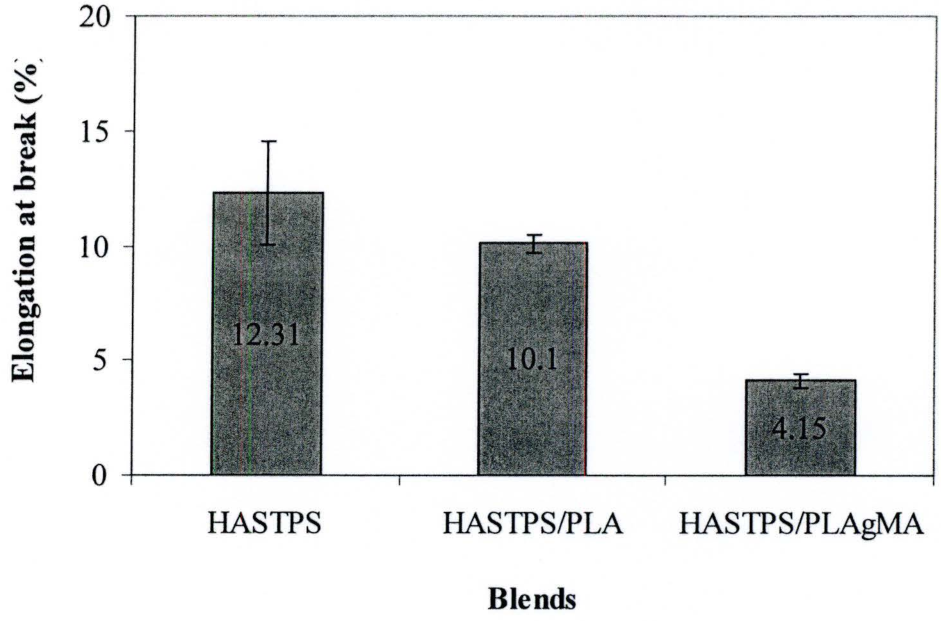
Nanoclay (Cloisite 30B) was applied in the system to improve the mechanical properties. Mechanical properties of thermoplastic cornstarch/PLAgMA blended with various contents of Cloisite 30B were investigated. Blending ratios are shown in Table 3.2. Table 4.8 and Figure 4.14 illustrated the results of tensile testing, indicating all the samples filled with clay showed an improvement of their tensile strengths and moduli with respect to the unfilled samples. Tensile strength increased from 7.165 MPa to 8.139 MPa and modulus increased from 440.3 MPa to 606.2 MPa as the clay concentration increased from 0% to 5%. Tensile strength of blend with 5% clay approach to the tensile


Tensile strength (MPa)
0
2
4
6
8
10
0.768
3.287
7.165
HASTPS
HASTPS/PLA
HASTPS/PLAgMA
Blends

(a)

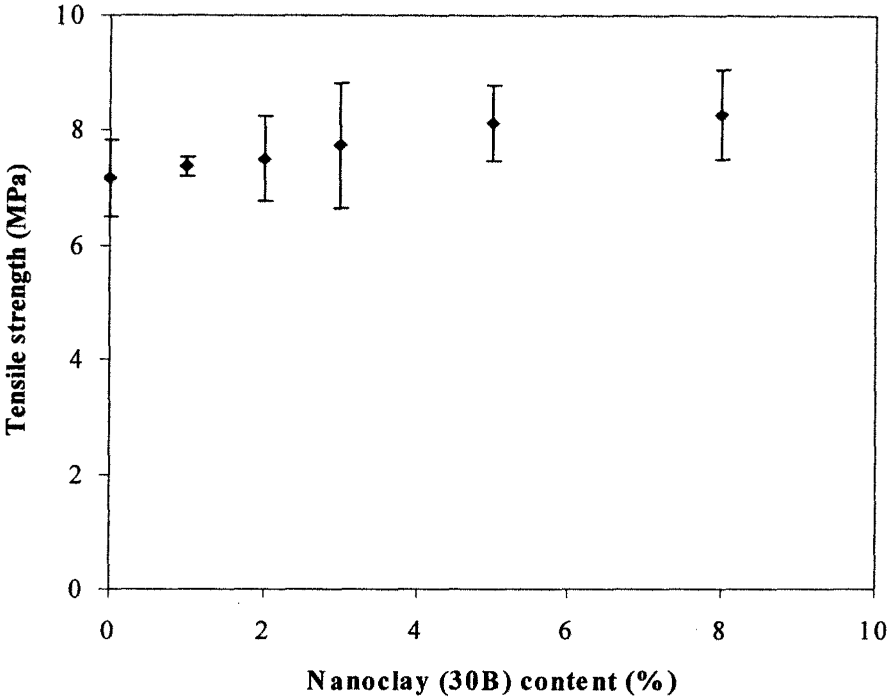

Modulus (MPa)
0
200
400
600
16.9
156.8
440.3
HASTPS
HASTPS/PLA
HASTPS/PLAgMA
Blends

(b)

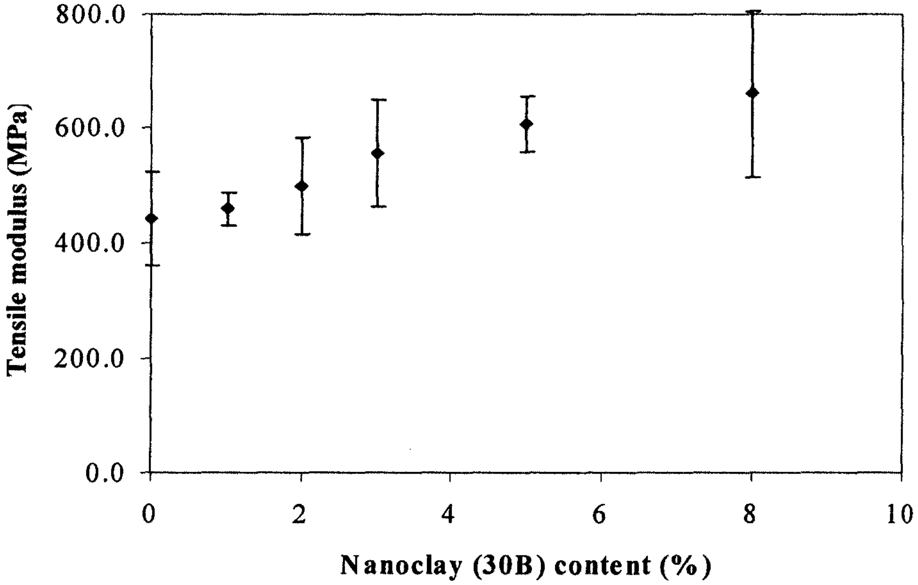


(c)

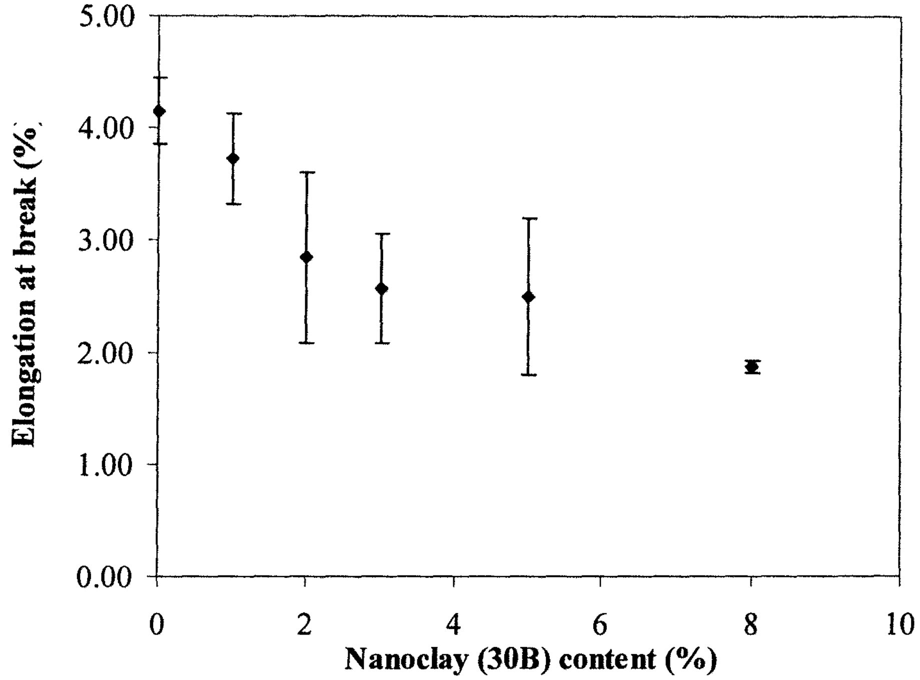
Figure 4.13 Comparison of mechanical properties of plasticized high amylose cornstarch (HASTPS), HASTPS/PLA and HASTPS/PLAgMA; (a) tensile strength, (b) modulus, and (c) elongation at break. (Blending ratios: HAS/glycerol/water: 50/36/14 wt/wt, HASTPS/PLA: 70/30 wt/wt and HASTPS/PLAgMA: 70/30 wt/wt)


10
8
6
4
2
0
Tensile strength (MPa)
0
2
4
6
8
10
Nanoclay (30B) content (%)

(a)


800.0
600.0
400.0
200.0
0.0
Tensile modulus (MPa)
0
2
4
6
8
10
Nanoclay (30B) content (%)

(b)



(c)

Figure 4.14 Mechanical properties of thermoplastic high amylose cornstarch (HASTPS)/ PLAgMA blended with various nanoclay contents; (a) tensile strength, (b) modulus, and (c) elongation at break. (Blending ratios: HAS/glycerol/water: 50/36/14 wt/wt, HASTPS/PLAgMA: 70/30 wt/wt and Cloisite 30B ratios are 0%, 1%, 2%, 3%, 5% and 8%, wt%, respectively.)

Table 4.8 Effect of nanoclay (Cloisite 30B) on mechanical properties of thermoplastic high amylose cornstarch/PLAgMA blends

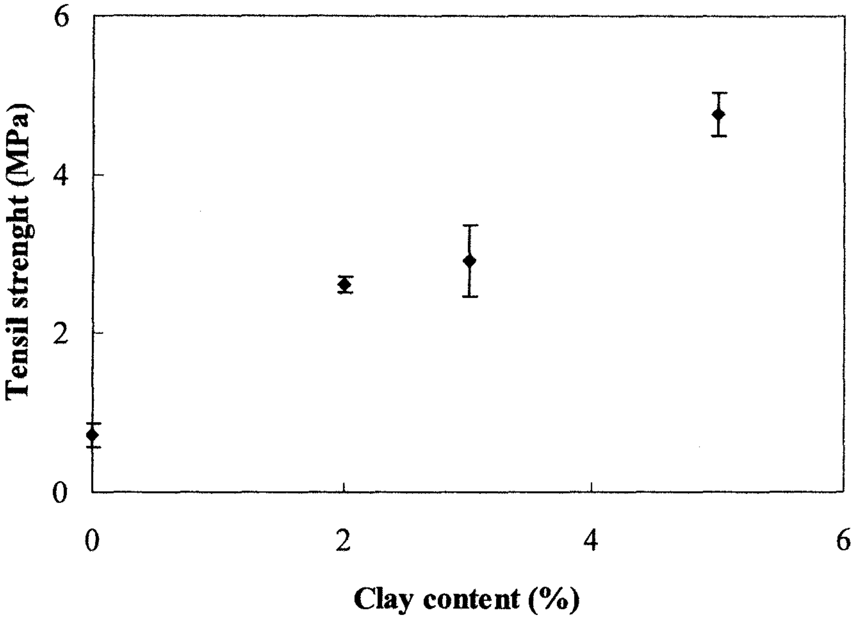
No	Starch Type	Blends	Ratio of Blends	Clay content wt%	Mechanical Properties		
					Tensile strength MPa	Modulus MPa	Elongation at break %
1	H.A.S	HAS-TPS36	100/0	0	0.768±0.095	16.9±3.9	12.31±2.25
2	H.A.S	HAS-TPS36/PLA	70/30	0	3.287±0.528	156.8±19.5	10.10±0.41
3	H.A.S	HAS-TPS36/PLAgMA	70/30	0	7.165±0.674	440.3±81.3	4.15±0.30
4	H.A.S	HAS-TPS36/PLAgMA	70/30	1	7.366±0.158	457.6±29.5	3.73±0.40
5	H.A.S	HAS-TPS36/PLAgMA	70/30	2	7.506±0.740	497.2±84.4	2.85±0.76
6	H.A.S	HAS-TPS36/PLAgMA	70/30	3	7.729±1.083	555.0±94.0	2.57±0.49
7	H.A.S	HAS-TPS36/PLAgMA	70/30	5	8.139±0.668	606.2±49.0	2.51±0.70
8	H.A.S	HAS-TPS36/PLAgMA	70/30	8	8.286±0.795	660.2±146.6	1.87±0.05

strength of low-density polyethylene (LDPE) but the modulus exceeds LDPE (tensile strength of 11.7 MPa and modulus of 393 MPa for LDPE); nevertheless, tensile strength and modulus are much smaller than polystyrene (tensile strength of 43.9 MPa and modulus of 3000 MPa for PS). However, elongation at break decreased to 1.87% from 10.10% as the concentration of clay increased from 0% to 8%. Similarly, plasticized normal cornstarch/PLAgMA blends filled with Cloisite 30B also exhibited an improvement in tensile strength and modulus. Elongation at break shows a decrease as the concentration of Cloisite 30B increases as well as HASTPS/PLAgMA/ Cloisite 30B blends (as shown in Table 4.9 and Figure 4.15)

Cloisite 30B is a type of organoclay with a good dispersion in the PLA matrix and it can form a nanocomposite system with PLA (Pluta, 2006). However, the dispersion of Cloisite 30B in a starch matrix is not as good as in PLA. Park et al (2002) thought that Cloisite 30B is hydrophobic and does not match with the polarity of TPS, indicating the lack of compatibility between TPS and Cloisite 30B. Interestingly, PLAgMA might act as a compatibilizer to enhance the dispersion of Cloisite 30B into TPS matrix. This is a possible reason why the tensile strength and modulus of the samples filled with Cloisite 30B improved compared to the unfilled sample. The reduction of elongation may be due to the interaction between clay and polymer matrices, which may lead to reduced polymeric chain mobility making the material more rigid (Modesti, 2005).

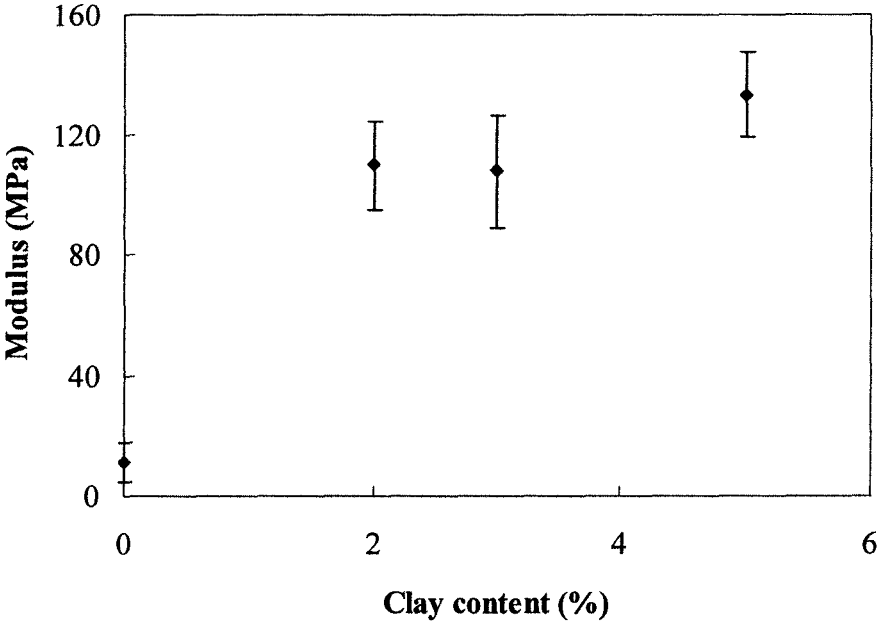
Table 4.9 Effect of nanoclay (Cloisite 30B) on mechanical properties of thermoplastic high amylose cornstarch/PLAgMA blends

No	Starch Type	Blends	Ratio of Blends	Clay content wt%	Mechanical Properties		
					Tensile strength MPa	Modulus MPa	Elongation at break %
1	N. S.	NS-TPS36/PLAgMA	70/30	0	0.726±0.141	11.2±6.7	18.09±5.05
2	N. S.	NS-TPS36/PLAgMA	70/30	2	2.609±0.107	109.5±15.0	10.67±1.50
3	N. S.	NS-TPS36/PLAgMA	70/30	3	2.914±0.460	107.5±18.5	5.76±0.13
4	N. S.	NS-TPS36/PLAgMA	70/30	5	4.766±0.276	133.0±14.2	3.96±0.57



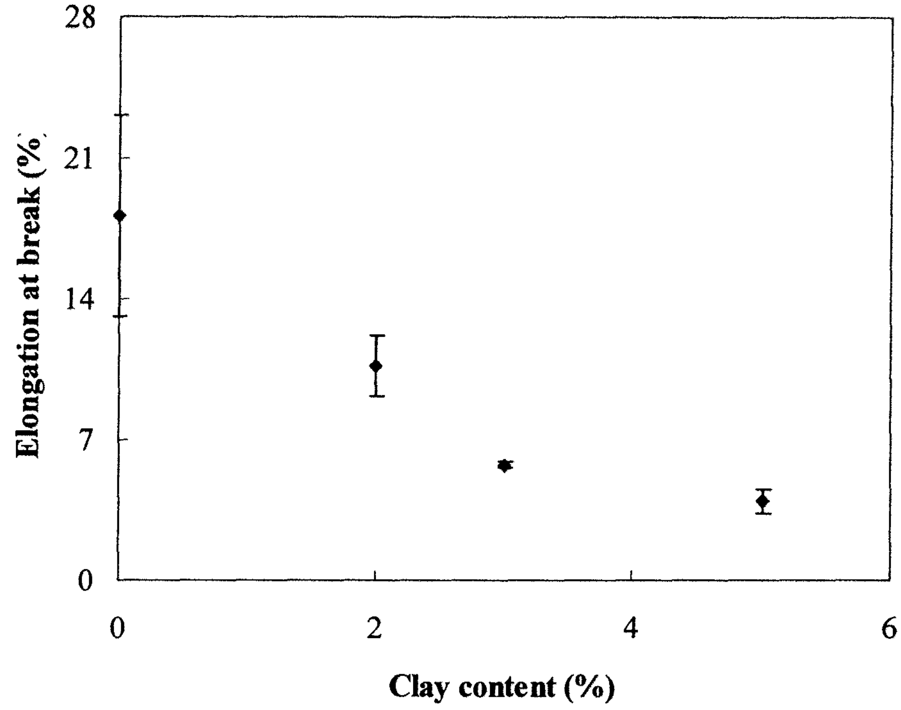
6
4
2
0
Tensil strenght (MPa)
0
2
4
6
Clay content (%)

(a)



160
120
80
40
0
Modulus (MPa)
0
2
4
6
Clay content (%)

(b)



(c)

Figure 4.15 Mechanical properties of thermoplastic normal cornstarch (NSTPS)/ PLAgMA blended with various nanoclay contents; (a) tensile strength, (b) modulus, and (c) elongation at break. (Blending ratios: HAS/glycerol/water: 50/36/14 wt/wt, HASTPS/PLAgMA: 70/30 wt/wt and Cloisite 30B ratios are 0%, 2%, 3%, and 5%, wt%, respectively.)

The effects of blending time on mechanical properties of blends were evaluated and the testing results are shown in Table 4.10. A longer blending time can provide clay a better dispersion and a greater interaction in material system, but it can cause thermal degradation as blending time is longer than 6 min (Huang, 2005). The greater interaction leads to improvement both in tensile strength and modulus but it could also be responsible for the lower elongation at break (Modesti et al, 2005).

Table 4.10 Effect of blending time on mechanical properties of thermoplastic high amylose cornstarch/PLAgMA/Cloisite 30B (70/30/2 wt/wt) blends

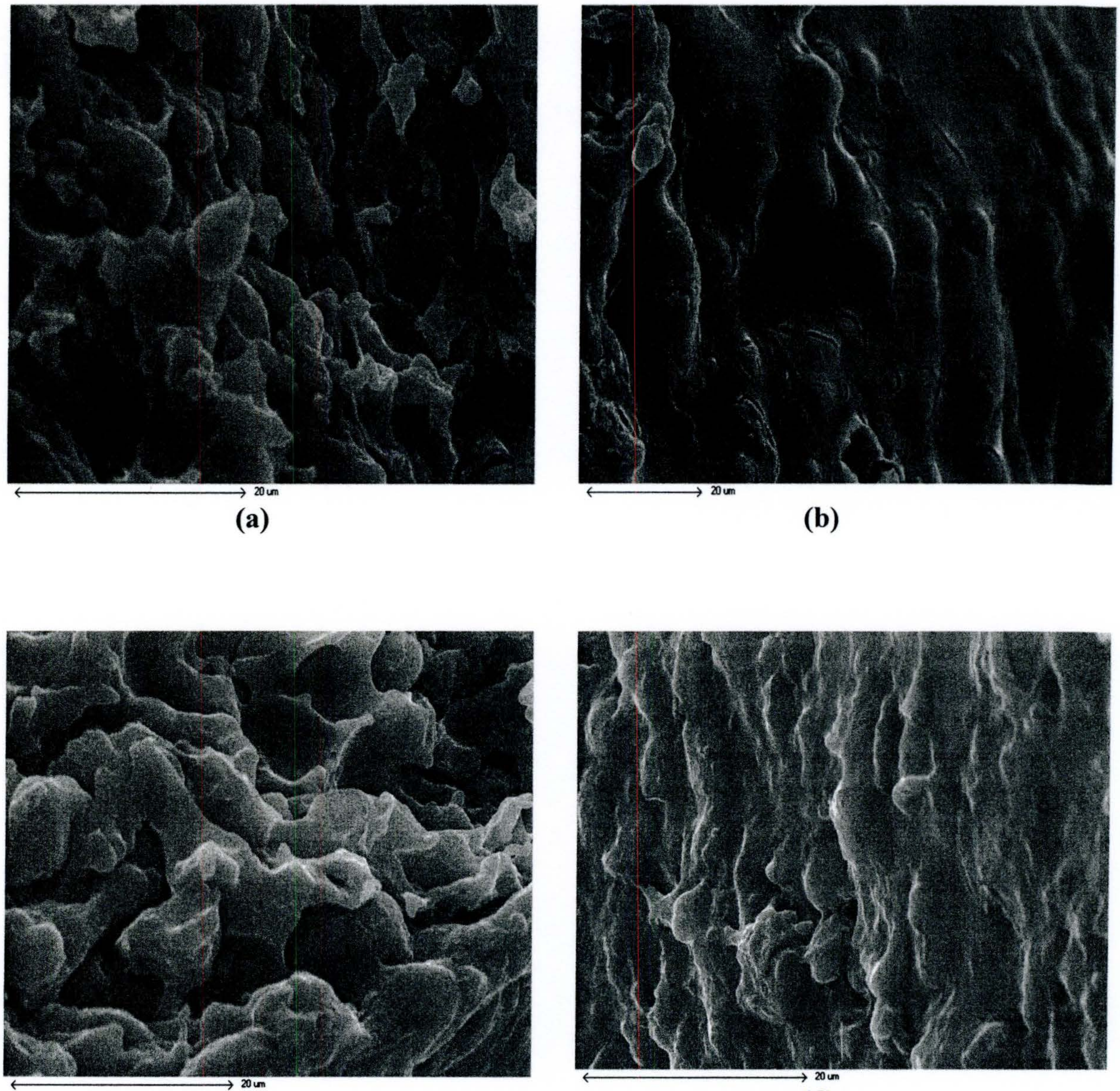
No	Blends	Ratio of Blends wt/wt	Clay content wt%	Blending time min	Mechanical Properties		
					Tensile strength MPa	Modulus MPa	Elongation at break %
1	HASTPS-PLAgMA	70/30	2	4	6.772±0.409	434.3±52.9	3.06±0.64
2	HASTPS-PLAgMA	70/30	2	6	7.506±0.740	497.2±84.4	2.85±0.76

4.1.4 Morphological Properties

Mechanical properties of polymer blends are highly related to their morphology. Morphologies of selected samples were observed on a Philips scanning electron microscope (SEM) and the images are shown in Figure 4.16 and Figure 4.17.

For MA compatibilized thermoplastic high amylose cornstarch/PLA blends (in Figure 4.16 (a) and (b)), SEM micrographs show a very good compatible morphology without cavities and edges resulting from poor interfacial adhesion. Images of thermoplastic normal cornstarch indicate the same behavior (in Figure 4.16 (c) and (d)). This result implied that the reaction between hydroxyl groups on the starch molecule and anhydride groups on MA increased the adhesion between starch and PLA phase. This result also explained why the blends compatibilized by MA show higher tensile strength and modulus than the blends unfilled by MA do (see section 4.1.3).

