

PREPARATION OF MALEIC ANHYDRIDE GRAFTED POLY(LACTID ACID) (PLA)  
AND ITS COMPATIBILIZATION EFFECTS ON PLA/SOY PROTEIN COMPOSITES

By

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Abstract

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Derived from renewable resources, Polylactide (PLA) exhibits good mechanical properties relative compared with polyolefins. Blending PLA with natural polymers such as soy protein concentrate (SPC) results in PLA materials of reduced cost, enhanced thermal properties and integral biodegradability. In this research, PLA/SPC composites were prepared in a single-step compounding process. A novel approach was used in this work for the preparation of PLA/SPC composites, which processed SPC as a plastic component in mixing with PLA but produced in situ formed PLA/SPC composites. In order to improve mechanical and physical properties, maleic anhydride (MA) grafted PLA (PLA-g-MA) was prepared and used as to compatibilize the PLA/SPC composites.

The preparation of PLA-g-MA was carried out in a co-rotating twin-screw extruder by free radical melt grafting reaction. An electron-donating monomer styrene (St) was added to active the MA monomer. The effects of MA/St molar ratio, initiator concentration, monomer concentration, processing temperature and screw speed on the grafting reaction were

investigated in details. The grafted copolymer was characterized by Nuclear Magnetic Resonance (NMR) and Fourier Transform Infrared Spectroscopy (FT-IR).

To investigate the compatibilization effect on the morphological, tensile and dynamic mechanical properties of PLA/SPC composites, PLA-g-MA was added to the composites at levels of 1, 2, and 4% on total. The grafting degree of MA was changed from 0.25% to 0.89%. Compatibilizer was found to be indispensable to achieve PLA/SPC composites of high mechanical and physical properties. The tensile properties of the compatibilized PLA/SPC composites were significantly higher than that of the uncompatibilized one. Fracture morphology was investigated through scanning electron microscopy (SEM) and indicates enhanced interfacial adhesion.

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## **Abbreviation**

SPC	Soy Protein Concentrate
PLA	Poly(lactic acid)
MA	Maleic Anhydride
PLA-g-MA	Poly(lactic acid)-g-Maleic Anhydride
GPC	Gel Permeation Chromatography
NMR	Nuclear Magnetic Resonance
FT-IR	Fourier Transform Infrared Spectroscopy
DMA	Dynamic Mechanical Analysis
DSC	Differential Scanning Calorimetry
SEM	Scanning Electron Microscopy

## Chapter 1 Introduction

### 1.1 Biobased plastics

#### 1.1.1 *State-of-the-art biobased plastics*

Biobased plastics (bio-plastics) have received widespread attention over the last two decades, primarily due to two major reasons: first, the growing environmental crisis and secondly, the realization that our petroleum resource is finite. Generally, bio-plastics can be classified into three categories according to the feedstock resources of the major polymer components:

- (1) The first group includes natural polymers which are used directly for plastics, such as starch, protein and cellulose.
- (2) The second group consists of thermoplastics polymers which are totally derived from renewable feedstock, such as poly(lactic acid) (PLA) and polyhydroxyalkanoates (PHAs).
- (3) The third group is comprised of polymers which are partially derived from renewable feedstock, such as polyurethanes based on plant oil-derived polyols and poly(trimethylene terephthalate) synthesized using the glycerol-derived 1-3-propane diol (Feng 2010).

The Technology Road Map for Plant/Crop-based Renewable Resources 2020, sponsored by the U.S Department of Energy (DOE), has targeted to achieve 10% of basic chemical building blocks arising from plant-derived renewable sources by 2020, with development concepts in place by then to achieve a further increase to 50% by 2050 (Plant 1999). Bio-plastics may soon be competing with commodity plastics, as a result of the sales growth of more than 20-30% per year and improvement in their overall properties (Scott 2000). However,

the high cost of bio-plastics is still a challenge. Actually, this is not due to the raw material cost for synthesis; rather it is mainly resulted from the low volume of production.