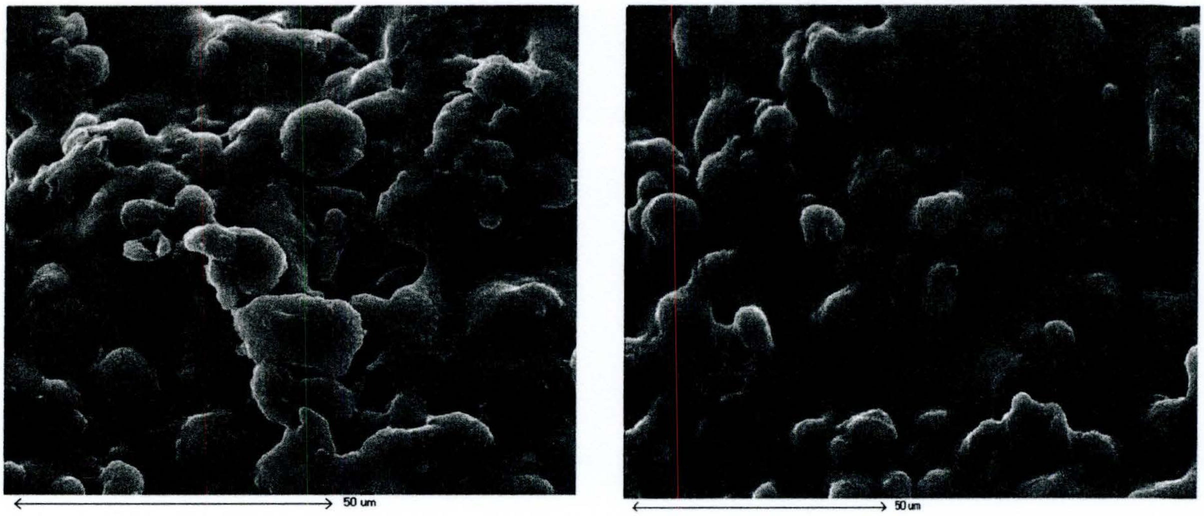
The effect of blending time on the morphological properties was evaluated. Figure 4.17 showed the images of SEM of blends prepared under blending times of 4 minutes and 6 minutes. Diameters of the granules of starch in 4-minutes blends were approximately 10-12 μm but that of 6-minute blends showed 5-8 μm diameters, which is much smaller than 4-minute blends did. The better mechanical properties were exhibited in blend with 6-minutes blending time also because of its smooth and uniform morphology.



(a) (b)

(c) (d)

Figure 4.16 Comparisons of SEM images of thermoplastic starch/PLA and MA compatibilized thermoplastic starch/PLA blends: (a) HAS-TPS/PLA, (b) HAS-TPS/PLAgMA, (c) NS-TPS/PLA, and (d) NS-TPS/PLAgMA. TPS/PLA blend ratio (wt/wt): 70/30, MA and L101 content (wt%): 2% and 0.25% PLA basis, respectively.



(a) **(b)**

Figure 4.17 Comparisons of SEM images of thermoplastic high amylose cornstarch/PLA/Cloisite 30B prepared under the different blending time on Haake rheomixer: (a) 4min, and (b) 6min. HAS-TPS/PLAgMA/Cloisite 30 ratio: 70/30/2 wt/wt.

4.1.5 Water Resistance

The contact angle formed between a water droplet placed at the surface of a material and the kinetics of spreading are related to the hydrophobicity of material. For TPS, the water droplet is very rapidly absorbed because the hydroxyl group in starch can form a hydrogen bond with water (Averous et al, 2000). The contact angles of HASTPS/PLAgMA/clay and NSTPS/PLAgMA/clay blends were measured and illustrated in Figure 4.18 and Figure 4.19, respectively. For blends of HASTPS/PLAgMA /clay, the initial angles are 50.7°, 59.5° and 66.2° as the contents of clay are filled at 2%, 3% and 5%, respectively but the drop rates for three formulations stay at the same level (shown in Figure 4.18). For blends NSTPS/PLAgMA/clay, the initial angles are 62.0° and 70.3° as the contents of clay are 3% and 5% (shown in Figure 4.19). A slight increase was achieved as clay increased for both types of cornstarch. In all cases, the water droplet was penetrated into the samples and it was believed to be absorbed by the component of starch.

In order to increase the hydrophobicity, AKD, a type of sizing agent, was introduced into the material system. Normally, AKD acted as a sizing agent was widely used in sizing treatment of paper products to improve the hydrophobicity of the paper. In this work, two treatment methods were applied: surface sizing and internal sizing. The test results of surface sizing are shown in Figure 4.20. Compared to untreated samples, treated samples exhibited an improvement in hydrophobicity for both types of starch. For the blends that included HAS, the evolution of contact angle with time is slower

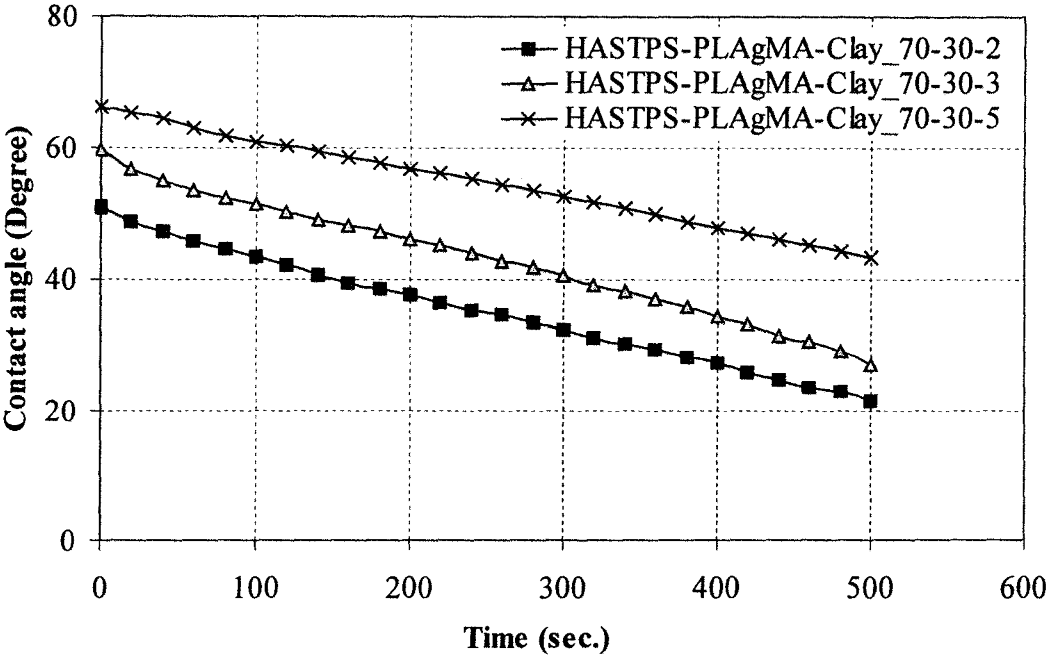


Figure 4.18 Contact angles of thermoplastic high amylose cornstarch/PLAgMA/Cloisite 30B. Ratio of TPS/PLAgMA: 70/30, wt/wt. Concentration of Cloisite 30B: 2%, 3%, and 5% (wt%) respectively.

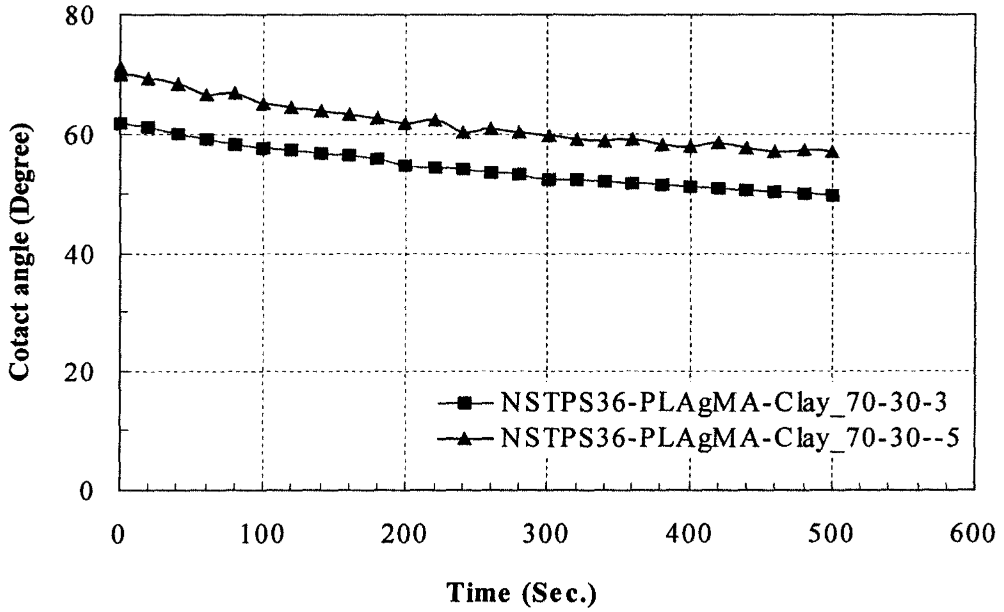
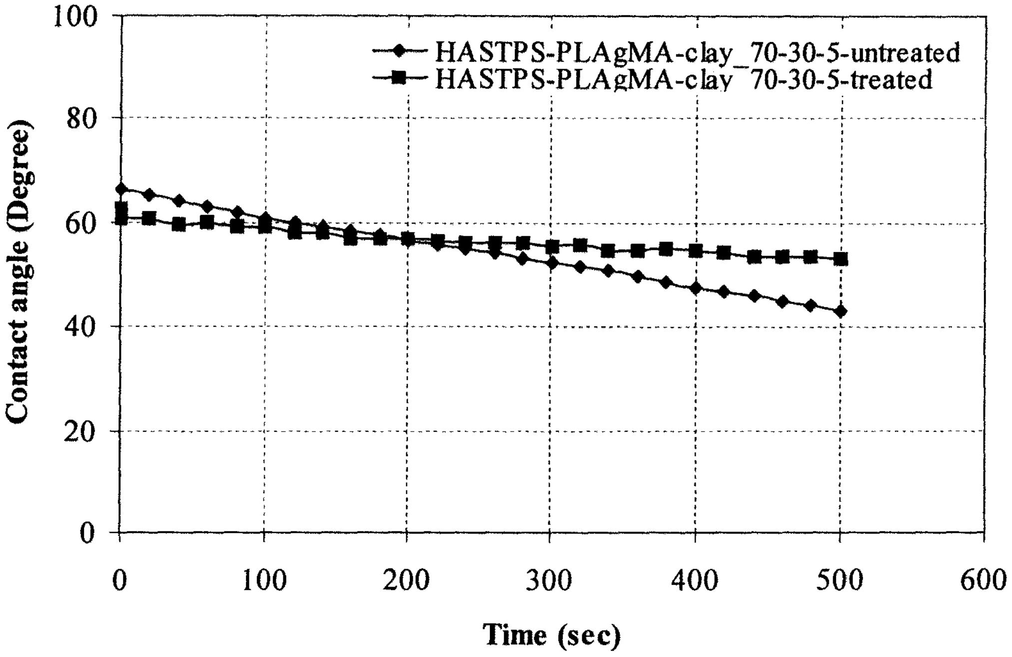
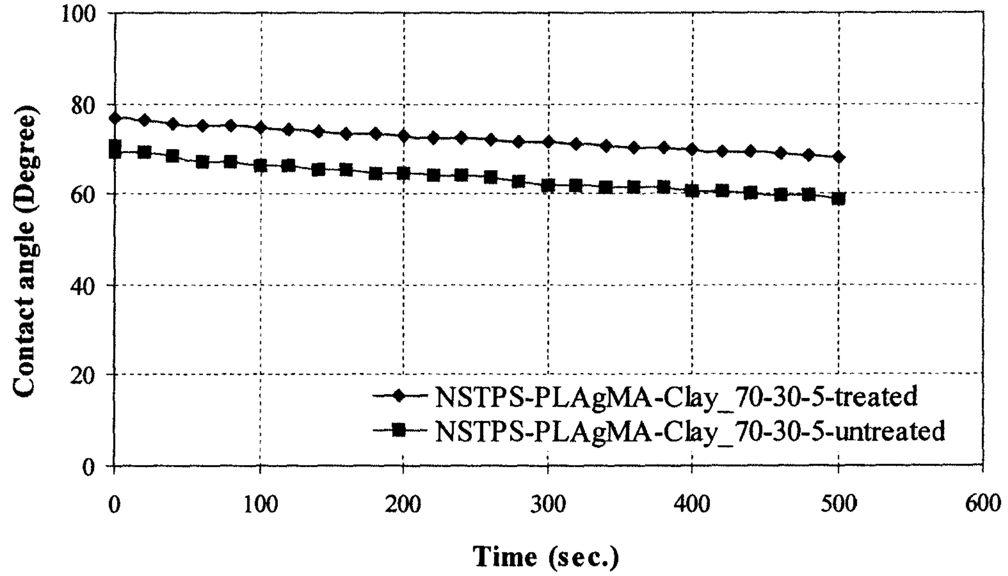


Figure 4.19 Contact angles of thermoplastic normal cornstarch/PLAgMA/Cloisite 30B. Ratio of TPS/PLAgMA: 70/30, wt/wt. Concentration of Cloisite 30B: 3% and 5% (wt%).



(a)



(b)

Figure 4.20 Effect of AKD surface sizing on contact angles of TPS/PLAgMA/Cloisite 30B blends, (a) high amylose cornstarch, (b) normal cornstarch. Ratio of TPS/PLAgMA: 70/30, wt/wt. Concentration of Cloisite 30B: 5%, wt%.

and more constant (illustrated in Figure 4.20a). For the blends involved NS, the sample treated by AKD showed higher initial angle than the one untreated did. The initial angles were increased from 69.5 to 76.7 after surface treatment by AKD.

Similar to the reaction between AKD and cellulose in the paper sizing process, AKD also easily reacts with hydroxyl functional groups on starch molecular chains. Figure 4.21 shows the possible reaction of AKD with starch, but this reaction needs more work to prove.

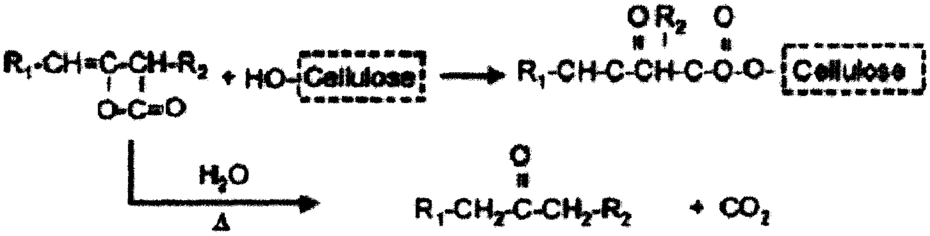
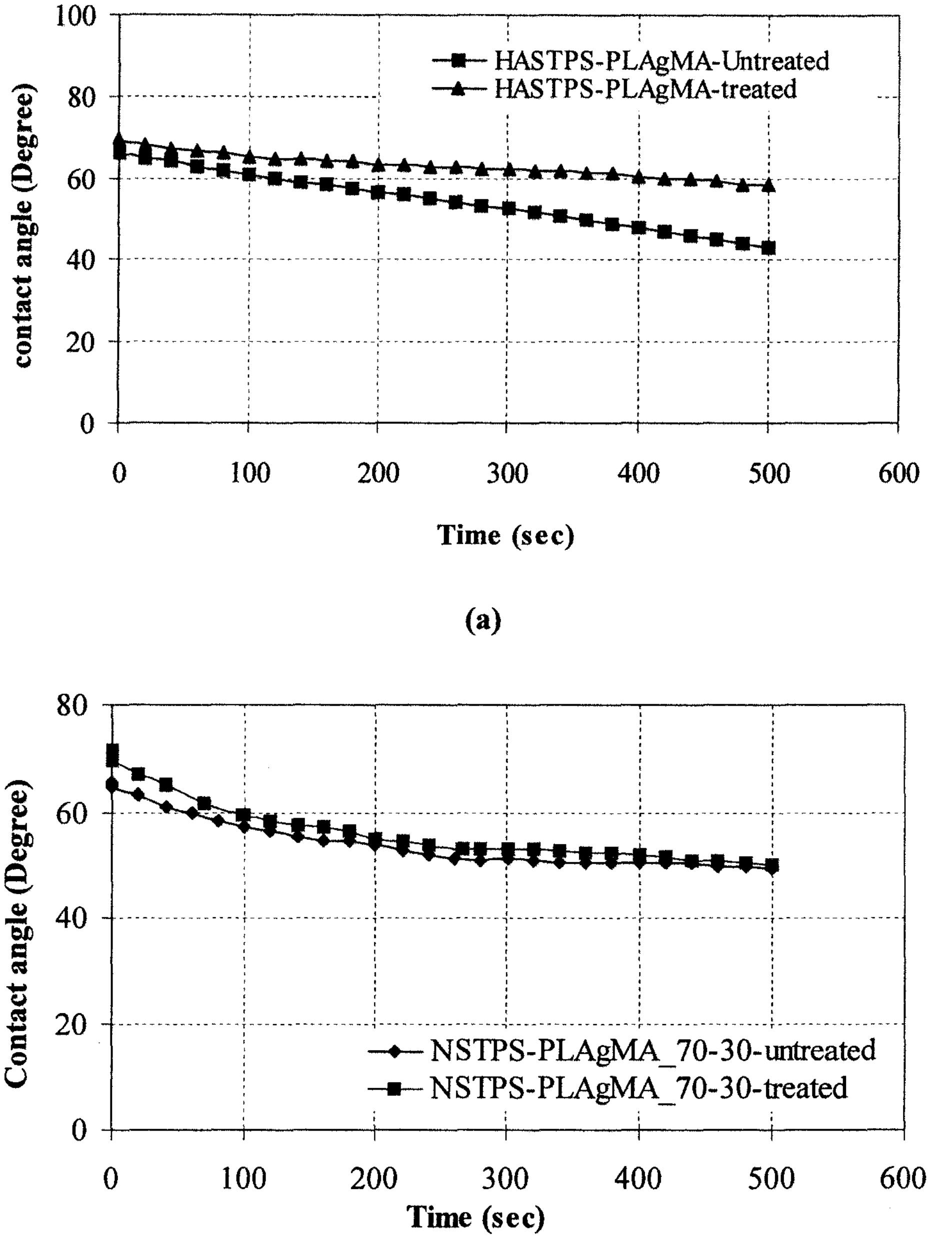


Figure 4.21 Possible reaction between AKD and starch

The internal sizing treatment was performed but no significant improvement on hydrophobicity was found as shown in Figure 4.22.



(a)

(b)

Figure 4.22 Effect of AKD internal sizing on contact angles of TPS/PLAgMA blends, (a) high amylose cornstarch, (b) normal cornstarch. Ratio of TPS/PLAgMA: 70/30, wt/wt. Concentration of AKD: 0.1% starch basis, wt%.

4.2 Structure and Properties of Thermoplastic Pulse Starches and PLAgMA Blends with Nanoclay

In this research work, three types of pulse starches were studied: mung bean, lentil and pea. Pulse starches were plasticized in the presence of water and glycerol to form thermoplastic pulse starches. Similar to the studies with cornstarch, rheological, thermal and mechanical properties and hydrophobicity of blends filled with pulse starches were investigated.

4.2.1 Thermal Properties

The thermal properties of thermoplastic pulse starch/PLAgMA were evaluated using DSC. The DSC thermograms of blends in a second thermal scan are recorded and the data read from DSC thermograms were listed in Table 4.11.

The glass transition temperatures (T_g), crystallization temperatures (T_c) and melting temperature (T_m) for blends (70/30 wt/wt) of thermoplastic bean starch/PLAgMA, lentil starch/ PLAgMA and pea starch/PLAgMA were studied. The results indicated that three types of plasticized pulse starches blended with PLAgMA exhibited a very similar thermal behavior. Compared to the thermal transition temperature and DSC thermogram of PLAgMA (Figure 4.3), the similar thermal behavior (as shown in Figure 4.23) indicated the same results from the investigations of cornstarch were achieved: the thermal behaviors are mainly dominated by the component of PLAgMA.

However, the melting enthalpy and crystallization enthalpy of bean starch showed much lower values than other two pulse starches, which may be attributed to the molecular structure and granular size of bean starch.

Table 4.11 DSC characteristics of thermoplastic pulse starch/PLAgMA/nanoclay blends

Starch Type	Blends	Ratio of Blends wt/wt	Clay content wt%	T_g (°C)	T_c (°C)	Crystallization enthalpy, J/g	T_m (°C)	Melting enthalpy J/g
Bean	Be-TPS/PLAgMA	70/30	0%	59.7	116.0	5.945	153.1	5.546
	Be-TPS/PLAgMA	70/30	5%	60.5	116.8	5.744	154.0	7.630
Lentil	Len-TPS/PLAgMA	70/30	0%	59.5	115.6	10.02	153.5	9.280
	Len-TPS/PLAgMA	70/30	5%	59.6	115.7	9.83	153.9	8.715
Pea	Pe-TPS/PLAgMA	70/30	0%	60.2	115.7	9.269	153.7	8.326
	Pe-TPS/PLAgMA	70/30	5%	59.2	109.9	10.86	153.7	10.080

All DSC data were read from the second thermal scan in DSC thermograms. T_g, T_c and T_m are glass transition temperature, crystallization temperature and melting temperature, respectively.

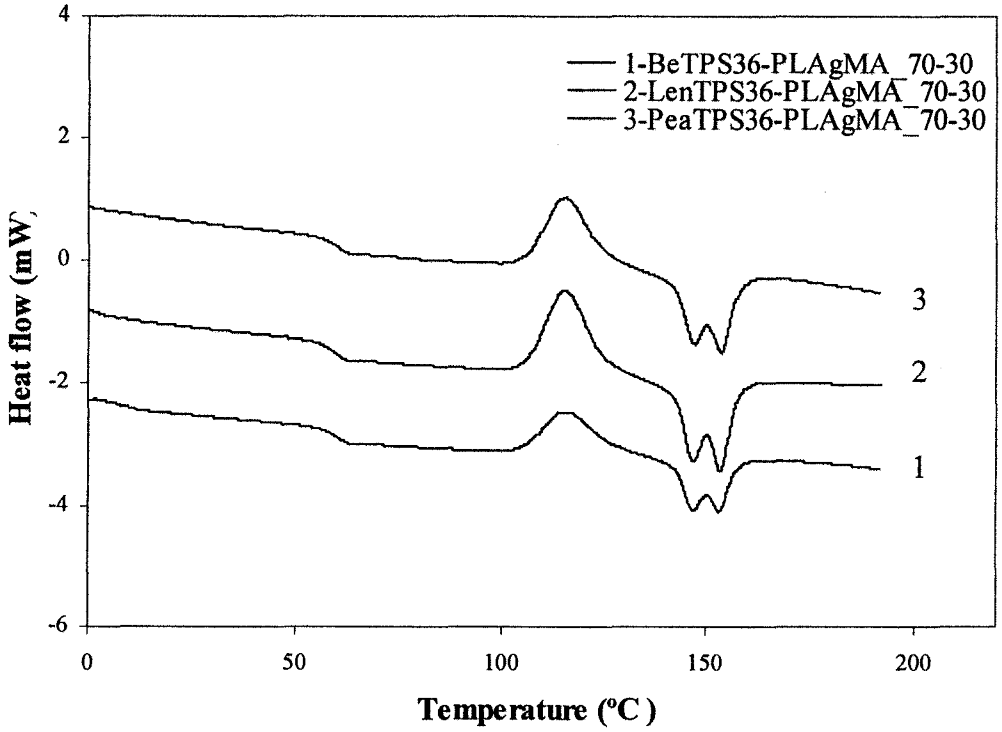


Figure 4.23 DSC thermograms of three types of thermoplastic pulse starch (TPPS)/ PLAgMA blends in a second thermal scan. Starch/water/glycerol ratio (wt/wt): 50/14/36; TPPS/PLAgMA ratio (wt/wt): 70/30.

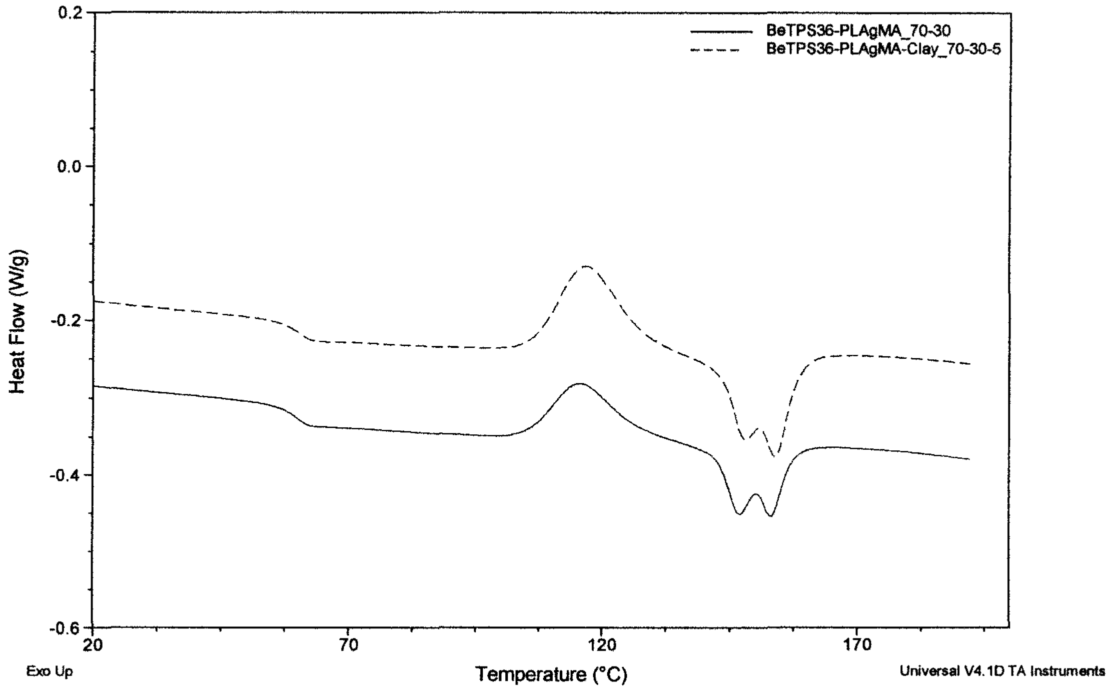


Figure 4.24 DSC thermograms of thermoplastic bean starch (TPBS)/PLAgMA blend and TPBS/PLAgMA/Cloisite 30B blend in a second thermal scan. Bean starch/water/glycerol ratio (wt/wt): 50/14/36; TPBS/PLAgMA ratio (wt/wt): 70/30 and Cloisite 30B content: 5%, wt%.

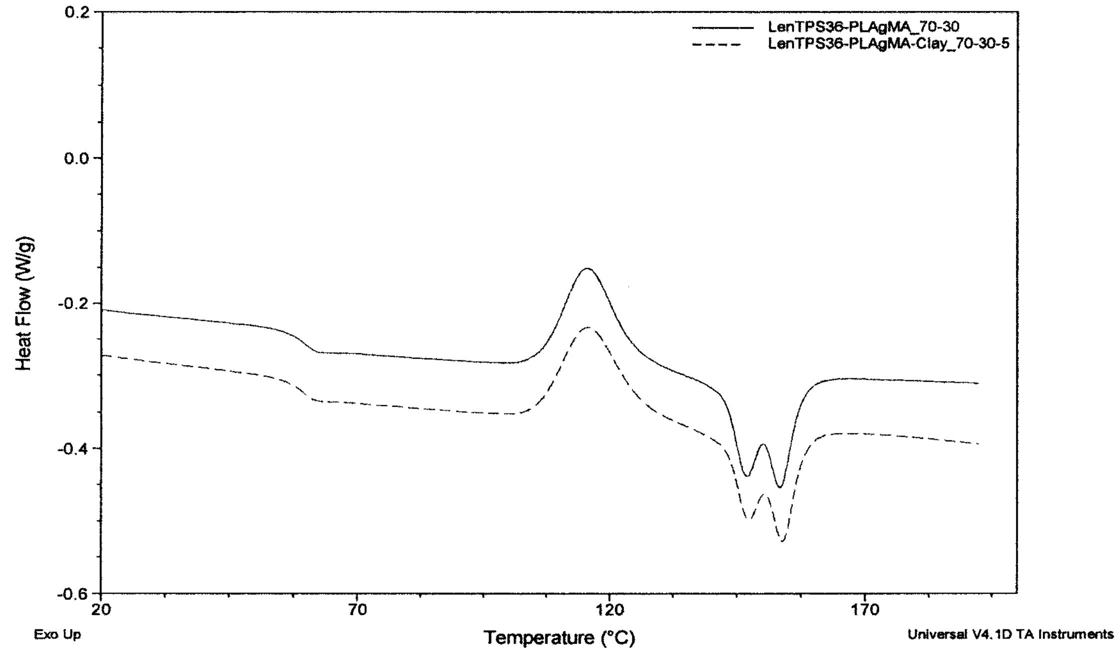


Figure 4.25 DSC thermograms of thermoplastic lentil starch (TPLS)/PLAgMA blend and TPBS/PLAgMA/Cloisite 30B blend in a second thermal scan. Lentil starch/water/ glycerol ratio (wt/wt): 50/14/36; TPLS/PLAgMA ratio (wt/wt): 70/30 and Cloisite 30B content: 5%, wt%.

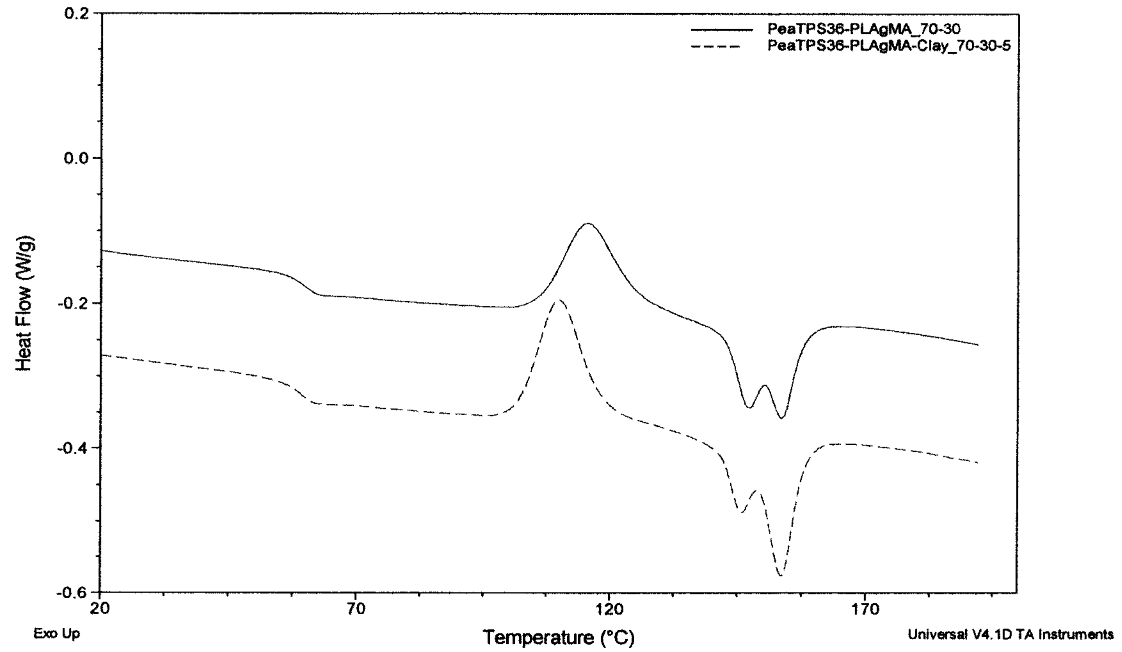


Figure 4.26 DSC thermograms of thermoplastic pea starch (TPPeS)/PLAgMA blend and TPPS/PLAgMA/Cloisite 30B blend in a second thermal scan. Pea starch/water/ glycerol ratio (wt/wt): 50/14/36; TPPeS/PLAgMA ratio (wt/wt): 70/30 and Cloisite 30B content: 5%, wt%.

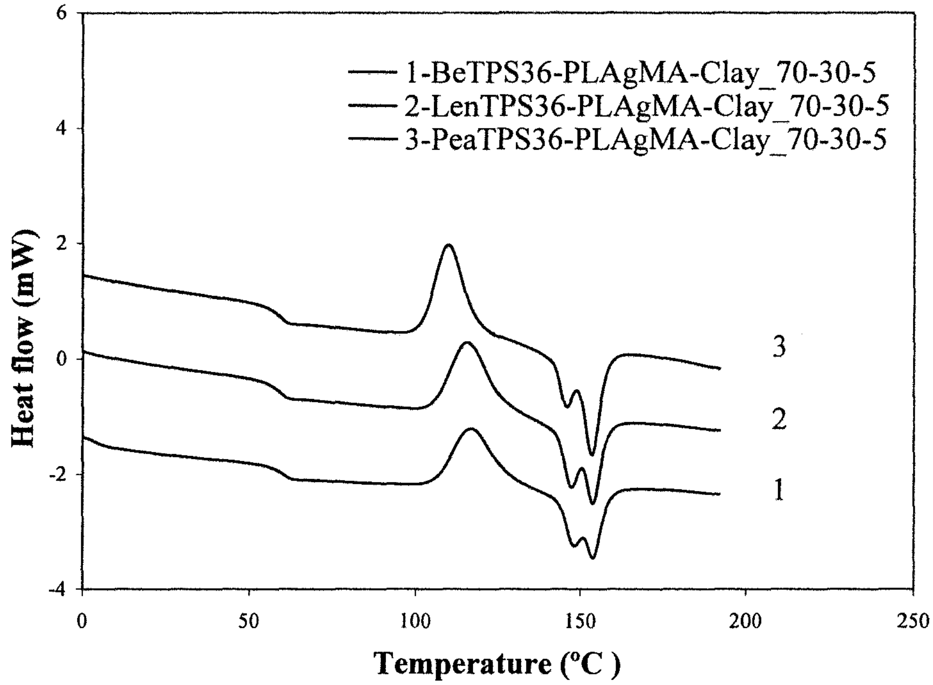


Figure 4.27 DSC thermograms of three types of thermoplastic pulse starch (TPPS)/ PLAgMA/Cloisite 30B blends in a second thermal scan. Starch/water/glycerol ratio (wt/wt): 50/14/36; TPPS/PLAgMA ratio (wt/wt): 70/30; Cloisite 30B concentration: 5% wt%

Nanoclay (Cloisite 30B) was also used to improve the properties of blends. The effects of nanoclay on thermal properties of thermoplastic pulse starch/ PLAgMA blends were also analyzed on DSC. DSC thermograms in the second thermal scan were shown from Figure 4.24 to Figure 4.26. Figure 4.27 showed comparison of thermal behaviors of three types of thermoplastic pulse starch blends filled with 5% of Cloisite 30B. The effects of nanoclay (Cloisite 30B) on thermal properties are very slight except pea starch. Crystallization temperature of pea decreased from 115.7° C to 109.9° C in presence of Cloisite 30B. The difference may be attributed to some physical properties of pea starch such as granular size, molecular structures and molecular weight distribution.

4.2.2 Rheological Properties

The effects of nanoclay on the rheological behaviors of thermoplastic pulse starch/ PLAgMA were investigated at 150° C. As illustrated by Figures 28-30, the thermoplastic pulse starch materials exhibited shear-thinning behaviors, which can be expressed by power-law equation as shown in Eq. 4-2. The power-law parameters calculated from power-law equation were shown in Table 4.12. Consistency values of TPPS/PLAgMA blends are 1915 Pa.s^n, 7917 Pa.s^n and 12219 Pa.s^n for bean, lentil and pea starch, respectively. The values are increased to 10127 Pa.s^n, 11614 Pa.s^n and 18522 Pa.s^n in the presence of 5% Cloisite 30B.

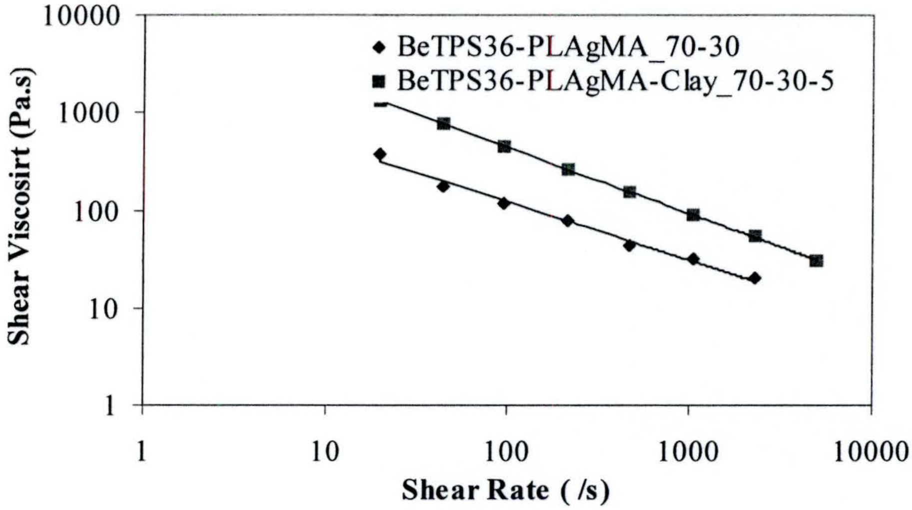


Figure 4.28 Rheological properties of thermoplastic bean starch (TPBS)/PLAgMA(70/30) blends with 5% of Cloisite 30B (starch/glycerol/water ratio: 50/36/14 wt/wt) (Temperature on Rosand: 150° C)

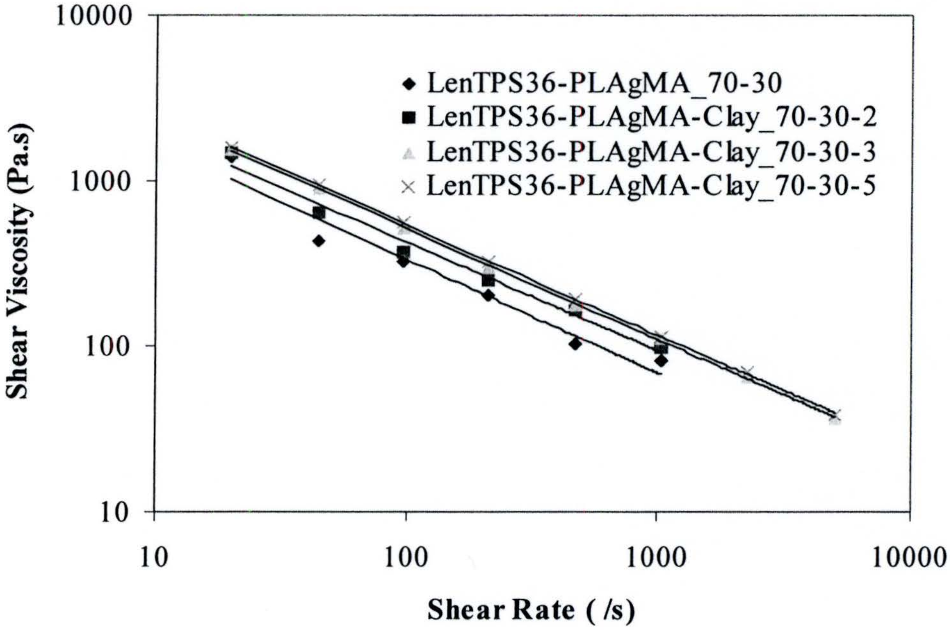


Figure 4.29 Rheological properties of thermoplastic lentil starch (TPLS)/PLAgMA (70/30) blends with 5% of Cloisite 30B (starch/glycerol/water ratio: 50/36/14 wt/wt) (Temperature on Rosand: 150° C)

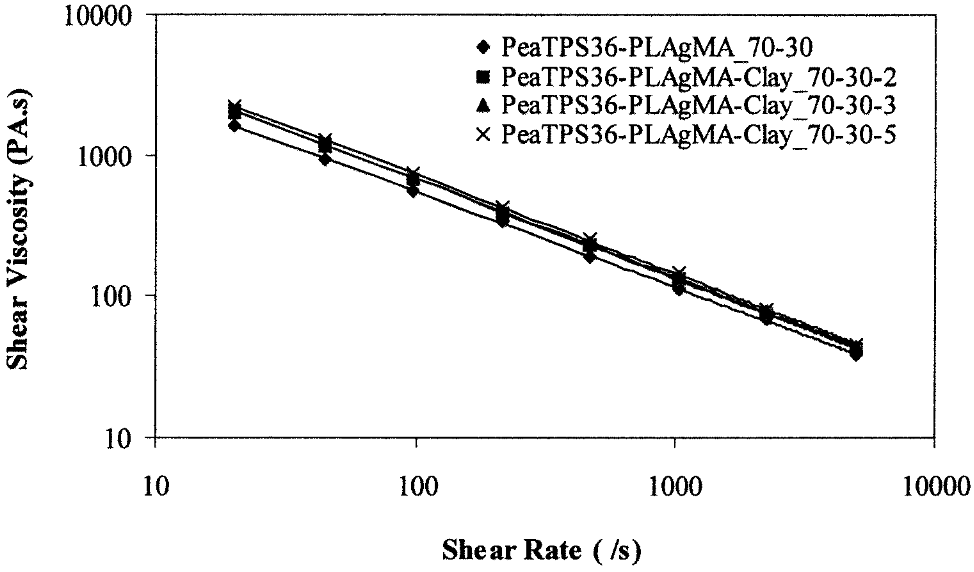


Figure 4.30 Rheological properties of thermoplastic pea starch (TPPeS)/PLAgMA (70/30) blends with 5% of Cloisite 30B (starch/glycerol/water ratio: 50/36/14 wt/wt) (Temperature on Rosand: 150° C)

Table 4.12 Power-law parameters for thermoplastic pulse starch/PLAgMA/Cloisite 30B blends

Starch Type	Blends	Content of Cloisite 30B (%)	Consistency index, m, Pa.s^n	Power law index, n	R^2
Bean	BeTPS-PLAgMA_70-30	0	1915	0.4017	0.9893
	BeTPS-PLAgMA-30B_70-30-5	5	10127	0.3194	0.9999
Lentil	LenTPS-PLAgMA-30B_70-30	0	7917	0.3135	0.9526
	LenTPS-PLAgMA-30B_70-30-2	2	8568	0.3472	0.9808
	LenTPS-PLAgMA-30B_70-30-3	3	11133	0.3316	0.9997
	LenTPS-PLAgMA-30B_70-30-5	5	11614	0.3340	0.9999
Pea	PeaTPS-PLAgMA_70-30	0	12219	0.3245	0.9998
	PeaTPS-PLAgMA-30B_70-30-2	2	17041	0.2967	0.9999
	PeaTPS-PLAgMA-30B_70-30-3	3	16731	0.3026	0.9998
	PeaTPS-PLAgMA-30B_70-30-5	5	18522	0.2958	0.9999

Temperature: 150° C

All the blends filled with Cloisite 30B showed an increase of their shear viscosities in comparison to the unfilled blends. This result may be attributed to the high dispersion of Cloisite 30B in the polymeric matrix but it needs to be proofed.

4.2.3 Mechanical Properties

Mechanical properties of thermoplastic pulse starches (TPPS) and TPPS/ PLAgMA blended with Cloisite 30B were studied on an Instron tensile testing machine. Figures 4.31, 4.32 and 4.33 show tensile strength, tensile modulus and elongation at breaks respectively. For bean and lentil starch, tensile strength and modulus were significantly improved in the presence of PLAgMA with respect to the blends of pulse starches plasticized by glycerol/water (36/14 wt/wt). But the improvement of tensile strength for bean starch was slight. Table 4.13 presented the mechanical properties of pulse starches quantitively. Tensile strengths of plasticized pea and lentil were increased from 1.717 MPa and 1.264 MPa to 4.371 MPa and 3.084 MPa as blending with PLAgMA (ratio of TPS/PLAgMA: 70/30 wt/wt). Moduli were increased to 159.9 MPa and 156.9 MPa from 8.059 MPa and 3.766 MPa. However, the improvement for bean starch was not as large as those two starches: modulus increased from 4.793 MPa to 86.07 MPa and tensile strength increased from 1.085 MPa to 1.295 MPa. The possible reason may be related to the bean molecular structure such as length of branch chains, molecular weight and distribution and reaction between bean starch and PLA in presence of Luperox 101. Little information is available concerning effects of bean molecular structure on mechanical properties.

Table 4.13 Mechanical properties of thermoplastic pulse starch and its blends with PLAgMA and Cloisite 30B

No	Starch Type	Blends	Ratio of Blends wt/wt	Clay content wt%	Mechanical Properties		
					Tensile strength MPa	Modulus MPa	Elongation at break %
1	Pea	PeTPS36	100/0	0	1.717±0.297	8.059±2.6	79.73±7.23
2	Pea	PeTPS36/PLAgMA	70/30	0	4.371±0.298	159.9±12.9	8.13±2.46
3	Pea	PeTPS36/PLAgMA	70/30	2	5.245±0.418	264.3±70.8	4.75±1.18
4	Pea	PeTPS36/PLAgMA	70/30	3	5.288±0.822	259.9±29.8	4.27±1.34
5	Pea	PeTPS36/PLAgMA	70/30	5	6.215±0.297	329.2±46.8	3.87±0.34
6	Lentil	LenTPS36	100/0	0	1.264±0.084	3.766±0.6	94.32±7.07
7	Lentil	LenTPS36/PLAgMA	70/30	0	3.084±0.417	156.9±39.8	5.91±1.46
8	Lentil	LenTPS36/PLAgMA	70/30	2	3.554±0.169	162.0±7.7	7.47±1.99
9	Lentil	LenTPS36/PLAgMA	70/30	3	3.854±0.410	155.0±24.3	8.30±0.55
10	Lentil	LenTPS36/PLAgMA	70/30	5	4.719±0.235	222.7±32.8	9.55±1.88
11	Bean	BeTPS36	100/0	0	1.085±0.097	4.793±0.5	85.57±10.68
12	Bean	BeTPS36/PLAgMA	70/30	0	1.295±0.171	86.1±72.9	9.93±2.38
13	Bean	BeTPS36/PLAgMA	70/30	5	3.704±0.219	192.4±52.1	6.79±1.53

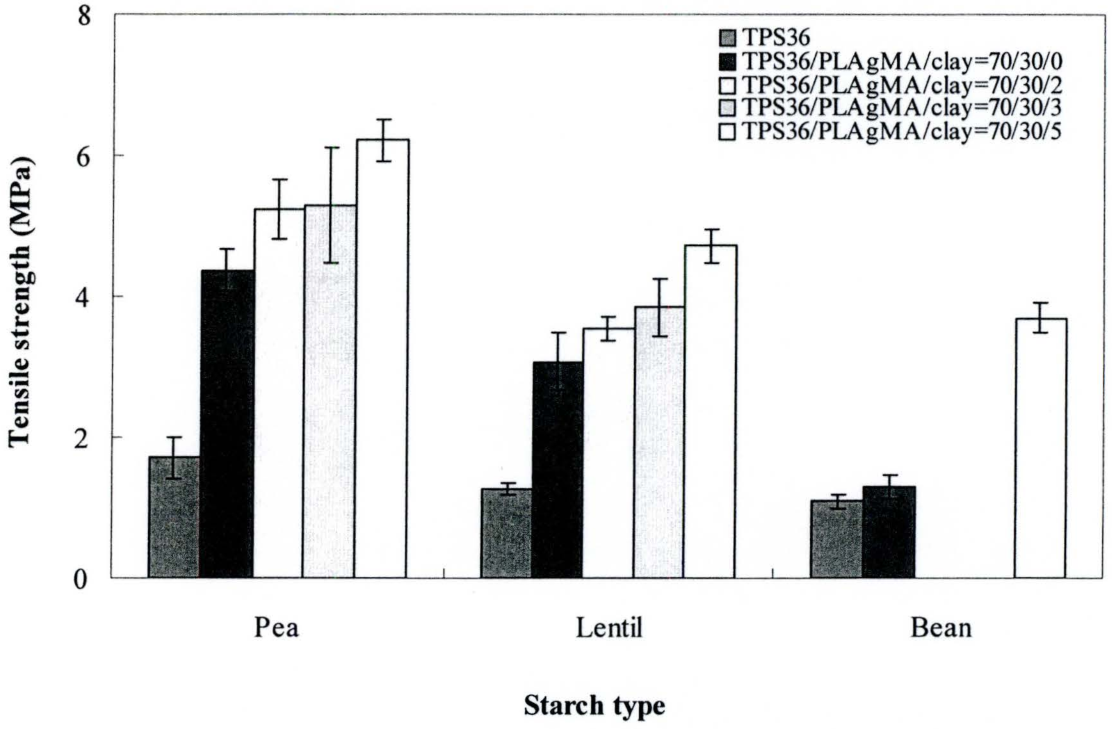


Figure 4.31 Comparison of tensile strength of thermoplastic pulse starch and its blends with PLAgMA and Cloisite 30B. Ratio of starch/glycerol/water: 50/36/14 wt/wt (TPS36: thermoplastic starch with 36%wt glycerol)