Bio-plastics have many advantages compared to petroleum-based plastics. Firstly, bio-plastics are totally and/or partially derived from renewable biomass sources, such as corn starch, vegetable oil and fermentation of bacteria. However, the feedstock of petroleum-based plastics, i.e. fossil carbons, is not renewable and is depleting very fast. The production and utilization of bio-plastics demonstrate a more sustainable philosophy. Secondly, bio-plastics are biodegradable and environmental-friendly. They are capable of undergoing decomposition, primarily through fermentation of microorganisms in the environment to metabolize the molecular structure of themselves, therefore maintain the carbon dioxide neutrality in the environment, while the residues of petroleum-based plastics after their usage may remain solid for hundreds of years, which is a severe issue only received public awareness recently.

### *1.1.2 Soy protein*

Soybean is a very important economic crop in the United States. It is a primary crop resource for oil and protein, both find wide applications in domestic and industrial products. Typically, soybean contains about 20% soy oil, 42% soy protein (SP), 33% carbohydrate, and 5% ash on a dry basis (Berk 1993). Food and Agriculture Organization (FAO) estimated that over 160 million tonnes of soybean was produced worldwide in the year 2000 (Kumar et al 2002). The leading producer was the USA, which accounted for 49% of the total production. SP is mainly available in three grades, i.e. soy flour (SF), soy protein concentrate (SPC), and soy protein isolate (SPI), containing ca. 50, 70, 90% protein, respectively (Feng 2010). The

composition details of the three grades has been summarized in Table 1.1(Kinsella 1979).

**Table 1.1** Composition of different soy protein products

g/100 g product	Soy flour	Soy protein concentrate (SPC)	Soy protein isolate (SPI)
Protein (as is)	48	64	92
Fat (min)	0.3	0.3	0.5
Moisture (max)	10	10	<5
Fibre (crude)	3.0	4.5	<1
Ash	7	7	4
Carbohydrate	31-32	14-15	—

In recent years, many attempts have been focused on research of SP as a promising natural polymer for plastics use. The first report on using SP for plastics can be traced back to 1930s and 1940s when Ford Motor Company attempted to use blends of soy meal and phenol-formaldehyde resin for manufacturing trunks (Brother et al 1939). Since then little progress has been made on SP plastics due to the low-cost of the petroleum-based plastics; not until the 1990s did SP-based plastics regain research interest due to its environmentally benign advantages (Zhang et al 2010). The potential uses of soy plastics as commodity products (spoon, bag, toys) have been successfully demonstrated (Paetau et al 1994). Besides the application of neat SP plastics, SP can also be used as filler for thermoplastics due to its low cost and good biodegradability. These thermoplastics include Polycaprolactone (John et al 1999) (Zhong et al 2001), Polylactide (Fang et al 2009) (Zhang et al 2006), and poly(butylene adipate-co-terephthalate) (Chen et al 2009).