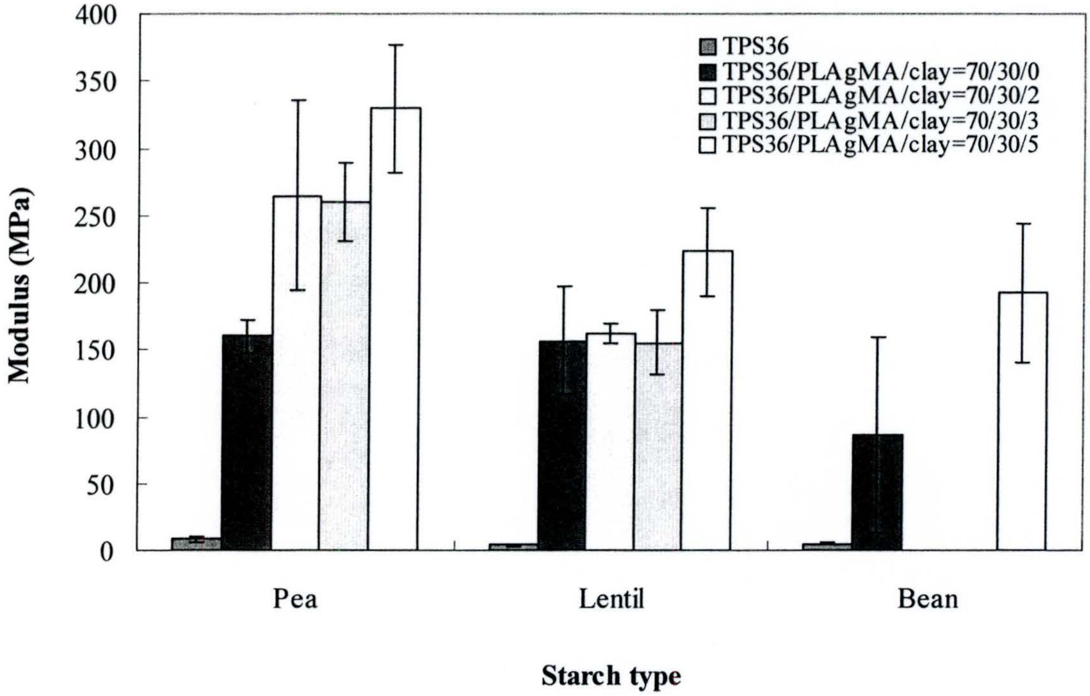


Figure 4.32 Comparison of modulus of thermoplastic pulse starch and its blends with PLAgMA and Cloisite 30B. Ratio of starch/glycerol/water: 50/36/14 wt/wt (TPS36: thermoplastic starch with 36%wt glycerol)

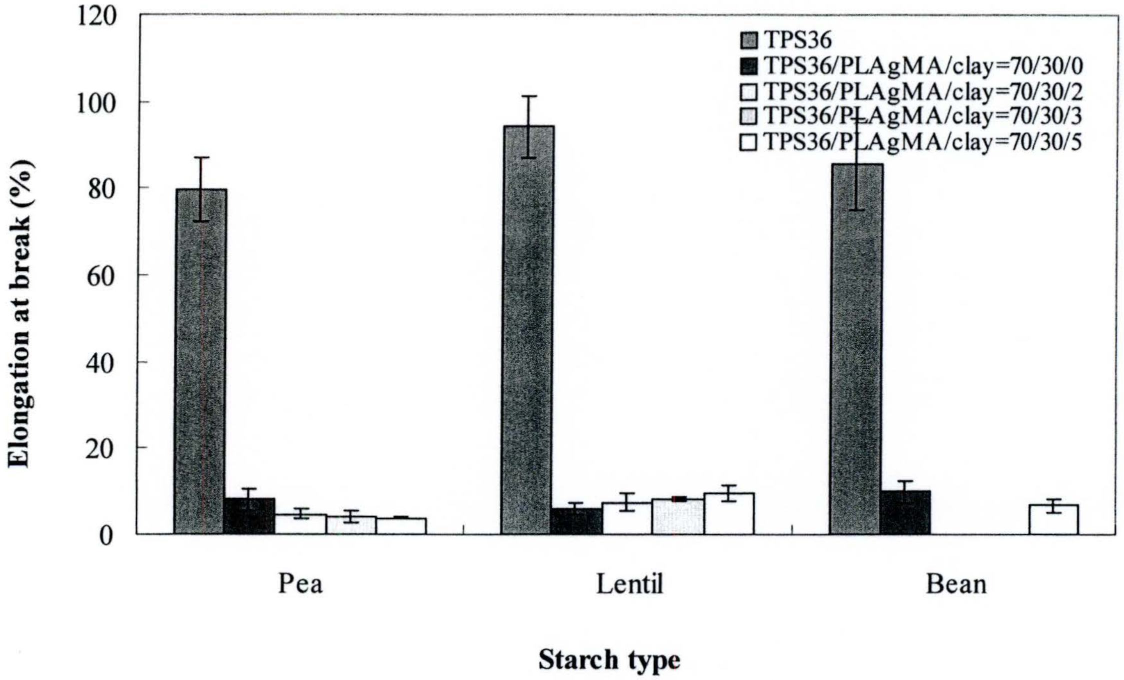


Figure 4.33 Comparison of elongation at break of thermoplastic pulse starch and its blends with PLAgMA and Cloisite 30B. Ratio of starch/glycerol/water: 50/36/14 wt/wt (TPS36: thermoplastic starch with 36%wt glycerol)

For all blends filled with Cloisite 30B, tensile strength and modulus increased as content of clay increased. This result is consisted with the behaviors of cornstarch when filling with clay. But lentil starch presented an opposite behavior on elongation at break: elongation at break was increased from 5.91% to 9.55% as content of Cloisite 30B increased from 0% to 5%. A further investigation is needed to understand why the difference exists between starches.

4.2.4 Water Resistance

Contact angles of a water droplet on the sample surface were measured for different type of pulse starches and are presented in Figures 4.34 - 4.36.

For thermoplastic pulse starch/PLAgMA, initial angles were 54.61°, 52.44° and 52.27° for bean, lentil and pea starch, respectively. When the blends filled with 5% Cloisite 30B, the initial angles were increased to 60.45°, 61.87° and 75.04° respectively. The hydrophobicity was improved when blends filled in 5% of Cloisite 30B. Similar to cornstarch, water droplet penetrated into the sample and combined with the component of starch. But when the blends filled with clay, the silicate layers can act as barriers to prevent water from entering. That may be the reason why hydrophobicity of blends was enhanced in presence of Cloisite 30B.

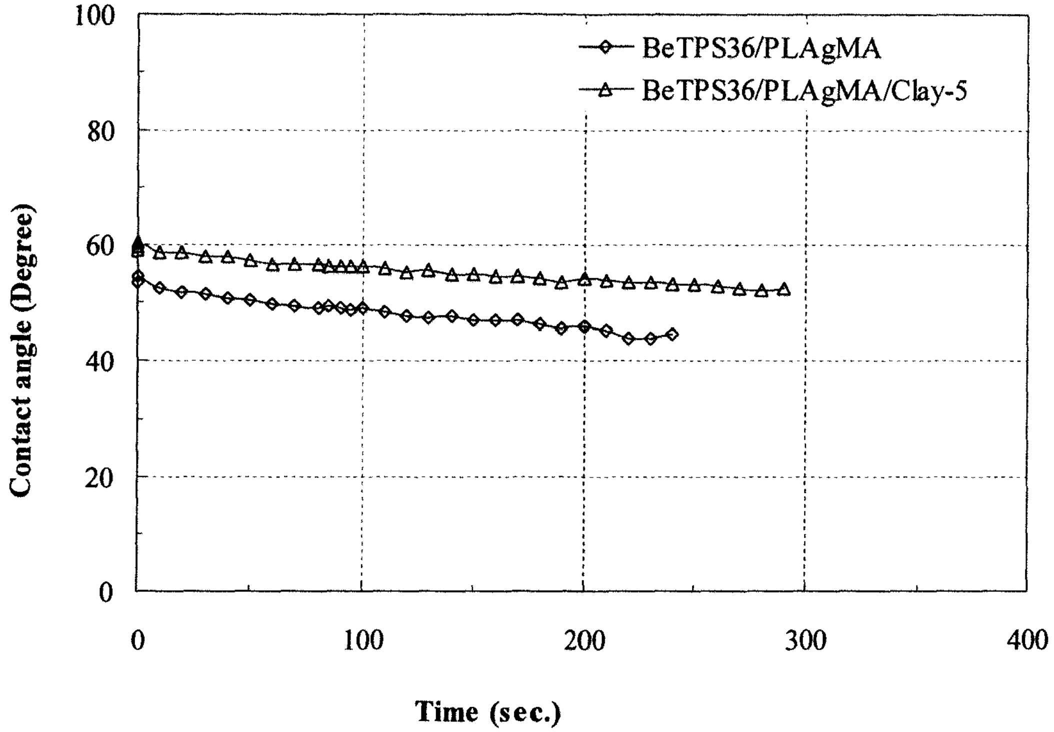


Figure 4.34 Comparison of contact angles of thermoplastic bean starch (BeTPS36)/ PLAgMA and BeTPS36/PLAgMA/Cloisite 30B. Ratio of BeTPS36/PLAgMA: 70/30, wt/wt. Concentration of Cloisite 30B: 5% (wt%).

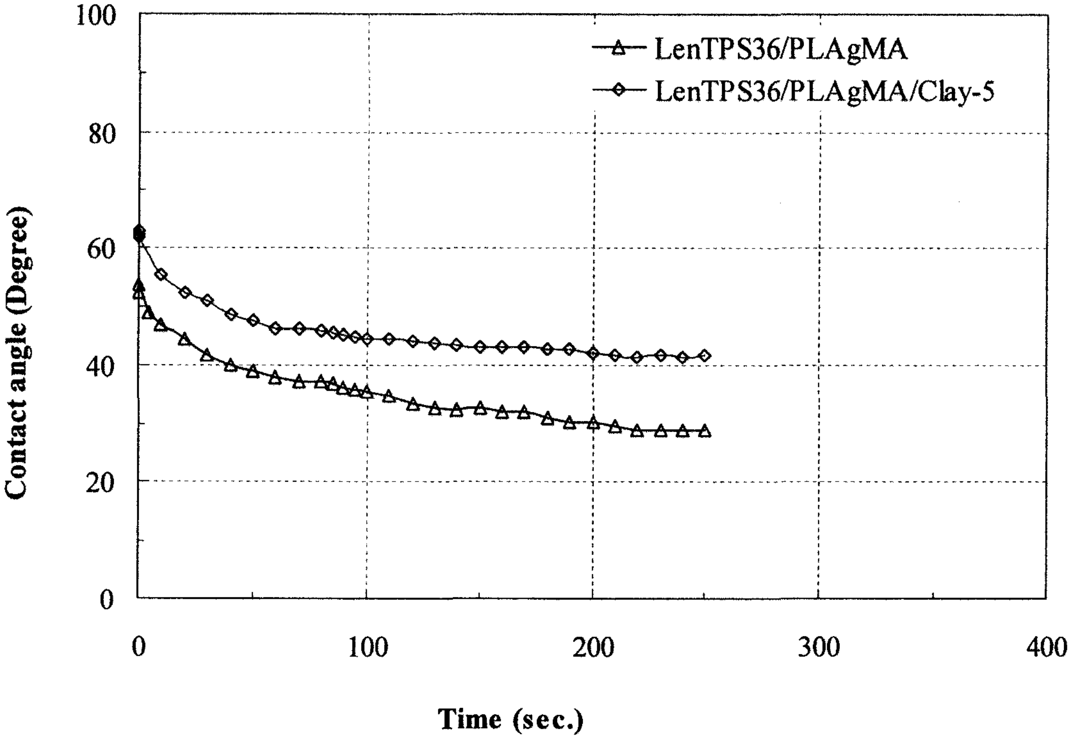


Figure 4.35 Comparison of contact angles of thermoplastic lentil starch (LenTPS36)/ PLAgMA and LenTPS36/PLAgMA/Cloisite 30B. Ratio of LenTPS36/PLAgMA: 70/30, wt/wt. Concentration of Cloisite 30B: 5% (wt%).

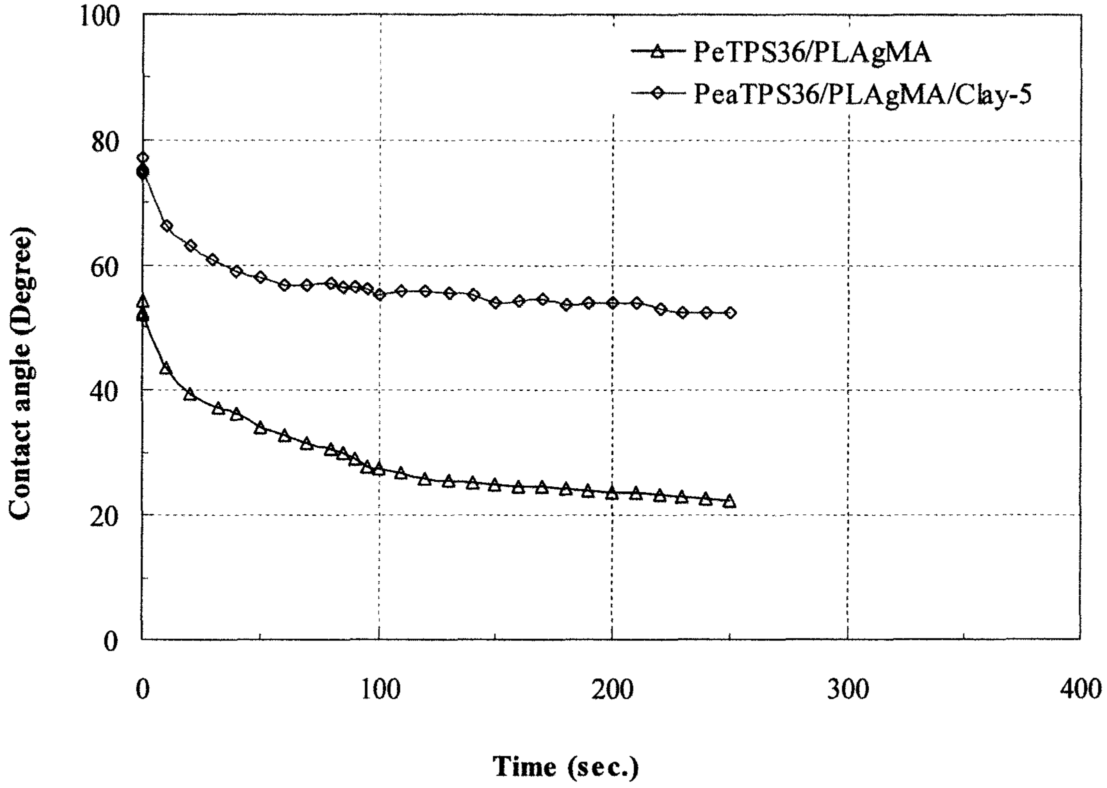


Figure 4.36 Comparison of contact angles of thermoplastic pea starch (PeTPS36)/ PLAgMA and PeTPS36/PLAgMA/Cloisite 30B. Ratio of PeTPS36/PLAgMA: 70/30, wt/wt. Concentration of Cloisite 30B: 5% (wt%).

Chapter 5

Conclusions

Three types of pulse starches and two types of cornstarches were used in this research. Starch was blended with water and glycerol to form thermoplastic starch (TPS). Poly (lactic acid) (PLA) was used to improve the properties of TPS. Maleic anhydride (MA) acted as a coupling agent to increase the miscibility of the PLA phase with the TPS phase. Cloisite 30B, a type of organoclay, was filled into material system to improve the properties of blends. The thermal, rheological, mechanical and morphological properties of blends were investigated. In order to enhance the hydrophobicity, alkyl ketene dimer (AKD) was used as a sizing agent. Two types of sizing methods were applied.

5.1 Corn Starch

DSC investigation showed that the action of water removal from TPS had little or no effect on the thermal behavior of the TPS and PLA blends. PLA grafted by maleic anhydride showed a lower glass transition temperature (T_g) and melting temperature (T_m) and a higher crystallization temperature (T_c) in comparison with PLA did. Blending time had very slight effect on thermal properties. Cloisite 30B had no significant effect on thermal behaviors of TPS/PLA blends at concentrations less than 5 wt%.

The presence of MA caused TPS/PLA to exhibit a lower shear viscosity than the blends with pure PLA. Thermoplastic cornstarch/PLAgMA/Cloisite 30B blends presented shear-thinning behaviors at 150° C when concentration of clay was less than 5 wt%. No significant effect on rheological properties was detected when the blending time was extended from 4 min to 6 min but the thermal degradation was occurred as blending time extended longer than 6 min (according to the previous research). For thermoplastic cornstarch/PLAgMA/Cloisite 30B blends, high amylose cornstarch demonstrated a higher shear viscosity than normal cornstarch in the same blending ratio.

Coupling agent MA significantly improved the tensile strength and modulus of blends. When blends of TPS/PLAgMA filled with Cloisite 30B (up to 5 wt%), the tensile strength and modulus were remarkably improved so as to approach to the level of LDPE, but the elongation at break is decreased. The blends with 6-min blending time exhibited higher tensile strength and modulus and lower elongation at break than the blends with 4-min blending time.

An improvement in morphology was obtained for TPS blended with PLAgMA compared to TPS blended with pure PLA. Blends of TPS/PLAgMA exhibit more homogeneous morphologies and smaller TPS particle size than blends of TPS/PLA. Therefore, we surmise that MA improved the interfacial adhesion between TPS and PLA phase. The smaller TPS particle size was found in the longer blending time (6min).

Starch is a hydrophilic material and water droplet on the surface of TPS is readily absorbed but the water droplet contact angle for TPS/PLAgMA was significantly improved compared to TPS alone due to the hydrophobicity of PLAgMA component. The existence of clay in blends improved the hydrophobicity of blends because the layer of silicate acts as a barrier to prevent water from going through the surface. In surface sizing, the samples treated by AKD showed higher hydrophobicity than the untreated samples. However, internal sizing blended into the material showed very little improvement in hydrophobicity.

5.2 Pulse Starch

Thermoplastic pulse starch/PLAgMA blends exhibited similar thermal behavior as thermoplastic cornstarch/PLAgMA blends; the thermal behaviors were mainly dominated by the PLAgMA component. For pulse based starches, blends of bean starch showed lower melting enthalpy and crystallization enthalpy than pea and lentil starch. Cloisite 30B had no significant effect on thermal behavior of thermoplastic pulse starch/PLAgMA blends.

At 150° C, all thermoplastic pulse starch/PLAgMA blends showed shear-thinning behaviors, which can be expressed by power law equation. Shear viscosity increased as blends had higher percentages of filler with Cloisite 30B.

Tensile strength and modulus improved remarkably for blends of pea and lentil starch when MA acted as coupling agent was used in blends, but the improvement for blends of bean starch was slight. The addition of Cloisite 30B improved the tensile strength and modulus, but elongation at break decreased.

The initial contact angle of a water droplet in the surface of thermoplastic pulse starch/ PLAgMA sample was less than 55°, but it increased up to 75° as nanoclay (Cloisite 30B) was added to the blends up to 5% by weight.

Chapter 6

Recommendations

The ultimate goal of this research should is to make thermoplastic starch basis materials available for producing the packaging applications such as film. Based on the fact that some mechanical properties of TPS/PLAgMA/clay blend approach the properties of LDPE, future research work should thoroughly evaluate some properties and enhance the properties, which is weak for making such as film and tray,

(1) Ductility improvement

Although the tensile strength and modulus were improved to reach the level of LDPE, the elongation at break was still too low (2-4%). Ductility improvement, which is important for the thin packaging applications, such film, should be studied.

(2) Barrier properties evaluation

Nanoclays in the material system proved to enhance the mechanical properties of blends. Meanwhile, theoretically, the addition of nanoclay should benefit for improving barrier properties if structures of nanocomposites were formed. So the barrier property evaluation for blends should be performed.

(3) Pulse starch research

Further studies should be done on the relation between molecular structure of pulse based starches and final properties.

(4) Hydrophobicity improvement

Hydrophobicity was improved as AKD was introduced to material system. The mechanism of reaction should be studied.

(5) Biodegradability research

The biodegradability of materials should be studied. The effects of nanoclay on biodegradability should be evaluated.

Appendix A

DSC measurements on cornstarch, pulse starch and their blends

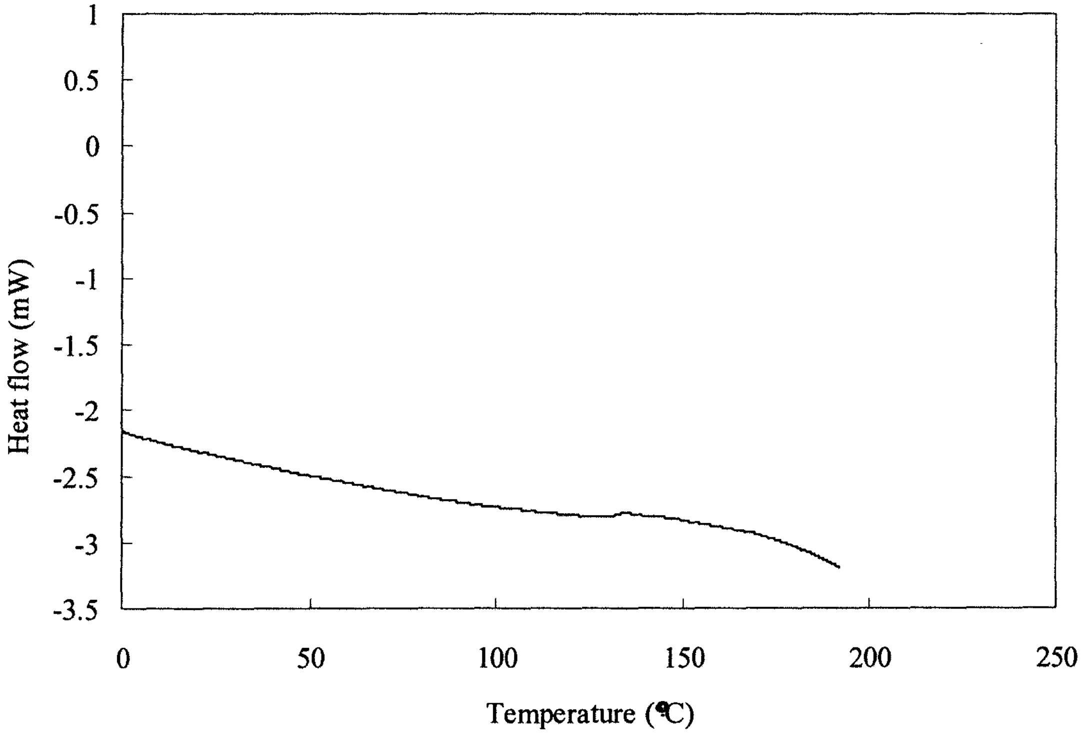


Figure A1 DSC thermogram of thermoplastic high amylose cornstarch in a second thermal scan. Blending ratio: HAS/glycerol/water = 50/36/14 wt/wt.

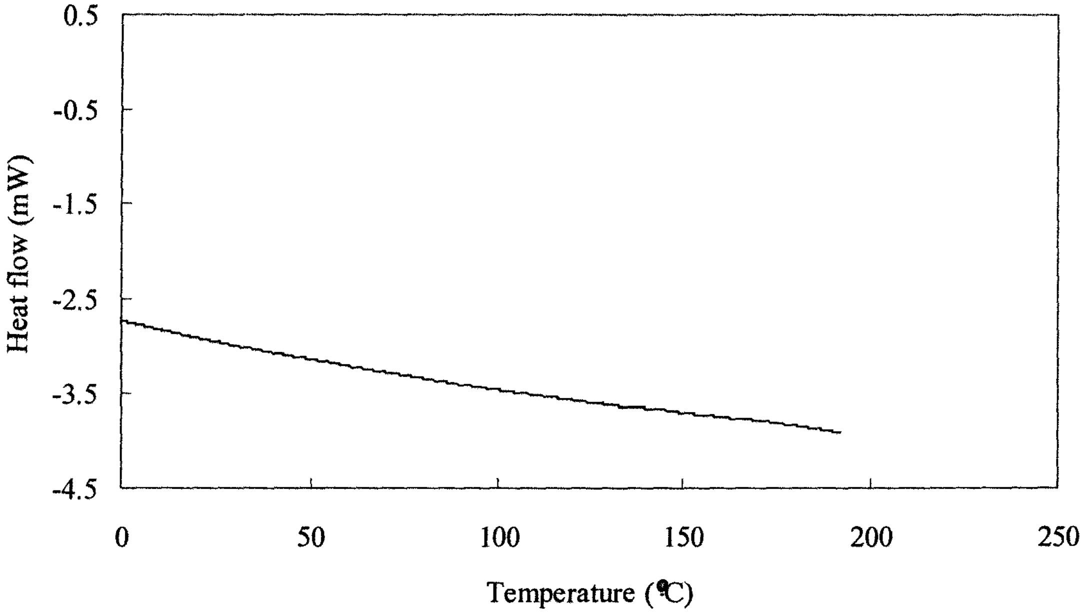


Figure A2 DSC thermogram of thermoplastic high amylose cornstarch after water removal in a second thermal scan. Blending ratio: HAS/glycerol/water = 50/36/14 wt/wt.

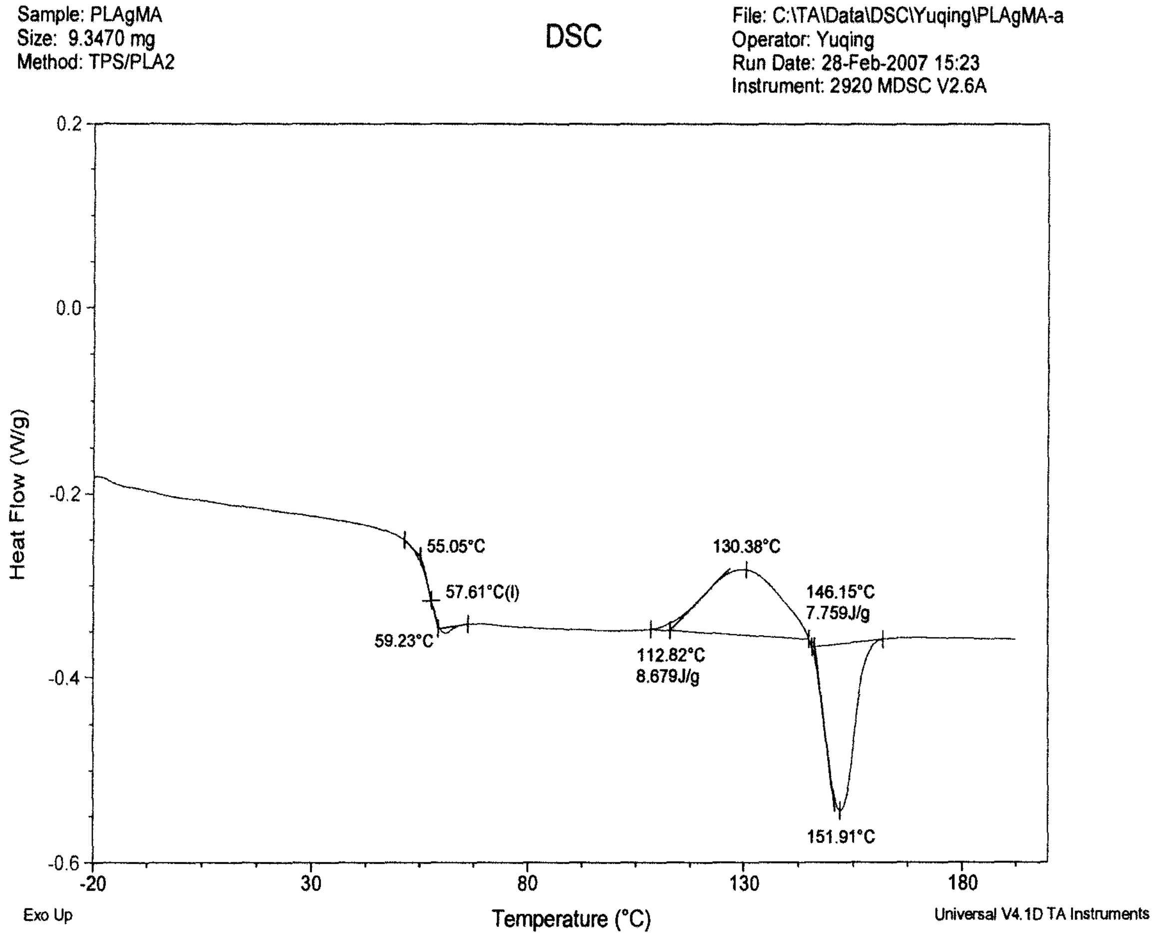


Figure A3 DSC thermogram of PLA grafted by maleic anhydride (PLAgMA) in a second thermal scan. Blending ratio: PLA/MA/L101 = 100/2/0.25 wt/wt.

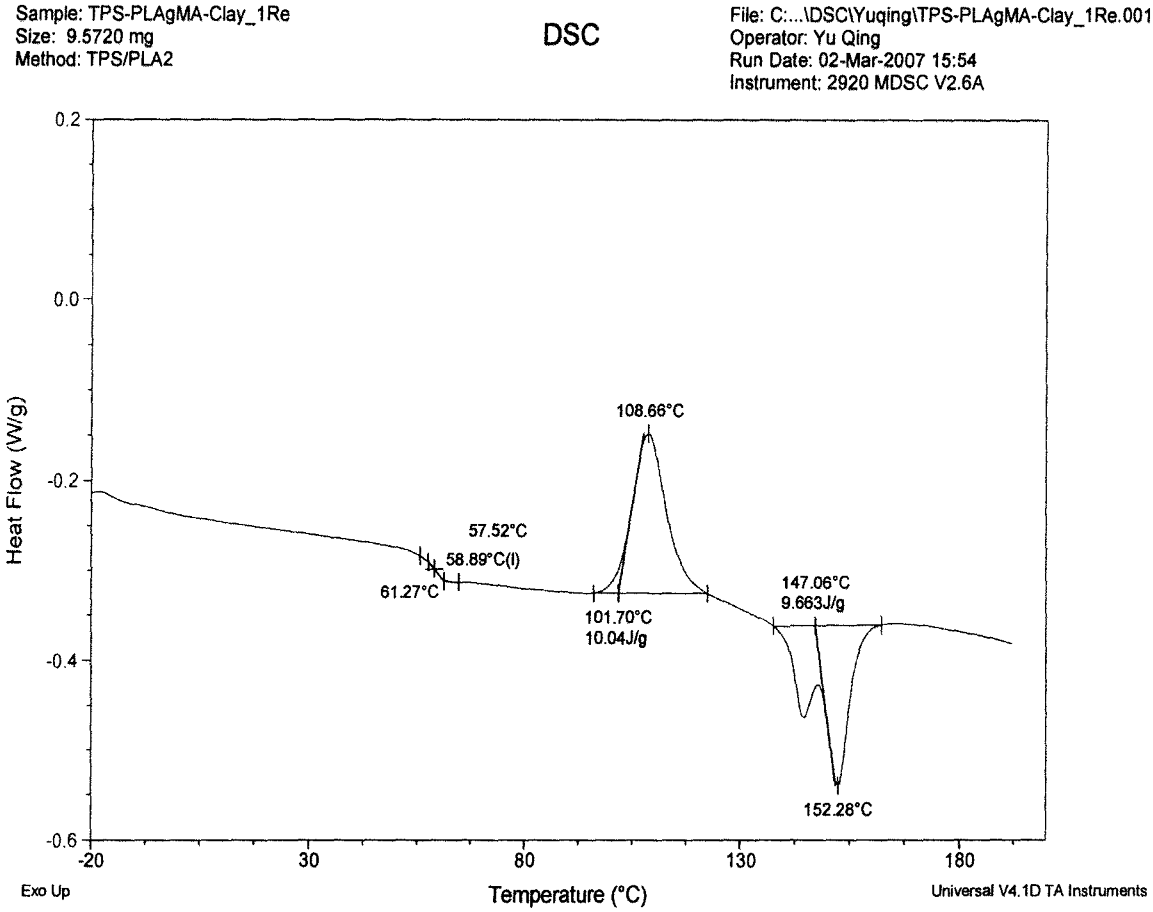


Figure A4 DSC thermogram of thermoplastic high amylose cornstarch/PLAgMA/ Cloisite 30B in a second thermal scan. Blending ratio: HASTPS/PLAgMA/Cloisite30B = 70/30/1 wt/wt.

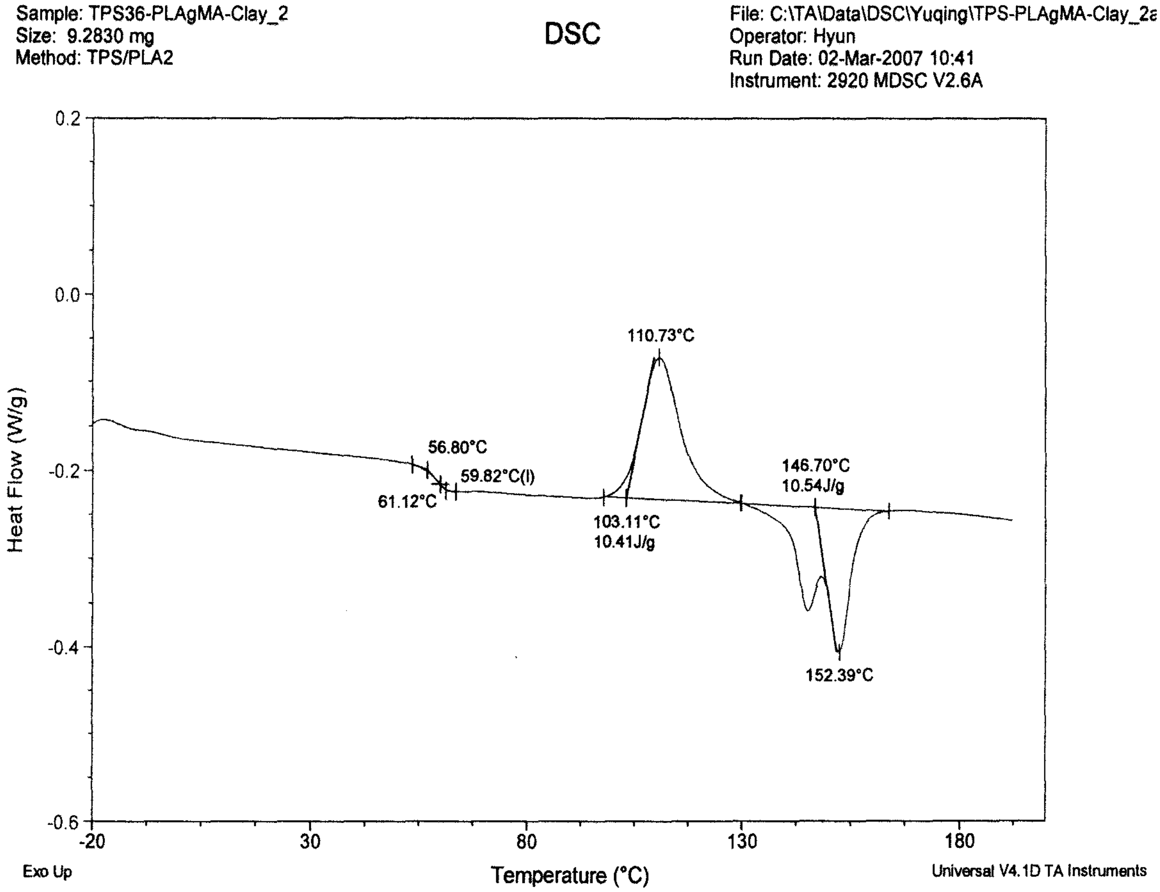


Figure A5 DSC thermogram of thermoplastic high amylose cornstarch/PLAgMA/ Cloisite 30B in a second thermal scan. Blending ratio: HASTPS/PLAgMA/Cloisite30B = 70/30/2 wt/wt.

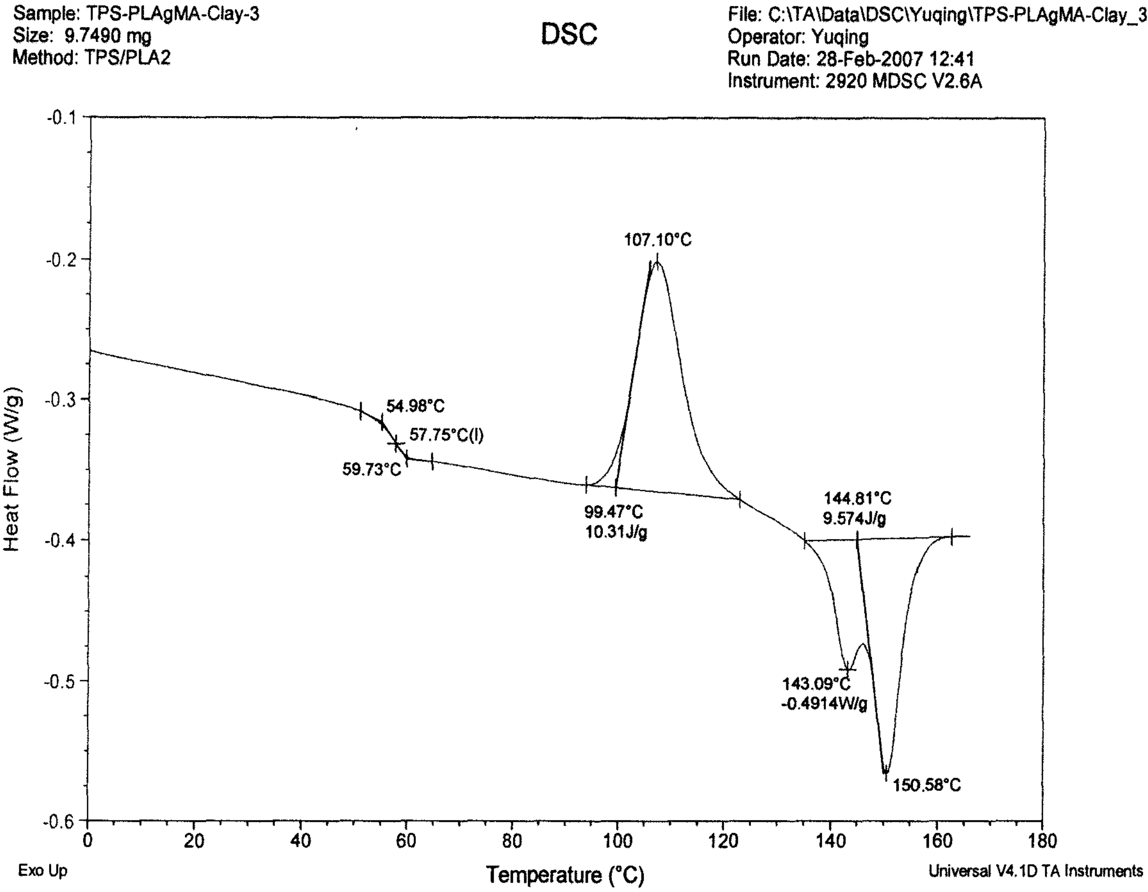


Figure A6 DSC thermogram of thermoplastic high amylose cornstarch/PLAgMA/ Cloisite 30B in a second thermal scan. Blending ratio: HASTPS/PLAgMA/Cloisite30B = 70/30/3 wt/wt.

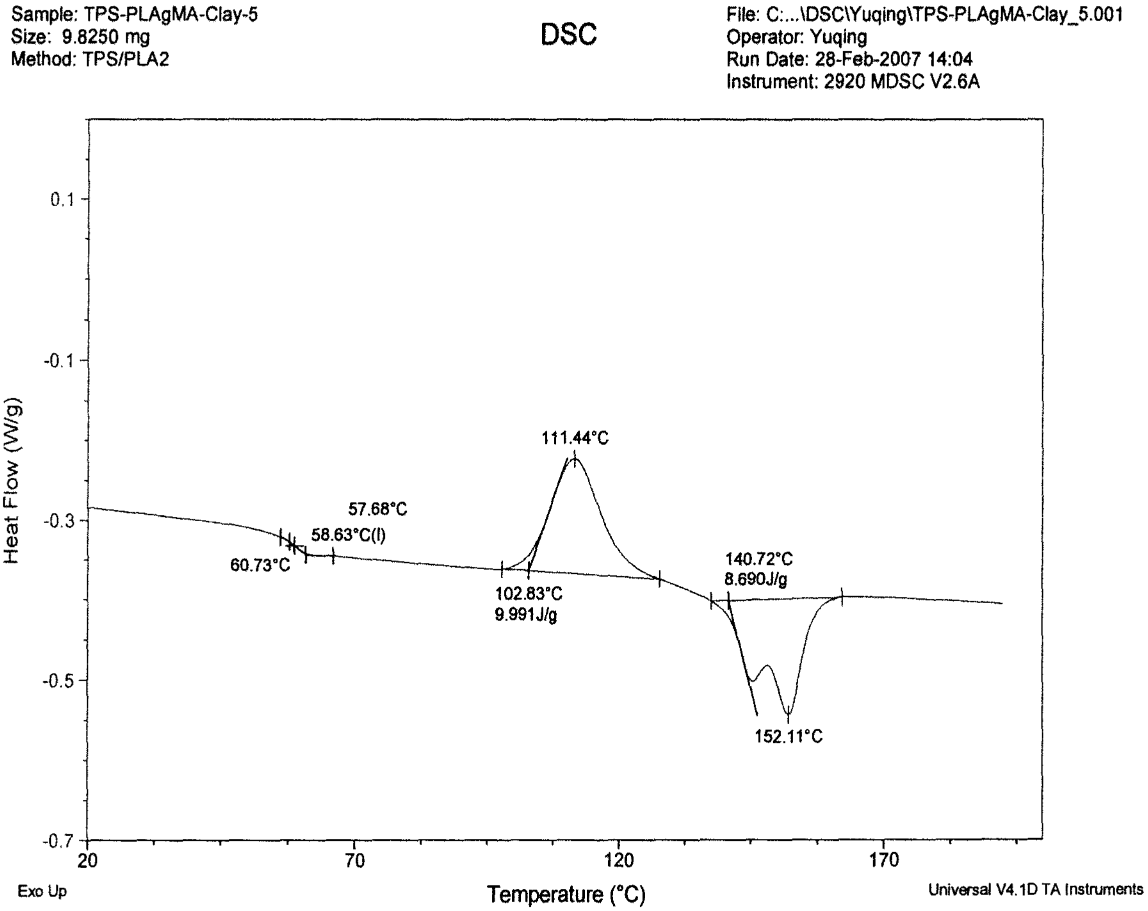


Figure A7 DSC thermogram of thermoplastic high amylose cornstarch/PLAgMA/ Cloisite 30B in a second thermal scan. Blending ratio: HASTPS/PLAgMA/Cloisite30B = 70/30/5 wt/wt.

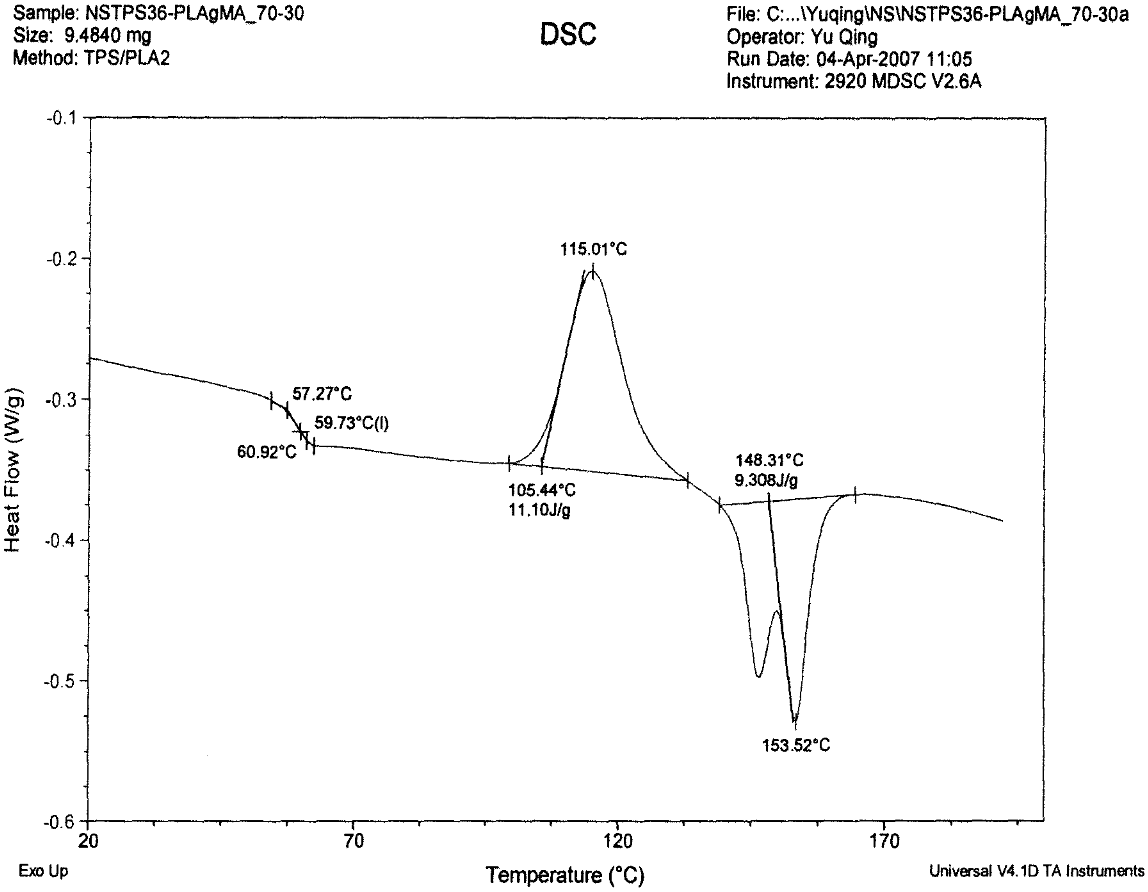


Figure A8 DSC thermogram of thermoplastic normal cornstarch/PLAgMA in a second thermal scan. Blending ratio: NSTPS/PLAgMA = 70/30 wt/wt.

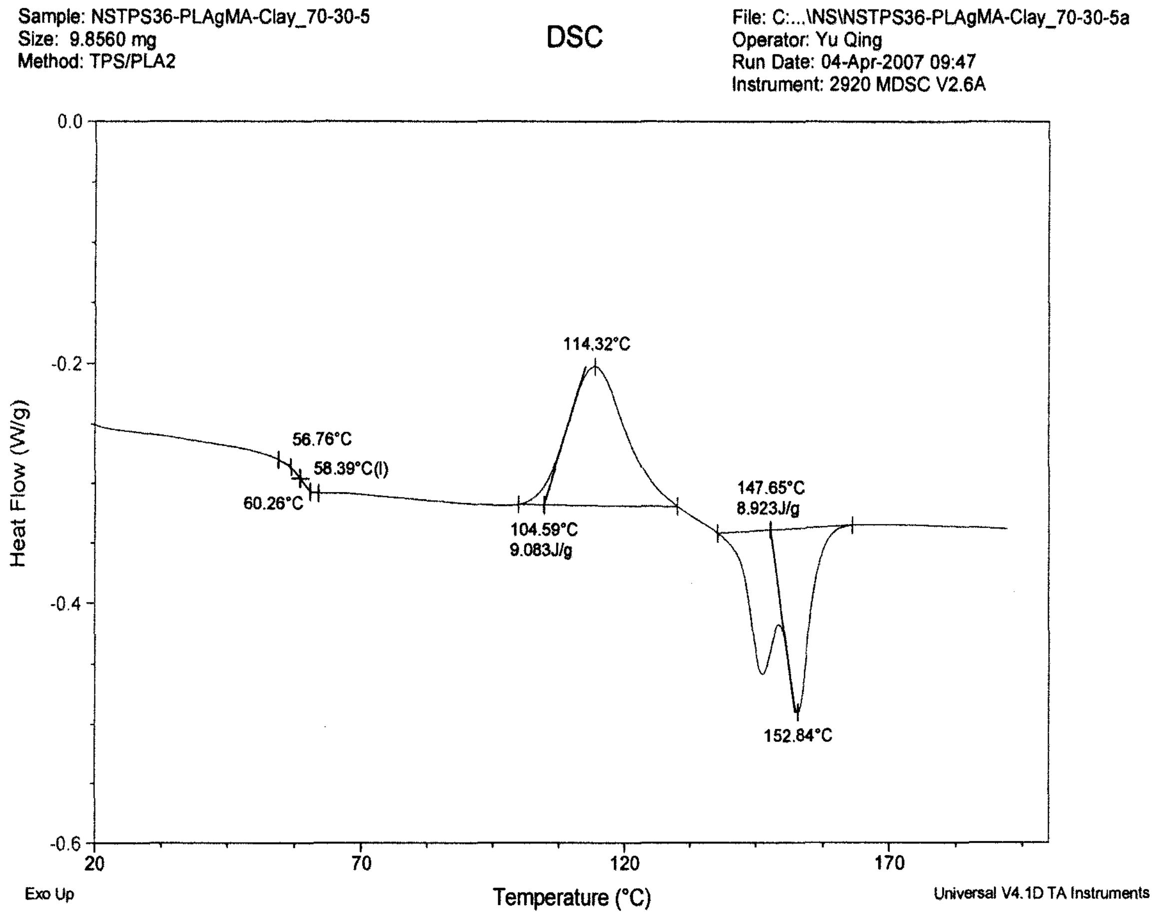


Figure A9 DSC thermogram of thermoplastic normal cornstarch/PLAgMA/ Cloisite 30B in a second thermal scan. Blending ratio: NSTPS/PLAgMA/Cloisite30B = 70/30/5 wt/wt.