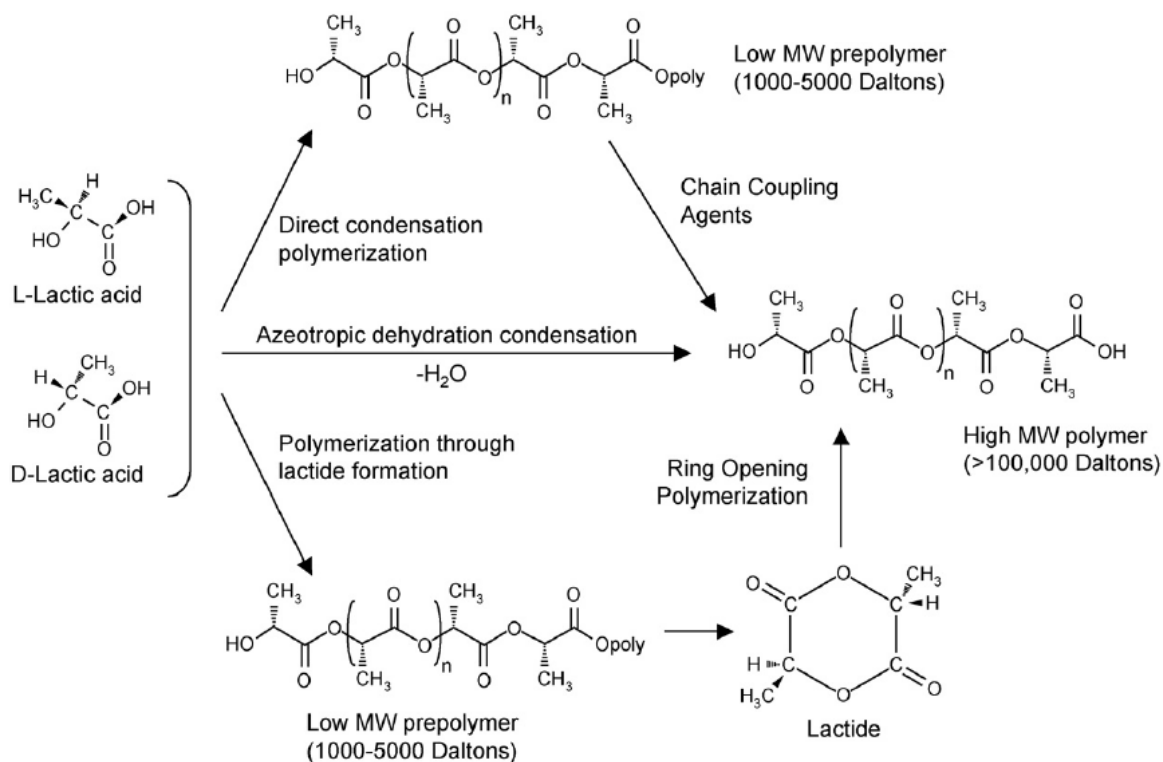


### *1.1.3 Introduction of PLA*

Bio-plastics are still in its early stage of applications, and so far PLA is the only one that is commercially produced on a relatively sizable scale (Feng 2010). PLA belongs to the family of aliphatic polyesters with the basic constitutional unit lactic acid, which can be manufactured by carbohydrate fermentation or chemical synthesis. Currently, the majority of lactic acid production is based on the fermentation processes, which can be classified into two methods: heterofermentative method and homofermentative method, respectively. Since homofermentative pathway leads to greater yields of lactic acid and lower levels of byproducts, it is mainly used by industry (Kharas et al 1994). Lactic acid is the simplest hydroxyl acid with an asymmetric carbon atom and it exists in two optically active configurations, the L(+) and D (-) isomers (Auras et al 2004). Depending on the proportion of the isomers, PLA of variable material properties can be derived. In general, there are three methods which can be used to produce high molecular weight PLA (above 100,000 Daltons) as shown in Figure 1.1:

- (1) Direct condensation polymerization: Since this method is an equilibrium reaction, by-product water needs to be removed to drive the reaction to the right. Although it is the least expensive route, it is very difficult to obtain a solvent-free high molecular weight PLA. Therefore, the use of chain coupling agents and adjuvants adds cost and complexity to the process (Kricheldorf et al 1996).
- (2) Azeotropic dehydration condensation: No chain extenders or adjuvants are needed in this method. Details of this technique can be found in the literature (Hartmann 1998) .
- (3) Polymerization through lactide formation: Firstly, lactic acid is prepolymerized to obtain

an intermediate low molecular weight PLA, which is then catalytically depolymerized through an intramolecular transesterification reaction to produce the cyclic lactide. Then, high molecular weight PLA is formed by ring-opening polymerization of the lactide.



**Figure 1.1** Synthesis of high molecular weight PLA via azetropic condensation, chain extension, and righ-opening polymerization, adapted from Hartmann (Hartmann 1998).

The new techniques which allow economical production of high molecular weight PLA polymer, as well as its high tensile strength and modulus, biodegradability and availability characteristics have broadened its use in industry. PLA is 100% biodegradable, can be recycled over 7-10 times and has a high tensile strength of 70 MPa and tensile modulus of 3 GPa (Zenkiewicz et al 2009). It can be processed by many conventional thermoplastics processing techniques, such as film extrusion, injection molding, blow molding, and thermoforming

(Rasal et al 2010). Moreover, from the perspective of energy savings, the production of PLA requires 25-55% less fossil resources than the traditional petroleum-based polymers.