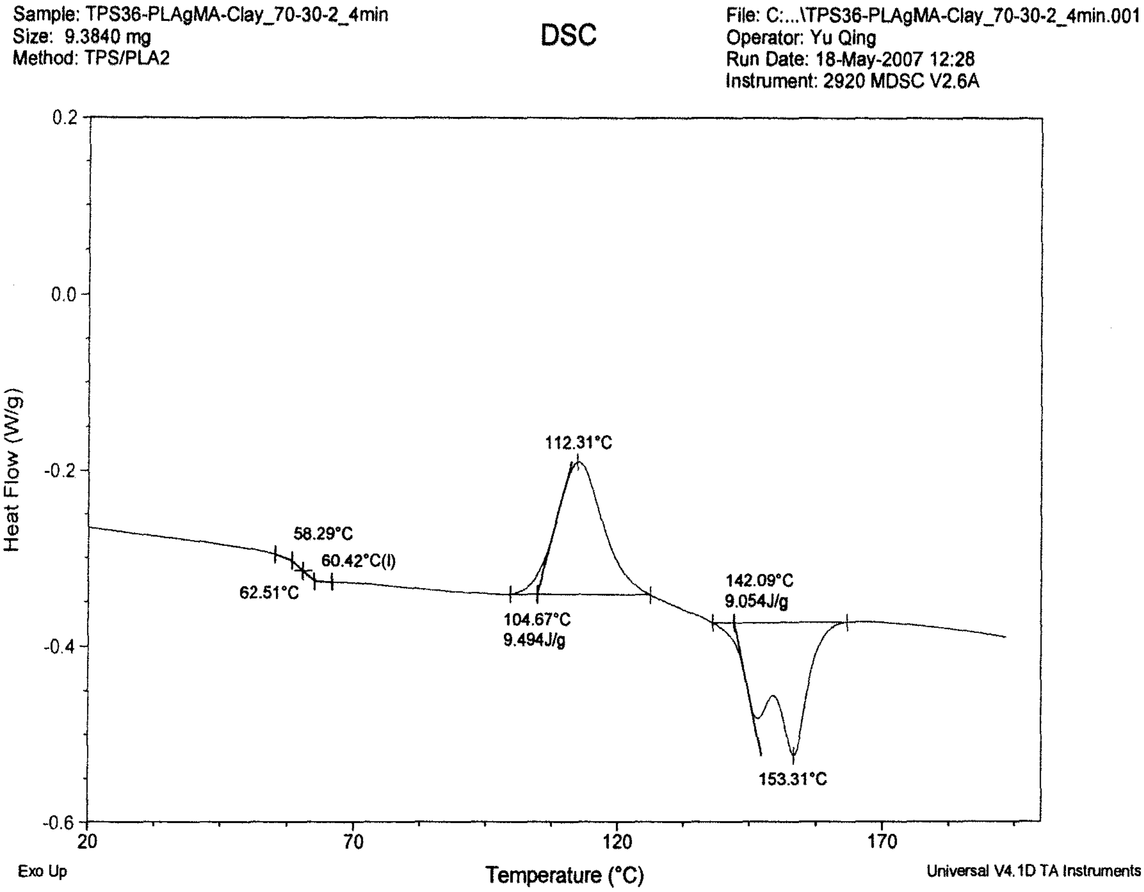


Figure A10 DSC thermogram of thermoplastic high amylose cornstarch/PLAgMA/ Cloisite 30B in a second thermal scan. Blending ratio: HASTPS/PLAgMA/Cloisite30B = 70/30/2 wt/wt. Blending time on Haake: 4 min

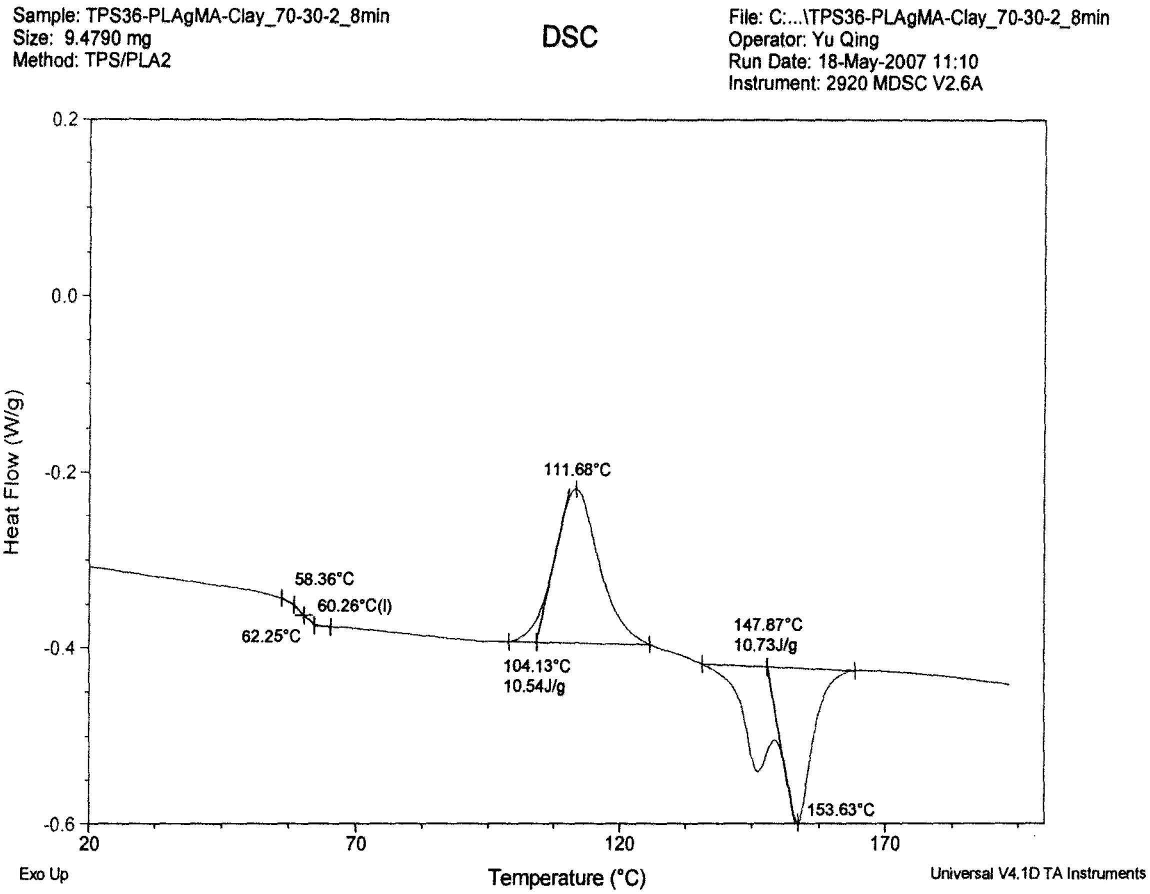


Figure A11 DSC thermogram of thermoplastic high amylose cornstarch/PLAgMA/ Cloisite 30B in a second thermal scan. Blending ratio: HASTPS/PLAgMA/Cloisite30B = 70/30/2 wt/wt. Blending time on Haake: 8 min

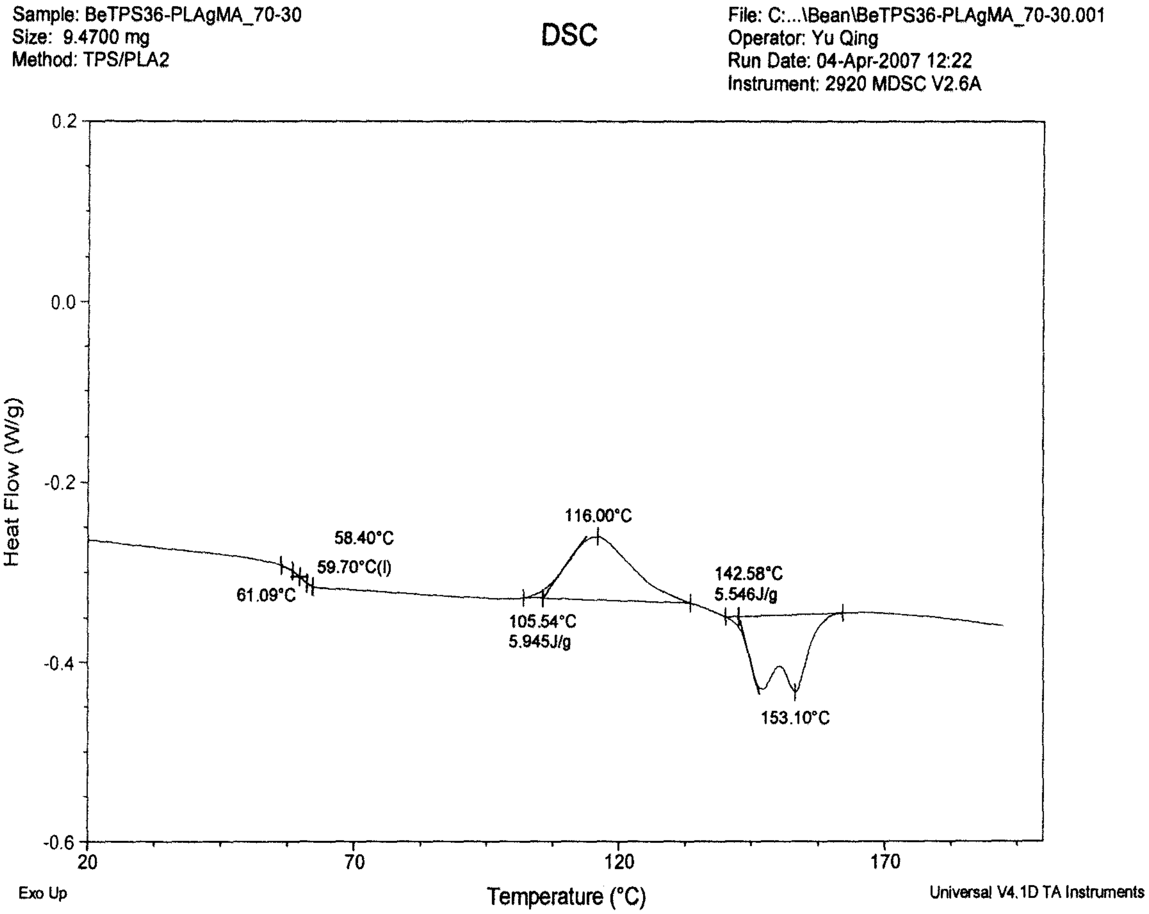


Figure A12 DSC thermogram of thermoplastic bean starch/PLAgMA in a second thermal scan. Blending ratio: BeTPS/PLAgMA = 70/30 wt/wt.

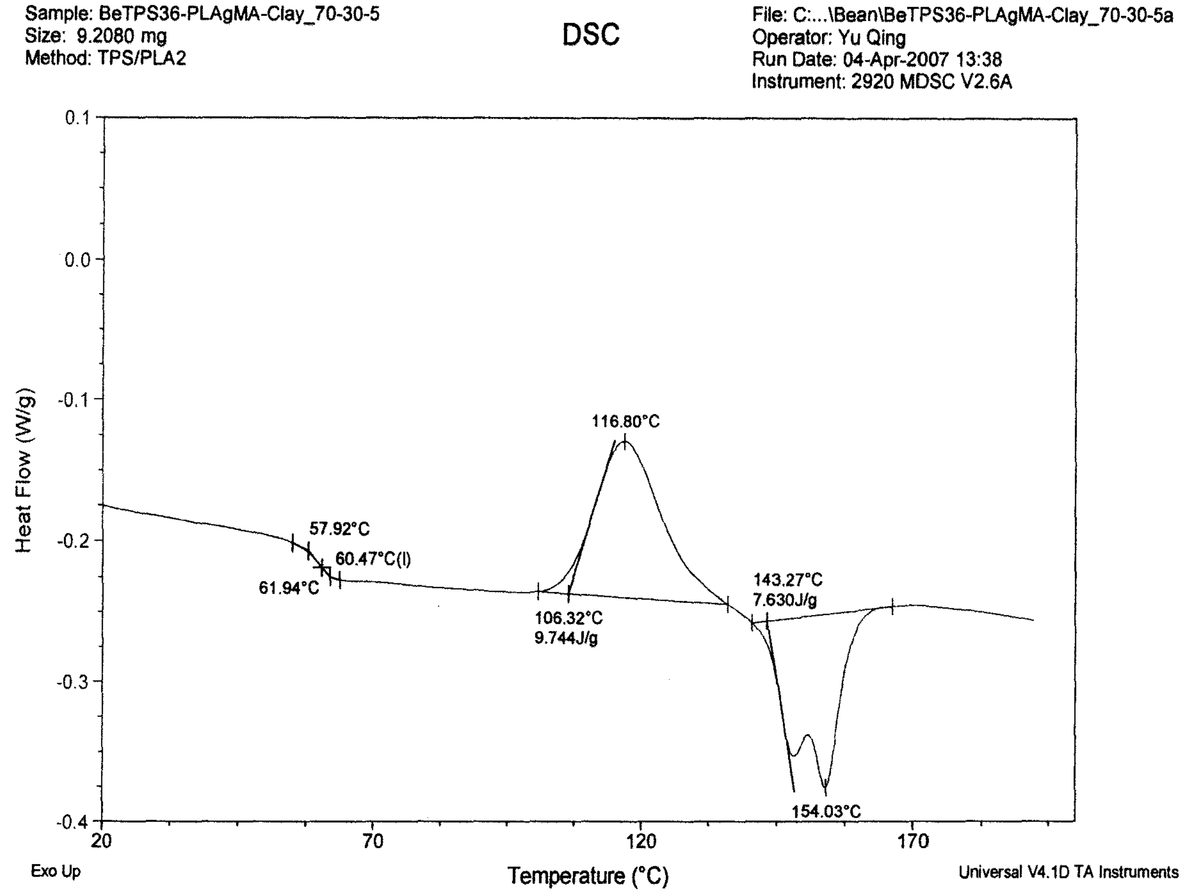


Figure A13 DSC thermogram of thermoplastic bean starch/PLAgMA/ Cloisite 30B in a second thermal scan. Blending ratio: BeTPS/PLAgMA/Cloisite30B = 70/30/5 wt/wt.

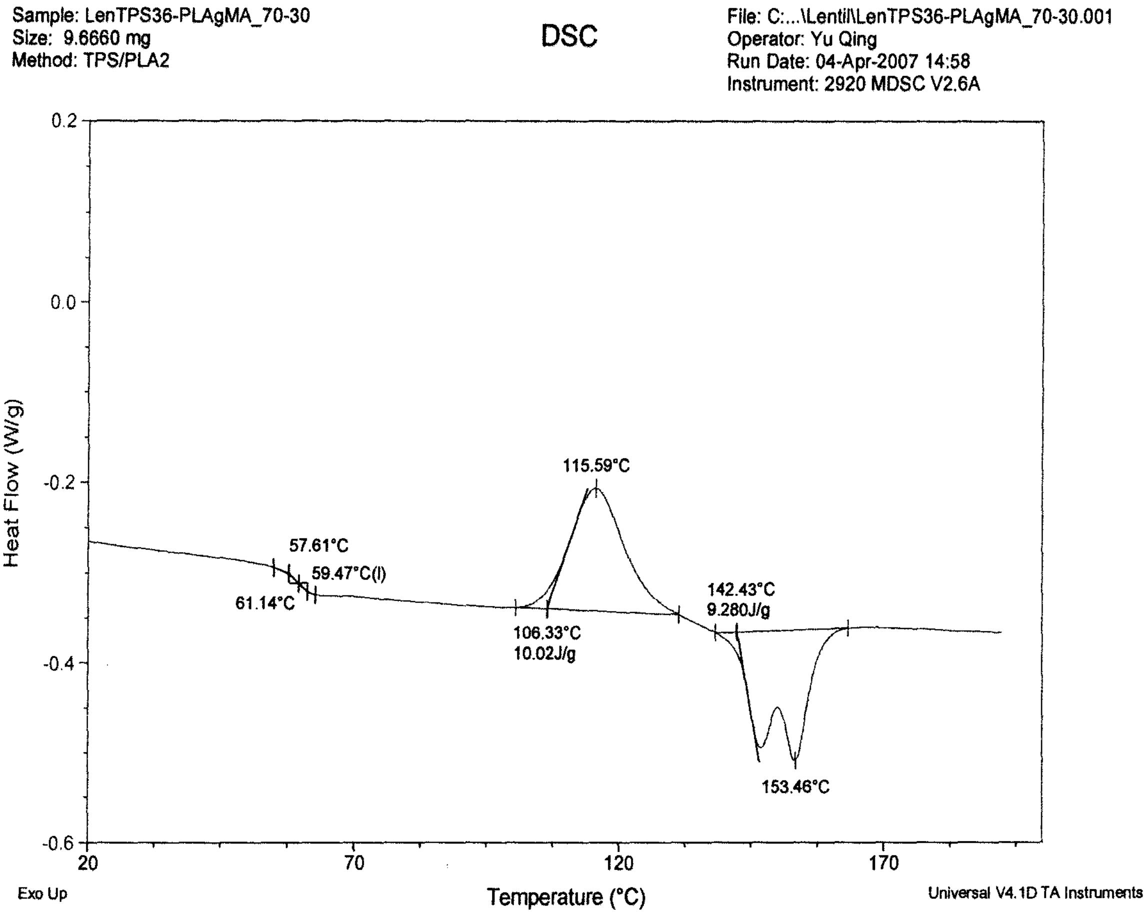


Figure A14 DSC thermogram of thermoplastic lentil starch/PLAgMA in a second thermal scan. Blending ratio: LenTPS/PLAgMA = 70/30 wt/wt.

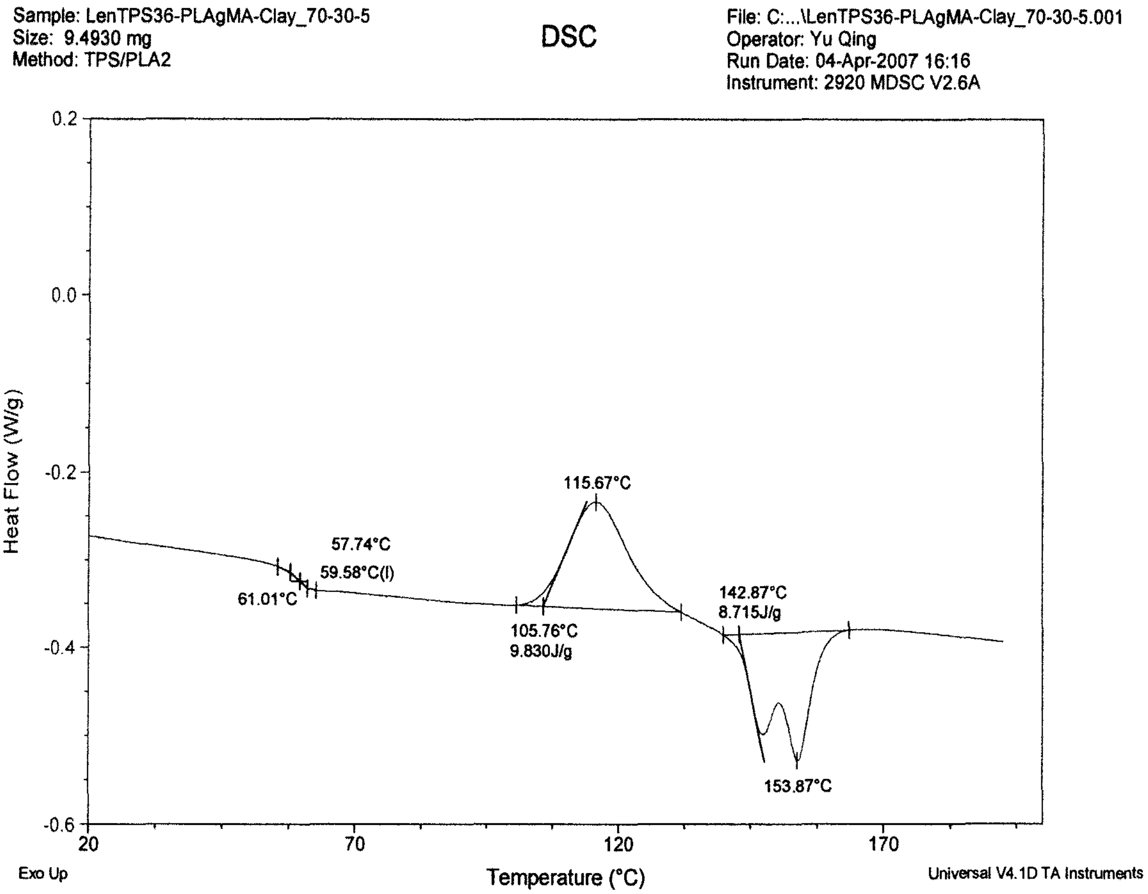


Figure A15 DSC thermogram of thermoplastic lentil starch/PLAgMA/ Cloisite 30B in a second thermal scan. Blending ratio: LenTPS/PLAgMA/Cloisite 30B = 70/30/5 wt/wt.

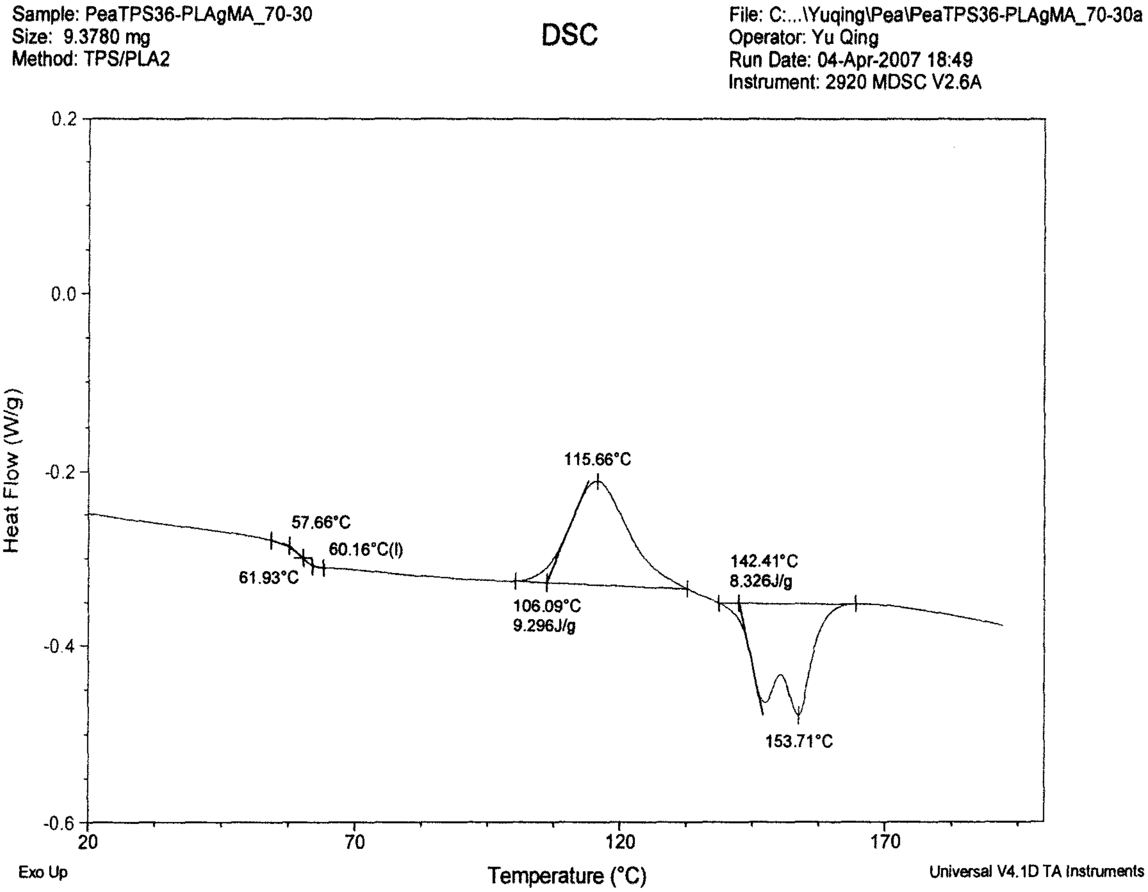


Figure A16 DSC thermogram of thermoplastic pea starch/PLAgMA in a second thermal scan. Blending ratio: PeTPS/PLAgMA = 70/30 wt/wt.

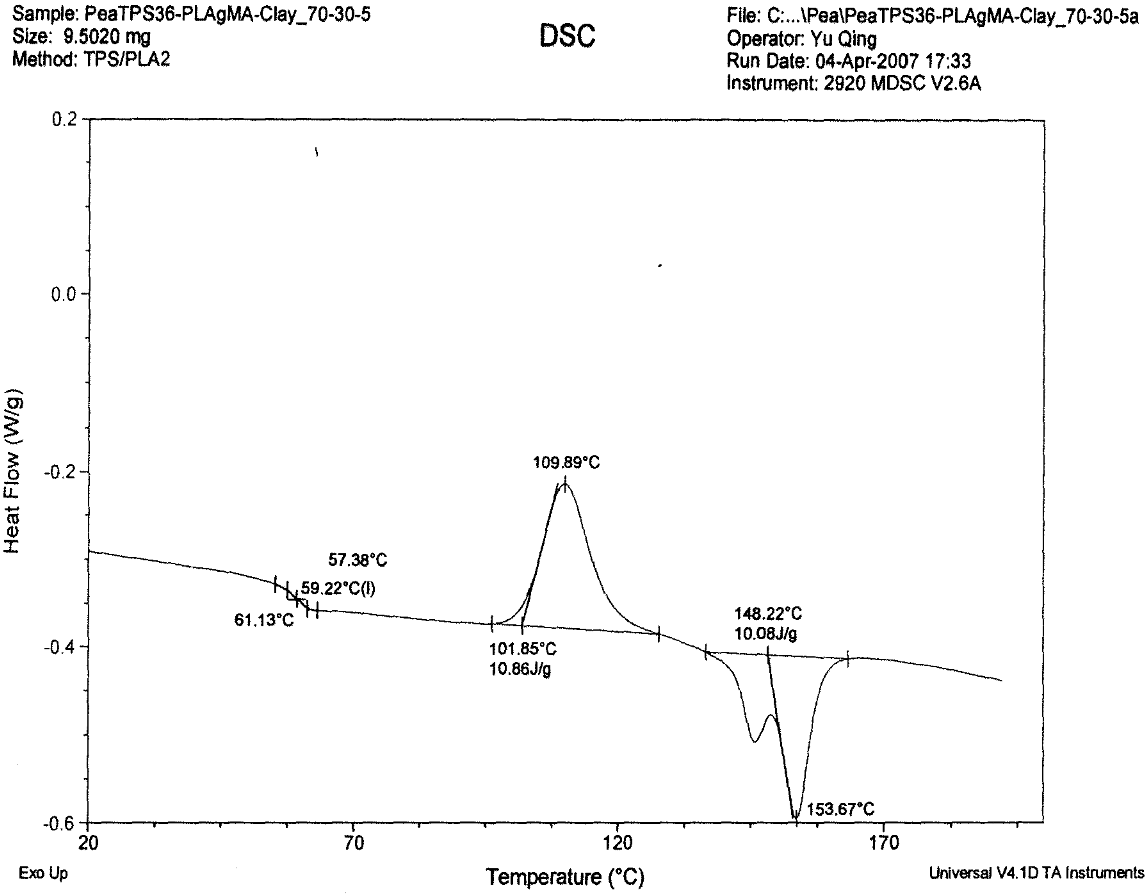


Figure A17 DSC thermogram of thermoplastic pea starch/PLAgMA/ Cloisite 30B in a second thermal scan. Blending ratio: PeTPS/PLAgMA/Cloisite 30B = 70/30/5 wt/wt.

Appendix B

Rheological properties of thermoplastic starch and their blends with PLAgMA and nanoclay[a,b]

Samples				Shear rate /s	Shear viscosity Pa.s
Starch type	Blends	Ratio of blends wt/wt	Clay content %		
HAS	HASTPS/PLAgMA	70/30	0	20	1272.34
				44.01	699.87
				96.86	398.11
				213.18	229.09
				469.18	141.25
				1032.37	85.11
				2272.34	48.98
HAS	HASTPS/PLAgMA	70/30	1	20	1445.44
				45.18	851.14
				102.04	501.19
				230.40	288.40
				520.38	199.53
				1148.15	104.71
				2654.01	60.26
				5998.76	33.11
HAS	HASTPS/PLAgMA	70/30	2	20	1994.73
				45.18	1185.93
				102.04	721.00
				230.86	431.82
				521.31	259.40
				1176.67	123.59
				2657.74	76.46
				5998.76	42.00
HAS	HASTPS/PLAgMA	70/30	3	20	2511.89
				45.18	1412.54
				102.04	812.83
				230.40	489.78
				502.34	302.00
				1288.25	154.88
				2591.64	95.50
				5998.76	53.70
HAS	HASTPS/PLAgMA	70/30	5	20	2691.53
				43.25	1698.24
				102.04	977.24
				217.77	616.60
				520.38	371.54
				1309.18	181.97
				2656.81	114.82
				6002.48	67.61

Samples				Shear rate /s	Shear viscosity Pa.s
Starch type	Blends	Ratio of blends wt/wt	Clay content %		
HAS	HASTPS/PLAgMA	70/30	8	20	3235.94
				44.01	2238.72
				103.04	1412.54
				213.18	870.96
				534.56	489.78
				1032.37	309.03
				2654.61	181.97
				4998.97	
HAS	HASTPS/PLAgMA 4 min-Haake	70/30	2	20	1584.89
				44.01	901.85
				96.86	553.57
				213.18	361.84
				469.18	201.68
				1033.31	117.49
				2272.34	66.07
				5002.69	38.02
HAS	HASTPS/PLAgMA with water	70/30	0	20	316.69
				44.01	164.22
				96.86	83.08
				212.71	37.83
				470.11	20.21
				1033.31	13.20
				2272.34	8.13
				4998.97	5.42
HAS	HASTPS/PLA water removal	70/30	0	20	1073.24
				44.01	751.64
				96.86	599.18
				213.18	396.16
				469.18	271.28
				1032.37	181.42
				2272.34	111.20
				4998.97	65.51
NS	NSTPS/PLAgMA	70/30	0	20	233.72
				44.01	164.45
				96.86	90.49
				213.18	50.35
				468.25	38.06
				1033.31	33.30
				2272.34	20.96

Samples				Shear rate /s	Shear viscosity Pa.s
Starch type	Blends	Ratio of blends wt/wt	Clay content %		
NS	NSTPS/PLAgMA	70/30	2	20	669.54
				44.01	315.07
				96.86	175.12
				212.71	129.44
				469.18	69.78
				1032.37	49.46
				2272.34	32.76
				5000.83	21.20
NS	NSTPS/PLAgMA	70/30	3	20	712.24
				44.01	323.23
				96.86	206.39
				213.18	160.36
				469.18	85.28
				1033.31	59.37
				2270.48	37.80
				5000.83	24.43
NS	NSTPS/PLAgMA	70/30	5	20	680.93
				44.01	522.92
				96.86	317.55
				213.18	194.47
				470.11	120.69
				1032.37	64.32
				2271.41	40.25
				4998.97	26.08
Bean	BeTPS/PLAgMA	70/30	0	20	379.83
				44.01	176.21
				96.86	115.61
				212.71	77.34
				470.11	43.73
				1032.37	31.68
				2272.34	20.14
Bean	BeTPS/PLAgMA	70/30	5	20	1328.21
				44.01	778.67
				96.86	442.60
				213.64	259.07
				469.18	156.29
				1032.37	88.63
				2272.34	53.32
				5000.83	30.74

Samples				Shear rate /s	Shear viscosity Pa.s
Starch type	Blends	Ratio of blends wt/wt	Clay content %		
Lentil	LenTPS/PLAgMA	70/30	0	20	1388.08
				44.01	428.49
				96.86	320.59
				213.18	201.56
				469.18	102.37
				1032.37	81.19
Lentil	LenTPS/PLAgMA	70/30	2	20	1482.58
				44.01	630.96
				96.86	374.16
				213.18	247.79
				469.18	165.60
				1032.37	97.74
Lentil	LenTPS/PLAgMA	70/30	3	20	1522.18
				44.01	886.12
				96.86	521.72
				212.71	302.70
				470.11	178.34
				1032.37	111.19
				2272.34	64.96
				5000.83	36.78
Lentil	LenTPS/PLAgMA	70/30	5	20	1567.31
				44.01	939.33
				96.86	553.27
				213.18	325.25
				468.25	192.43
				1032.37	114.91
				2272.34	69.32
				5000.83	38.98
Pea	PeTPS/PLAgMA	70/30	0	20	1623.63
				44.01	937.21
				96.86	547.77
				212.71	334.73
				469.18	190.81
				1031.44	113.07
				2272.34	67.45
				4998.97	37.90

Samples				Shear rate /s	Shear viscosity Pa.s
Starch type	Blends	Ratio of blends wt/wt	Clay content %		
Pea	PeTPS/PLAgMA	70/30	2	20	2073.07
				44.01	1194.57
				96.86	675.93
				213.18	389.40
				470.11	225.91
				1032.37	131.50
				2272.34	75.30
				5000.83	41.80
Pea	PeTPS/PLAgMA	70/30	3	20	2052.53
				44.01	1180.23
				96.86	693.30
				213.18	399.70
				469.18	233.63
				1031.44	133.49
				2271.41	77.59
				4998.97	42.67
Pea	PeTPS/PLAgMA	70/30	5	20	2249.16
				44.01	1270.97
				96.86	731.92
				213.18	427.96
				469.18	248.52
				1032.37	142.58
				2272.34	80.22
				4997.10	44.95

[a]: measurement condition: 150° C

[b]: Bagley correction and Rabinowitsch correction were applied in calculation of shear rate and shear viscosity

Appendix C

Contact angle measurements

Table C1 Contact angle of thermoplastic high amylose cornstarch/PLAgMA/Cloisite 30B blends

HASTPS/PLAgMA/Clay =70/30/2, wt/wt		HASTPS/PLAgMA/Clay =70/30/3, wt/wt		HASTPS/PLAgMA/Clay =70/30/5, wt/wt	
Graph Secs	Y_Axis Angle	Graph Secs	Y_Axis Angle	Graph Secs	Y_Axis Angle
0	50.83	0	59.46	0	66.19
0.033	50.74	0.033	59.47	0	66.19
20	48.59	20	56.66	20	65.09
40	47.16	40	54.92	40	64.22
60	45.52	60	53.32	60	62.81
80	44.43	80	52.21	80	61.72
100	43.19	100	51.27	100	60.84
120	41.95	120	50.03	120	60.09
140	40.54	140	49.01	140	59.22
160	39.49	160	47.9	160	58.38
180	38.46	180	47.06	180	57.56
200	37.63	200	45.97	200	56.73
220	36.58	220	44.92	220	55.88
240	35.38	240	43.94	240	55.05
260	34.52	260	42.63	260	54.22
280	33.49	280	41.84	280	53.35
300	32.23	300	40.54	300	52.48
320	31.17	320	39.16	320	51.55
340	30.08	340	38.1	340	50.77
360	29.25	360	36.89	360	49.70
380	28.22	380	35.84	380	48.71
400	27.12	400	34.44	400	47.75
420	25.78	420	33.23	420	46.88
440	24.63	440	31.55	440	45.96
460	23.49	460	30.54	460	44.96
480	22.77	480	29.11	480	44.13
500	21.28	500	26.97	500	43.14

Table C2 Contact angle of thermoplastic normal cornstarch/PLAgMA/Cloisite 30B blends

NSTPS36/PLAgMA/Clay 70/30/3, wt/wt		**NSTPS36/PLAgMA/Clay 70/30/5, wt/wt**	
Graph Secs	Y_Axis Angle	Graph Secs	Y_Axis Angle
0	61.83	0	69.75
0.033	61.81	0.033	70.97
0.067	61.89	0.067	70.33
0.1	61.98	0.1	70.32
20	61.25	20	69.16
40	59.95	40	68.39
60	59.14	60	66.71
80	58.23	80	66.78
100	57.75	100	65.19
120	57.47	120	64.66
140	56.71	140	64.06
160	56.41	160	63.48
180	55.99	180	62.82
200	54.81	200	61.78
220	54.36	220	62.43
240	53.99	240	60.49
260	53.51	260	61.00
280	53.16	280	60.33
300	52.33	300	59.63
320	52.39	320	59.16
340	51.91	340	58.90
360	51.82	360	59.07
380	51.51	380	58.42
400	51.01	400	57.86
420	50.72	420	58.70
440	50.56	440	57.65
460	50.16	460	57.21
480	49.94	480	57.30
500	49.67	500	57.24

Table C3 Contact angle of thermoplastic high amylose cornstarch/PLAgMA/Cloisite 30B blends surface treated by AKD (Ratio: HASTPS/PLAgMA/Clay=70/30/5 wt/wt)

Untreated		**Treated**	
Graph Secs	Y_Axis Angle	Graph Secs	Y_Axis Angle
0	66.19	0	62.46
0.033	66.19	0.033	60.80
20	65.09	20	60.86
40	64.22	40	59.38
60	62.81	60	59.77
80	61.72	80	59.13
100	60.84	100	59.01
120	60.09	120	58.23
140	59.22	140	58.23
160	58.38	160	57.00
180	57.56	180	56.93
200	56.73	200	56.87
220	55.88	220	56.49
240	55.05	240	56.27
260	54.22	260	56.07
280	53.35	280	56.22
300	52.48	300	55.43
320	51.55	320	55.85
340	50.77	340	54.74
360	49.70	360	54.75
380	48.71	380	54.94
400	47.75	400	54.54
420	46.88	420	54.42
440	45.96	440	53.60
460	44.96	460	53.71
480	44.13	480	53.38
500	43.14	500	53.37

Table C4 Contact angle of thermoplastic normal cornstarch/PLAgMA/Cloisite 30B blends surface treated by AKD (Ratio: NSTPS/PLAgMA/Clay=70/30/5 wt/wt)

Untreated		Treated	
Graph Secs	Y_Axis Angle	Graph Secs	Y_Axis Angle
0	70.60	0	76.73
0.033	69.80	0.033	76.76
0.067	69.70	0.067	76.74
0	69.51	0	76.74
20	69.40	20	76.15
40	68.29	40	75.52
60	67.31	60	75.18
80	67.32	80	74.84
100	66.31	100	74.55
120	66.15	120	74.3
140	65.28	140	73.74
160	65.55	160	73.46
180	64.52	180	73.15
200	64.62	200	72.83
220	63.82	220	72.34
240	64.08	240	72.24
260	63.42	260	71.94
280	62.85	280	71.66
300	62	300	71.33
320	61.9	320	70.98
340	61.46	340	70.74
360	61.61	360	70.29
380	61.29	380	70.19
400	60.68	400	69.69
420	60.64	420	69.43
440	60.08	440	69.19
460	59.53	460	68.89
480	59.78	480	68.62
500	58.89	500	68.18

Table C5 Contact angle of thermoplastic high amylose cornstarch/PLAgMA/Cloisite 30B blends internal treated by AKD (Ratio: HASTPS/PLAgMA/Clay=70/30/5 wt/wt)

Untreated		**Treated**	
Graph Secs	Y_Axis Angle	Graph Secs	Y_Axis Angle
0	66.19	0	69.98
0.033	66.19	0.033	69.1
20	65.09	20	68.22
40	64.22	40	67.52
60	62.81	60	67.04
80	61.72	80	66.26
100	60.84	100	65.46
120	60.09	120	65
140	59.22	140	64.72
160	58.38	160	64.4
180	57.56	180	64.15
200	56.73	200	63.61
220	55.88	220	63.34
240	55.05	240	63.09
260	54.22	260	62.86
280	53.35	280	62.57
300	52.48	300	62.32
320	51.55	320	62.05
340	50.77	340	61.82
360	49.7	360	61.52
380	48.71	380	61.35
400	47.75	400	60.29
420	46.88	420	60.19
440	45.96	440	59.94
460	44.96	460	59.28
480	44.13	480	58.76
500	43.14	500	58.62

Table C6 Contact angle of thermoplastic normal cornstarch/PLAgMA blends internal treated by AKD (Ratio: NSTPS/PLAgMA =70/30 wt/wt)

Untreated		**Treated**	
Graph Secs	Y_Axis Angle	Graph Secs	Y_Axis Angle
0	65.53	0	71.47
0.0334	64.73	0.0334	69.44
0.067	65.00	0.067	69.48
0.1	64.85	0.1	69.47
20	63.02	20	66.78
40	60.96	40	65.00
60	59.80	69	61.74
80	58.40	98	59.59
100	57.07	100	59.60
120	56.50	120	58.40
140	55.40	140	57.66
160	54.50	160	57.08
180	54.60	180	56.30
200	53.70	200	55.14
220	52.70	220	54.57
240	52.00	240	53.96
260	51.30	266	53.20
280	50.80	280	53.00
300	51.10	300	53.20
320	50.80	320	52.93
340	50.60	340	52.70
360	50.60	360	52.46
380	50.60	380	52.17
400	50.60	400	51.78
420	50.46	420	51.46
440	50.44	440	50.99
460	49.90	460	50.86
480	49.67	480	50.46
500	49.42	500	50.19

Table C7 Contact angle of thermoplastic normal cornstarch/PLAgMA blends internal treated by different concentrations of AKD (Ratio: NSTPS/PLAgMA =70/30 wt/wt)

AKD-0%[a]		**AKD-0.05%[b]**		**AKD-0.075%[c]**		**AKD-0.1%[d]**	
Graph Secs	Y_Axis Angle	Graph Secs	Y_Axis Angle	Graph Secs	Y_Axis Angle	Graph Secs	Y_Axis Angle
0	65.53	0	70.12	0	72.8	0	71.47
0.0334	64.73	0.0333	70.11	0.0333	73.81	0.0334	69.44
0.0667	65	0.0667	70.09	0.0666	73.88	0.0667	69.48
0.1	64.85	0	70.1	0.1	73.75	0.1	69.47
20	63.02	20	67.76	20	71.25	20	66.78
40	60.96	40	66.23	40	68.42	40	65
60	59.8	60	64.59	60	66.84	69	61.74
80	58.4	80	63.29	80	65.73	98	59.59
100	57.07	100	62.7	100	65.44	100	59.6
120	56.5	120	62.48	120	64.9	120	58.4
140	55.4	140	60.83	140	63.73	140	57.66
160	54.5	160	60.43	160	63.42	160	57.08
180	54.6	180	60.24	180	63.37	180	56.3
200	53.7	200	59.85	200	62.97	200	55.14
220	52.7	220	58.9	220	62.92	220	54.57
240	52	240	58.22	240	62.5	240	53.96
260	51.3	260	57.91	260	61.93	266	53.2
280	50.8	280	57.57	280	61.89	280	53
300	51.1	300	56.8	300	61.91	300	53.2
320	50.8	320	56.5	320	61.35	320	52.93
340	50.6	340	56.3	340	61.32	340	52.7
360	50.6	360	55.6	360	60.53	360	52.46
380	50.6	380	54.7	380	60.64	380	52.17
400	50.6	400	54.01	400	60.35	400	51.78
420	50.46	420	53.78	420	60.55	420	51.46
440	50.44	440	53.2	440	59.59	440	50.99
460	49.9	460	52.98	460	59.18	460	50.86
480	49.67	480	52.85	480	58.4	480	50.46
500	49.42	500	52.56	500	58.21	500	50.19

[a, b, c, d]: denote the AKD concentration are 0%, 0.75%, 0.5% and 0.1%wt (dry starch weight basis, respectively.

Table C8 Comparison of contact angle of thermoplastic bean starch/PLAgMA blends

BeTPS36/PLAgMA/Cloiste 30B 70/30/5, wt/wt		**BeTPS36/PLAgMA 70/30, wt/wt**	
Graph Secs	Y_Axis Angle	Graph Secs	Y_Axis Angle
0	58.95	0	53.61
0.0334	59.81	0.0333	54.64
0.0667	60.5	0.0667	54.49
0.1	60.45	0.1	54.61
10	58.78	10	52.54
20	58.48	20	51.88
30	58.01	30	51.32
40	57.81	40	50.66
50	57.32	50	50.43
60	56.72	60	49.53
70	56.4	70	49.36
80	56.41	80	48.88
85	56.2	85	49.41
90	56.1	90	49.05
95	56.14	95	48.56
100	56.13	100	49.12
110	55.84	110	48.11
120	55.28	120	47.67
130	55.44	130	47.41
140	54.96	140	47.65
150	54.98	150	46.8
160	54.47	160	46.98
170	54.39	170	46.77
180	54.18	180	46.08
190	53.56	190	45.51
200	53.97	200	45.8
210	53.94	210	45.14
220	53.61	220	43.85
230	53.5	230	43.65
240	53.08	240	44.5
250	52.98		
260	52.7		
270	52.5		
280	52.16		
290	52.5		

Table C9 Comparison of contact angle of thermoplastic lentil starch/PLAgMA blends

LenTPS36/PLAgMA 70/30, wt/wt		**LenTPS36/PLAgMA/Clay 70/30/5, wt/wt**	
Graph Secs	Y_Axis Angle	Graph Secs	Y_Axis Angle
0	53.74	0	62.69
0.0333	52.23	0.0334	62.01
0.0667	53.44	0.0667	61.75
0.1	48.96	0.1	61.87
10	46.86	10	55.35
20	44.5	20	52.35
30	41.5	30	50.82
40	40	40	48.5
50	39.01	50	47.29
60	37.9	60	46.2
70	37.2	70	46.21
80	37.22	80	45.71
85	36.8	85	45.38
90	36.16	90	45.14
95	36	95	44.67
100	35.5	100	44.5
110	34.7	110	44.24
120	33.6	120	43.95
130	32.91	130	43.73
140	32.46	140	43.47
150	32.6	150	43.15
160	32.25	160	43.12
170	32	170	42.9
180	31.1	180	42.64
190	30.39	190	42.5
200	30.21	200	41.98
210	29.58	210	41.76
220	28.9	220	41.2
230	28.9	230	41.64
240	29.1	240	41.3
250	28.9	250	41.6

Table C10 Comparison of contact angle of thermoplastic pea starch/PLAgMA blends

PeTPS36/PLAgMA 70/30, wt/wt		**PeaTPS36/PLAgMA/Clay 70/30/5, wt/wt**	
Graph Secs	Y_Axis Angle	Graph Secs	Y_Axis Angle
0	51.81	0	76.92
0.0334	51.89	0.0334	74.76
0.0667	54.11	0.0667	74.57
0.1	52.27	0.1	75.04
10	43.58	10	66.12
20	39.52	20	63.04
32	37.16	30	60.81
40	36.35	40	58.81
50	34.21	50	58.05
60	32.75	60	56.7
70	31.6	70	56.7
80	30.54	80	56.86
85	29.8	85	56.48
90	29.1	90	56.32
95	27.8	95	56.1
100	27.39	100	55.22
110	26.7	110	55.67
120	25.68	120	55.68
130	25.35	130	55.48
140	25.11	140	55.08
150	24.87	150	53.9
160	24.62	160	54.05
170	24.38	170	54.57
180	24.14	180	53.42
190	23.9	190	53.81
200	23.66	200	53.9
210	23.41	210	53.96
220	23.17	220	52.9
230	22.93	230	52.11
240	22.69	240	52.29
250	22.45	250	52.22

Appendix D

Experiments on Brazilian cornstarches

Cornstarches were purchased from Corn Products Brasil Ingredientes Industriais Ltda (Brazil). Blend ratios and experimental conditions were shown in Table D-1. Water and glycerol acted as plasticizers and ratio of water/glycerol was fixed at 15/35 (wt/wt) for each run. According to ASTM D882-02, the crosshead speed was set at 5 mm/min when testing mechanical properties on Instron tensile testing machine. Properties were shown in Table D-2.

Table D1 Blend ratios and experimental conditions

No	HAS	NS	WS	Amidex 4001*	High Amylose	Amidex 3001	PLA	Plasticizer	Mold Temp** (°C)
1	0	0	0.367	0.183	0	0	0.2	0.25	160
2	0	0	0.267	0.133	0	0	0.4	0.2	170
3	0	0	0.4	0	0	0	0.4	0.2	170

* Amidex 4001 contained 0-3wt% amylose and 97-100wt.% amylopectin with an average molecular weight (Mw) of 486,000 g/mol and a density of 0.5-0.7 g/cm3.