## **1.2 Problem Statement**

Currently, PLA is the only commercial biobased thermoplastic polymer which has been produced with sizable production rate and competitive cost compared with petroleum based polymers. Other biobased thermoplastic polymers are either of insignificant production rates or quite expensive or have both disadvantages. SP has demonstrated to be a promising plastic material. However, both PLA and SP have several barriers need to be overcome.

For SP to be used as bio-plastics, the major obstacles include:

- (1) Low moisture resistance.
- (2) High melt viscosity due to strong intra- and intermolecular interactions of SP which makes melt processing such as extrusion and injection molding difficult (Feng 2010).
- (3) Brittleness.

For PLA to be used as bio-plastics, the major disadvantages include:

- (1) Low thermal resistance: Though some grades of PLA are semi-crystalline, because they crystallize very low, the injection molded and extruded PLA products often exhibit very low crystallinity. On the other hand, the glass transition temperature of PLA is  $\sim 60^{\circ}\text{C}$ . Therefore, the heat distortion temperature is greatly limited.
- (2) Relatively high cost: Although PLA has been commercialized in industry, its price (\$1.2 -1.5/lb) is still more expensive than natural polymers such as starch, soy protein.

(3) Lack of reactive groups: PLA is chemically inert with no reactive groups on the main chain, making its surface modifications a very challenging task (Moad 2010).

*Since SP and PLA are complementary in many aspects of their properties, blending SP with PLA is an excellent approach to increase the processibility and moisture resistance of the SP plastics on one hand and to increase heat resistance and lower production cost on the other hand.* However, the hydrophilic SP and the hydrophobic PLA are thermodynamically immiscible. The interfacial adhesion between the two phases is expected to be inferior. Therefore, compatibilization is necessary to improve interfacial properties and control morphologies of the PLA/SP composites.

### **1.3 Compatibilization in polymer composites**

#### *1.3.1 Reactive Compatibilization*

It is well known that polymer/polymer blending is an effective method for improving the original physical properties of one or both of the components, or for preparing new polymeric materials that exhibit widely variable properties without parallel in homopolymers (Nishio 2006). Usually, there are two means to produce polymer composites, mixing them in the solutions, and blending the components in the molten state. The latter one is much more favorable in industry, since the production process can take place in conventional processing equipment with high yield. The market for polymer composites has increased dramatically during the last decades, mainly in the packaging, automotive and building area. However, most polymer composites are not immiscible. Polymer composites will be miscible only if free

energy of mixing is negative:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix}$$

The gain in entropy  $\Delta S_{mix}$  is negligible, and the free energy of mixing can only be negative if the heating of mixing,  $\Delta H_{mix}$  is negative, which requires specific interactions between the blend components. These interactions may range from strong ionic bonding to weak and nonbonding interactions, such as hydrogen bonding. Usually, only Van der Waals interactions occur, which explains why polymer miscibility is the exception rather than the rule (Koning et al 1998). In order to overcome the immiscible drawback in the polymer composites, and develop such melt-composites with satisfactory overall physic-mechanical properties, compatibilization is therefore required to optimize interfacial tension, to generate a dispersed phase of limited size and strong interfacial adhesion, and to improve the stress transfer between the component phases (Barlow et al 1984).

Generally, compatibilization is accomplished either by addition of a compatibilizer or introduction of reactive compatibilization. The former usually has a block structure, with one constitutive block miscible with one blend component and a second block miscible with the other blend component (Koning et al 1998). However, due to the lack of economically viable and industrially practical routes for synthesizing such additives, preformed block or graft copolymers have not been used extensively for compatibilization (Paul et al 2000). An attractive alternative route, reactive compatibilization, is to form the block or graft copolymer in situ during blend preparation via interfacial reaction of added functionalized polymeric components. For the added polymers, functional groups can be placed along the chain by

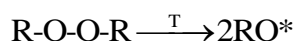
copolymerization or by grafting or at the chain end by special techniques (Datta et al 1996).

The formation of copolymers at the interface will significantly reduce the dimensions of the phase domains and interfacial tension, stabilize the phase morphology, and strengthen the interface.