** Mold Temp is the temperature on Rosand Capillary Rheometer

Table D2 Mechanical properties of blends

No.	Tensile Strength (MPa)	Modulus (MPa)	Elongation at Break (%)
1	9.79±3.76	1033.0±293.3	1.527±0.301
2	16.22±2.13	1102.0±318.3	2.203±0.292
3	17.54±1.70	1013.0±199.0	2.539±0.645

Reference

Ajili, S.H., Ebrahimi, N.G., "Miscibility of TPU (PCL diol)/PCL blend and it effect on PCL crystallinity, *Macromolecular Symposia*, (249-250) 623-627 (2007)

Albertsson, A-C., Varma, I-K., "Aliphatic polyester: synthesis, properties and applications", *Advances on Polymer Science*, 157 1-40 (2002)

Alexandre, M., Dubois, P., "Polymer-layered silicate nanocomposites: preparation, properties and uses of a new class of materials", *Materials Science and Engineering*, 28 1-63 (2000)

Arvanitoyannis I., Biliaderis, C. G., Ogawab, H. and Kawasakib, N. "Biodegradable films made from low-density polyethylene (LDPE), rice starch and potato starch for food packaging applications: Part 1", *Carbohydrate Polymers* 36, 89- 104 (1998)

Auras, R.A., Harte, B., Selke, S., Hernandez, R., 'Mechanical, physical and barrier properties of poly (lactide) films", *Journal of plastic film and sheeting*, 19 123-135 (2003)

Auras, R.A., Singh, S.P., Singh, J.J., "Evaluation of oriented poly (lactide) polymers vs. existing PET and oriented PS for fresh food service containers", *Packaging Technology and Science*, 18 207-216 (2005)

Avella, M., Vlieger, J.J.D., Errico, M.E., Fischer, S., Vacca, P., Volpe, M.G., "Biodegradable starch/clay nanocomposite films for food packaging applications", *Food Chemistry*, 93 467 - 474 (2005)

Averous, L. "Biodegradable multiphase system based on plasticized starch: a review", *Journal of Macromolecular Science Part C: Polymer Review*, C44 (3) 231-274 (2004)

Averous, L. and Boquillon, N. "Boicomposites based on plasticiaed starch: thermal and mechanical behaviors", *Carbohydrate Polymer* 56 111-122 (2004)

Avérous, L., and Fringant, C., "Association between plasticized starch and polyesters: processing and performances of injected biodegradable systems", *Polymer Engineering & Science*, 41 (5) 727-734 (2001)

Averous, L., Fauconnier, N., Moro, L.; Fringant, C., "Blends of thermoplastic starch and polyesteramide: processing and properties", *Journal of Applied Polymer Science*, 76 (7), 1117-1128 (2000)

Bagheri, R., "Effect of processing on the melt degradation of starch-filled polypropylene", *Polymer International*, 48 1257-1263 (1999)

Bastioli, C., Cerutti, A., Guanella, I., Romano, G.C., Tosin, M., "Physical state and biodegradation behaviors of starch-polycaprolactone systems", *Journal of Environmental Polymer Degradation*, 3 (2) 81-95 (1995)

Bohlmann, G.M., "Biodegradable packaging life-cycle assessment", *Environmental Progress*, 23 (4) 342-346 (2004)

Brook, M., Jiang, J., Heritage, P., Underdown, B., McDermott, M., "Silicone-modified starch/protein microparticles: protecting biopolymers with a hydrophobic coating", *Colloids and Surfaces B: Biointerfaces*, 9 285-295 (1997)

Cairncross, R.A., Ramaswamy, S., O'Connor, R., "Moisture sorption and transport in polylactide", *International Polymer Processing XXI* 1 33-37 (2007)

Califano, A.N., Anon, M.C., "Differential scanning calorimetry of mung bean starch", Journal of Food Science 55 (3) 771-773 (1990)

Carlson, D., Nie, L., Narayan, R., Dubois, P., "Maleation of polylactide (PLA) by reactive extrusion", *Journal of Applied Polymer Science*, 72 477–485 (1999)

Carvalho, A.J.F., Curveloa, A.A.S., Agnellib, J.A.M., "A first insight on composites of thermoplastic starch and kaolin", *Carbohydrate Polymers,* 45 189-194 (2001)

Carvalho, A.J.F., Zambon, M.D., Curvelo, A.A.S., Gandini, A., "Sizing exclusion chromatography characterization of thermoplastic starch composites: 1. Influence of plasticizer and fibre content", *Polymer Degradation and Stability*, 79 133-138 (2003)

Chen, B., Evans, J.R.G., "Thermoplastic starch–clay nanocomposites and their characteristics", *Carbohydrate Polymers,* 61 455–463 (2005)

Chiou, B-S., Yee, E., Glenn, G-M., Orts, W-J., "Rheology of starch-clay nano-composites", *Carbohydrate Polymers,* 59 467–475(2005)

Cinelli, P., Chiellini, P., E. Lawton, J. W., Imam, S. H., "Foamed articles based on potato starch, corn fibers and poly (vinyl alcohol)", *Polymer Degradation and Stability,* 91 (5) 1147-1155 (2006)

De Graaf, R. A. and Janssen, L. P. B. M., "Properties and manufacturing of a new starch plastic", *Polymer Engineering and Science*, 41, (3) 584-594 (2001)

Decker, E.L., Frank, B., Suo, Y., Garoff, S., "Physics of contact angle measurement", *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 156 177–189 (1999)

Dubois, P., and Narayan, R., Biodegradable compositions by reactive processing of aliphatic polyester/polysaccharide blends", *Macromolecular Symposia*, 198 233-243 2003

Feijoo, J. L., Cabedo, L., Gimenez, E., Lagaron, J. M., Saura, J. J., "Development of amorphous PLA-montmorillonite nanocomposites", *Journal of Materials Science* **40** 1785 – 1788 (2005)

Fischer, E.W., Sterzel, H.J., Wegner, G., Kolloid, Z.Z., *Polymer*, 251 980-990 (1972)

Fringant, C., Rinaudo, M., Foray, M.F., Bardet, M., "Preparation of mixed esters of starch or use of an external plasticizer: two different ways to change the properties of starch acetate films", *Carbohydrate Polymers*, 35 97-106 (1998)

Funke, U., Bergthaller, W., Lindhauer, M. G., "Processing and characterization of biodegradable products based on starch", *Polymer Degradation and stability*, 59, 293-296 (1998)

Garmabi, H., and Kamal, M.R., "Improved barriew and mechanical properties of laminar polymer blends", *Journal of Plastic Film &Sheeting,* 15 120-130 (1999)

Halley, P., Rutgers, R., Coombs, S., Kettels, J., Gralton, J., et al., "Developing biodegradable mulch films from starch based polymers", *Starch/Stärke* 53, 362-367 (2001)

Hiroi, R., Ray, S.S., Okamoto, M., Shiroi, T., "Organically modified layered titanate: a new nanofiller to improve the performance of biodegradable polylactide", *Macromolecular Rapid Communications*, 25 1359–1364 (2004)

Hoover, R., Ratnayake, W.S., "Starch characteristics of black bean, chick pea, lentil, navy bean and pinto bean cultivars grown in Canada" Food Chemistry, 78 489-498 (2002)

Huang, C-H., "Properties of thermoplastic starch/poly (lactic acid) blends", *Master Thesis*, McMaster University, (2005)

Huda, H.S., Mohanty, A.K., Misra, M., Drzal, L.T., Schut, E. "Effect of processing conditions on physico-mechanical properties of cellulose fiber reinforced poly (lactic acid)", *ANTEC* 1614-1618 (2004)

Huneault, M. and Li, H., "Morphology and properties of compatibilized polylactide/ thermoplastic starch blends", *Polymer*, 48 270-280 (2007)

Ikada, Y., Tsuji, H., "Biodegradable polyesters for medical and ecological Applications", Macromolecular Rapid Communications, 21, 117–132 (2000)

Jacobsen, S., Fritz, H.G., "Filling of poly (lactic acid) with native starch", *Polymer Engineering and Science*, 36, (22) 2799-2804 (1996)

Jacobsen, S., Fritz, H.G., "Plasticizing polylactide-the effect of different plasticizers on the mechanical properties", *Polymer Engineering And Science*, 39(7) 1303-1310 (1999)

Jang, W.Y., Shin, B.Y., Lee, T.J., Narayan, R., "Thermal properties and morphology of biodegradable PLA/starch compatibilized blends", *Journal of Industrial &Engineering Chemistry,* 13 (3) 457-464 (2007)

Jun, C-H., "Reactive blending of biodegradable polymers: PLA and starch", *Journal of Polymers and the Environment,* 8 (1) 33-37 (2000)

Kalambur, S., Rizvi, S.S.H., "Biodegradable and functionally superior starch - polyester nanocomposites from reactive extrusion", *Journal of Applied Polymer Science*, 96 1072 - 1082 (2005)

Kalybaba, M., Tabil L.G., Panigrahi, S., Crerar, W.J., Powell, T., Wang, B. "Biodegradable polymer: past, present, and future" An ASAE Meeting Present Paper Number: RRV03-0007

Ke, T., Sun, S. X., Seib, P., "Blending of poly (lactic acid) and starch containing varying amylose content", *Journal of Applied Polymer Science*, 89 3639-3646 (2003)

Ke, T., Sun, X., "Melting behavior and crystallization kinetics of satch and poly (lactic acid) composites" *Journal of Applied Polymer Science*, 89 1203-1210 (2003c)

Ke, T., Sun, X., "Physical Properties of Poly (Lactic Acid) and Starch Composites with Various Blending Ratios", *Cereal Chemistry*, 77 (6) 761–768 (2000)

Ke, T., Sun, X., "Starch, poly (lactic acid), and poly (vinyl alcohol) blends", *Journal of Polymers and the Environment*, 11 (1) 7-14 (2003a)

Ke, T., Sun, X., "Thermal and mechanical properties of poly (lactic acid) and starch blends with various plasticizers", *Transactions of the ASAE,* 44 (4) 945–953 (2001)

Ke, T., Sun, X., "Thermal and mechanical properties of poly (lactic acid)/starch/

methylenediphenyl diisocyanate blending with triethyl citrate", *Journal of Applied Polymer Science*, 88 2947-2955 (2003b)

Kim, C-H., Jung, K-M., Kim, J-S., Payk, J-K., "Modification of aliphatic polyesters and their reactive blends with starch", *Journal of Polymers and Environment*, 12 (3) 179-187 (2004)

Kotnis, M. A., O'Brien, B. S., and Willett, J. L., "Processing and Mechanical Properties of biodegradable Poly (hydroxybutyrate-co-valerate)-Starch Compositions", *Journal of Environmental Polymer Degradation*, 3 (2) 97-105 (1995)

Labrecque, L.V., Kumar, R.A., Dave, V., Gross, R.A., Mccarthy, S.P., "Citrate Esters as Plasticizers for Poly (lactic acid)", *Journal of Applied Polymer Science*, 66 1507–1513 (1997)

Laohakunjit, N., Noomhorm, A., "Effect of plasticizers onmechanical and barrier properties of rice starch film", *Starch/Stäke,* 56 348 – 356 (2004)

LeBaron, P. Wang, Z., Pinnavaia, T., "Polymer-layered silicate nanocomposites: an overview", *Applied Clay Science*, 15 11–29 (1999)

Liu, Q. "Food Carbohydrates: chemistry, physical properties, and applications", Ch. 7, 309-406 (2005)

Liu, W., Wang, Y-J., Sun, Z., "Crystallization behavior of starch-filled polypropylene", *Journal of Applied Polymer Science*, 92 484 – 492 (2004)

Lourdin, D., Bizot, H., Colonna, P., " 'Antiplasticization' in starch-glycerol film", *Journal of Applied Polymer Science*, 63 (8) 1047-1053 (1997)

Ma, X., Yu, J., " Formamide as the plasticizer for thermoplastic starch", *Journal of applied Polymer Science,* 93 1769-1773 (2004)

Maliger, R.B., McGlashan, S.A., Halley, P.J., Matthew, L.G., "Compatibilization of starch–polyester blends using reactive extrusion", *Polymer Engineering and Science*, 46 48–263 (2006)

Mano, J.F., Koniarova, D., Reis, R.L., "Thermal properties of thermoplastic starch/synthetic polymer blends with potential biomedical applicability", *Journal of Materials Science: Materials in Medicine*, 14 127-135 (2003)

Marmur, A., "Equilibrium contact angles: theory and measurement", *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 116 55-61 (1995)

Martin, O. and Averous, L., "Poly (lactic acid): plasticization and properties of biodegradable multiphase systems", *Polymer*, 42 (14), 6237–6247 (2001).

Martin, O., Schwach, E., Avérous, L., Couturier, Y., "Properties of biodegradable multilayer films based on plasticized wheat starch", *Starch/Stärke* 53 372-380 (2001)

McGlashan, S.A., and Halley, P.J., "Preparation and characterization of biodegradable starch-based nanocomposite materials", *Polymer International*, 52 1767-1773 (2003)

Mehta, R., Kumar, V., Bhunia, H., Upadhyay, S.N., "Synthesis of poly (lactic acid): a review", *Journal of Macromolecular Science Part C: Polymer Reviews*, 45 325-349 (2005)

Modesti, M., Besco, S., Lorenzetti, A., Zanirato, G., Rauli, F. "Reinforcing effect of organo-modified layered silicates in high-density polyethylene", *Journal of Nanoscience and Nanotechnology*, 5 (6) 958-963 (2005)

Okamoto, M., "Biodegradable polymer/layered silicate nanocomposites: a review", *Handbook of Biodegradable Polymeric Materials and Their Applications,* 1 1 - 45 (2005)

Pandey, J.K., Reddy, K.R., Kumar, A.P., Singh, R.P., " An overview on the degradability of polymer nanocomposites". *Polymer Degradation and Stability*, 88 234-250 (2005)

Pandey, J.K., Singh, R.P., "Green nanocomposites from renewable resources: effect of plasticizer on the structure and material properties of clay-filled starch", *Starch/Stäke* 57 8 - 15 (2005)

Paola, R.D.D, Asis, R. Aldo, M.A.J., "Evaluation of degree of starch gelatinization by a new enzymatic method", *Starch/Stärke* 55 403-409 (2003)

Park H-M., Li, X., Jin, C-Z., Park, C-Y., Cho, W-J., Ha, C-S., "Preparation and properties of biodegradable thermoplastic starch/clay hybrids", *Macromolecular Materials and Engineering*, 287 553-558 (2002)

Park, H-M., Lee, W-K., Park, C-Y., Cho, W-J., Ha, C-S., "Environmentally friendly polymer hybrids Part I Mechanical thermal , and barrier properties of thermoplastic starch/clay nanocomposites", *Journal of Materials Science*, 38 909-915 (2003)

Park, J.W., Im, S.S., Kim, S.H., Kim, Y.H., "Biodegradable polymer blends of poly (L-lactic acid) and gelatinized starch", *Polymer Engineering and Science,* 40 (12) 2539-2540 (2000)

Perez, C.J., Alvarez, V., Mondragon, I., Vazquez, A., "Mechanical properties of layered silicate/starch polycaprolactone blend nanocomposites", *Polymer International*, 56 686-693 (2007)

Plackett, D., "Maleated Polylactide as an Interfacial Compatibilizer in Biocomposites", *Journal of Polymers and the Environment*, 12 (3) 131-138 (2004)

Pluta, M., Galeski, A., Alexandre, M., Paul, M-A., Dubois, P., "Polylactide/ montmorillonite nanocomposites and microcomposites prepared by melt blending: structure and some physical properties", *Journal of Applied Polymer Science*, 86 1497-1506 (2002)

Pluta, M., Paul, M-A., Alexandre, M., Dubois, F., "Plasticized polylactide/clay nanocomposites. I. The role of filler content and its surface organo-modification on the physico-chemical properties", *Journal of Polymer Science: Part B: Polymer Physics* 44, 299 - 311 (2006)

Potschke, P. and Wallheinke, K., "Blends of thermoplastic polyurethane and maleic-anhydride grafted polyethylene. I: morphlogy and mechanical properties", *Polymer Engineering and Science*, 39 (6) 1035-1048 (1999)

Ratnayake, W.S., Hoover, R., Warkentin, T., "pea starch: composition, structure and properties- a review", *Starch/Stärke,* 54 217-234 (2002)

Ratner, B. D., Hoffman, A.S., Schoen, F.J., and Lemons, J.E., "Biomaterials Science: An introduction to materials in medicine", *Society of Biomaterials, Academic Press: San Diego*, Ch. 2, 37–130 (1996).

Ravnjak, D., Plazl, I., Moze, A., "Kinetics of colloidal alkylketene dimmer particles deposition on pulp fibers", *Colloid and Polymer Science*, 285 907-914 (2007)

Ray, S.S., Okamoto, M., "Biodegradable Polylactide and Its Nanocomposites:Opening a New Dimension for Plastics and Composites", *Macromolecular Rapid Communications* 24 815–840 (2003)

Ray, S.S., Yamada, K., Okamoto, M., Ueda, K., "Control of biodegradability of polylactide via nanocomposite technology", *Macromolecular Materials and Engineering*, 288, 203–208 (2003)

Rodriguez-Gonzalez, F. J., Ramsay, B. A. and Favis, B. D., "High performance HDPE/ thermoplastic starch blends: a sustainable alternative to pure polyethylene", *Polymer* 44, 1517–1526 (2003)

Rodriguez-Gonzalez, F. J., Ramsay, B. A. and Favis, B. D., "Rheological and thermal properties of thermoplastic starch with high glycerol content", *Carbohydrate Polymers,* 58 139-147 (2004)

Rodriguez-Gonzalez, F. J., Virgilio, N., Ramsay, B. A. and Favis, B. D., "Influence of melt drawing on the morphology of one- and two-step processed LDPE/thermoplastic starch blends", *Advances in Polymer Technology*, 22 (4) 297–305 (2003)

Rodriguez-veloz, O. and Kamal, M. R., “The development of laminar morphology in a co-rotating twin screw extruder”, *Advances in Polymer Technology*, 18 (2) 89–108 (1999)

Sarazin, P., Huneault, M.A., Orts, W., Favis, B.D., “Blends of polylactide with thermoplastic starch”, *ANTEC*, 2111-2114 (2005)

Schwach, E., Averous, L., “Starch-based biodegradable blends: morphology and interface properties”, *Polymer International*, 53 2115-2124 (2004)

Shen, W., Filonanko, Y., Truong, Y., Park, I.H., Brack, N., Pigram, P., Liesegang, J., “Contact angle measurement and surface energetics of sized and unsized paper”, *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 173 117–126 (2000)

Shen, W., Zhang, H., Ettl, R., “Chemical composition of ‘AKD vapour’ and its implication to AKD vapour sizing”, *Cellulose*, 12 641-652 (2005)

Sheth, M., Kumar, R.A., Dave, V., Gross, R.A., Mccarthy, S.P., “Biodegradable polymer blends of poly (lactic acid) and poly (ethylene glycol)”, *Journal of Applied Polymer Science*, 66 1495-1505 (1997)

Shibata, M., Someya, Y., Orihara, M., Miyoshi, m., “Thermal and mechanical properties of plasticized poly (L-lactide) nanocomposites with organo-modified montmorillonites” *Journal of Applied Polymer Science*, 99 (5) 2594-2602 (2006)

Sinclair, R.G., “The case for polylactic acid as a commodity packaging plastic”, *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, A33 (5) 585-597 (1996)

Smith J.K., Dow Corning Corp., *US Patent* No. 4495226, 1985.

Soest, J.J.G., Benes, K., Wit, D., “The influence of starch molecular mass on the properties of extruded thermoplastic starch” *Polymer* 37 (16) 3543-3552 (1996)

Stepto, R.F.T., " Understanding the processing of thermoplastic starch", *Macromolecular Symposia,* 571-577 (2006)

Stepto, R.F.T., "The processing of starch as a thermoplastic", *Macromolecular Symposia* 200, 255–264 (2003).

St-Pierre, N., Favis, B. D., Ramsay B. A., Ramsayt J. A. and Verhoogt H., "Processing and characterization of thermoplastic starch/polyethylene blends", *Polymer,* 38 (3), 647-655 (1997)

Sudesh, K. Abe, H., Dio, Y. "Synthesis, structure and properties of polyhydroxyalkanoates: biological polyesters", *Progress in Polymer Science,* 25 (10) 1503-1555 (2000)

Sun, X., Greg K. and Seib P., "Edible/biodegradable feed packaging materials", *Patent, U.S.* Patent No. 6,337,097 (1999).

Suyatma, N.E., Coinet, A., Tighzert, L., Coma, V., "Mechanical properties of biodegradable films made from chitosan and poly (lactic acid) blends", J*ournal of Polymer and the Environment,* 12 (1) 1-6 (2004)

Swinkels, J.J.M., "Composition and properties of commercial native starches", *Starch/Stärke,* 37 1–5 (1985).

Tanoue, S., Hasook, W., Iemoto, Y., Unryu, T., "Preparation of poly(lactic acid)/ poly (ethylene glycol)/organoclay nanocomposites by melt compounding", *Polymer Composites,* 256-263 2006

Ueda, T., Takagi, S., Nishida, M., Hishiki, N., Ogura, Nippon Starch Chemical Co., Jpn. Kokkyo Koho, *Japanese Patent,* No. 62218401. 1987

Vaidya, D.R., Bhattacharya, M.J., "Properties of blends of starch and synthetic polymers containing anhydride groups", *Journal of Applied Polymer Science,* 52 (5) 617-628 (1994)

Van Soest, J. J. G. and Borger, D. B. "Structure and properties of compression-molded thermoplastic starch materials from normal and high-amylose maize starches", *Journal of Applied Polymer Science*, 64 (4), 631-644

Velzen U.T., "R&D and innovation of bioplastics in the Netherlands", *IBAW - BCPN Meeting*, Agrotechnology & Food Innovations, Wageningen University, April 26, 2005

Vlachopoulos, J., "Introduction to polymer processing", McMaster University, Hamilton, Canada (2003).

Wagener, R., Reisinger, T., "A rheological method to compare the degree of exfoliation of nanocomposites", *Polymer,* 44 7513–7518 (2003)

Wang, H., Sun, X., Seib, P., "Properties of poly (lactic acid) blends with various starches as affected by physical aging", *Journal of applied Polymer Science,* 90 3683-3689 (2003)

Wang, H., Sun, X., Seib, P., "Strengthening blends of poly (lactic acid) and starch with methylenediphenyl diisocyanate", *Journal of Applied Polymer Science*, 82, 1761-1767 (2001)

Wang, X-L., Yang K-K., Wang, Y-Z., "Properties of starch blends with biodegradable polymer", *Journal of Macromolecular Science Part C: Polymer Reviews*, C43 (3) 385-409 (2003)

Wang, Y., Chen, F-B., Wu, K-C., Wang, J-C., "Shear rheology and melt compounding of compatibilized-polypropylene nanocomposites: effect of compatibilizer molecular weight". *Polymer Engineering And Science*, 289-302 (2006)

Wilhelm, H-M., Sierakowski M-R., Souza, G.P., Wypych, F., "Starch films reinforced with mineral clay", *Carbohydrate Polymers*, 52 101–110 (2003)

Willett, J.L., and Shogren, R.L., "Processing and properties of extruded starch/polymer foams", *Polymer*, 43 5935-5947 (2002)

Williams, D. F., "Definitions in Biomaterials", *Proceedings of a Consensus Conference of the European Society for Biomaterials*. Elsevier: New York, (1987).

Wool, R.P., and Sun, X.S., "Bio-based polymers and composites", *Academic Press Inc., U. S.*, Ch 11 369-411 (2005)

Wu, C-S., "A comparison of the structure, thermal properties, and biodegradability of polycaprolactone/chitosan and acrylic acid grafted polycaprolactone/chitosan", *Polymer*, 46 147-155 (2005)

Xie, F., Yu, L., Liu, H., Chen, L., " Starch modification using reactive extrusion", *Starch/Stäke*, 58 131-139 (2006)

Xie, F., Yu, L., Liu, H., Dean, K., "Effect of compatibilizer distribution on thermal and rheological properties of gelatinized starch/biodegradable polyesters blends", *International Polymer Processing*, XXI 4 374-380 (2006)

Yu, J., Chen, S., Gao, J., Zheng, H., Zhang, J., Lin, T., "A study on the properties of starch/glycerine blend", *Starch/Stärke,* 6 246-250 (1998)

Yu, J., Gao, J., Lin, T., "Biodegradable thermoplastic starch", *Journal of Applied Polymer Science*, 62 1491-1494 (1996)

Yu, L., Kealy, T., Chen, P., "Study of starch gelatinization in a flow field using simultaneous rheometric data collection and microscopic observation", *International Polymer Processing XXI* 3 383-389 (2006)

Zhang, H., Kannangara, D., Hilder, M., Ettl, R., Shen, W., "The role of vapour deposition in the hydrophobization treatmentof cellulose fibres using alkyl ketene dimers and lkenyl succinic acid anhydrides", *Colloids and Surfaces A: Physicochemical and Engineering Aspects,* 297 203–210 (2007)

Zhang, J-F. and Sun, X., "Physical characterization of coupled poly(lactic acid)/starch/maleic anhydride blends plasticized by acetyl triethyl citrate", *Macromolecular. Bioscience*, 4 1053–1060 (2004)

Zhang, J-F., Sun, X., "Mechanical and Thermal Properties of Poly(lactic acid)/Starch Blends with Dioctyl Maleate", *Journal of Applied Polymer Science,* 94 1697 - 1704 (2004)

Zhang, J-F., Sun, X., "Mechanical properties of poly(lactic acid)/starch composites compatibilized by maleic anhydride", *Biomacromolecules*, 5, 1446-1451 (2004)

Zimmerman, P.M. and Hercules, D.M., "Direct quantitation of alkylketene dimmers using time-of-flight secondary ion mass spectrometry", *Analytical Chemistry*, 67 (17) 2901-2905 (1995)