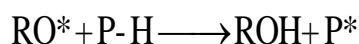
### 1.3.2 Free Radical Grafting Polymerization

Free radical grafting polymerization is a well-known method to modify otherwise apolar and/or chemically inert polymers for specific applications. The typical free radical grafting polymerization involves grafting of various monomers initiated by chemical initiators, plasma, and gamma radiation. A number of methods are now available in the literature to prepare the grafted copolymer, such as melt-grafting, solid state grafting, solution grafting, suspension grafting in aqueous solvents and redox-induced grafting (Carlson et al 1999). A free radical grafting system often contains three types of reactants: a polymer, unsaturated molecules like the vinyl monomer, and a free radical initiator (Cartier et al 1998). Irrespective of different chemical structures of the polymer substrates, a typical free radical grafting process consists of three basic steps as follows.

- (1) Formation of primary radicals ( $RO^*$ ). In this step (usually under high temperature condition), oxygen bond in the free radical initiators (usually a peroxide) ruptures, which lead to the formation of primary radicals.



- (2) Hydrogen abstraction. Macroradicals are formed during this step as a result of the abstraction of a hydrogen atom from the polymer substrate by the primary radicals.



(3) Subsequent reactions. The macroradicals can then react with monomer, which is the desired grafting reaction; they can also undergo crosslinking reaction if the macroradicals tend to react with each other, or chain fragmentation by  $\beta$ -scission (Cartier and Hu 1998). Some monomers with high reactivity might also homopolymerize themselves.

Various monomers have been utilized for free radical grafting polymerization. Among these functional monomers, Glycidyl methacrylate (GMA) and Maleic anhydride (MA) received most attention because of its widespread applications and distinct chemical structures. GMA is a very interesting monomer because of its bi-functional characters: a free-radically reactive double bond together with an epoxy group, which is capable of reacting with various other functional groups such as carboxyl, hydroxyl, anhydride and amine (Cartier et al 1998) (Huang et al 1998). MA is another monomer which has received substantial attention primarily due to its difficulty in homopolymerization during free radical grafting polymerization (Thompson et al 1998), and is therefore grafted with high efficiency without formation of homopolymer. Besides, it contains a double bond that is susceptible to radical reactivity and anhydride functional groups which could be used for subsequent chemical modifications. For instance, elastomers modified by MA is able to react with the amine terminal groups of polyamides leading to the in situ formation of amphiphilic copolymers at the interfaces between elastomers and polyamide (Gonzalez-Montiel et al 1995).

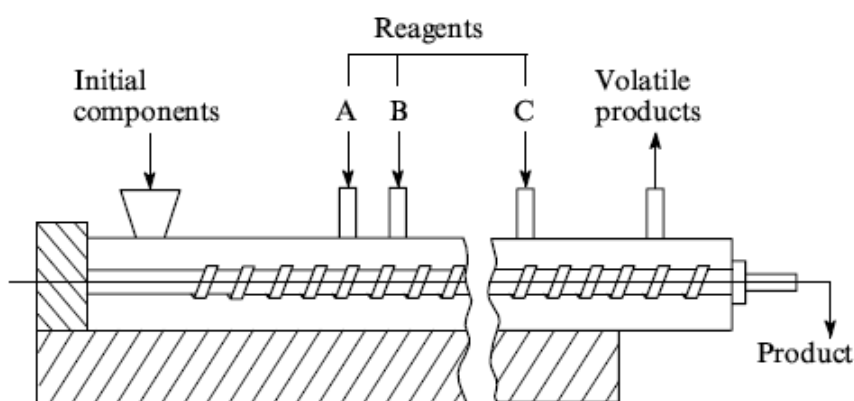
It is worth noting that the grafting degree of these monomers are usually low (Cartier and Hu 1998). As mentioned in the free radical grafting process, apart from reacting with monomers, the macroradicals formed from hydrogen abstraction might undergo chain scissions or crosslinking reactions which are undesirable for the original grafting purpose. Recently, various electron-rich co-monomers, in particular styrene (St), have been shown to be effective as coagents for improving grafting yields and reducing side reactions of the electron deficient monomers, in particular MA and GMA (Li et al 2001) (Moad 1999) (Samay et al 1995). It was also shown that the addition of St can improve the grafting degree of some other monomers such as hydroxyl ethyl methacrylate (HEMA) and methyl methacrylate (MMA), but not the grafting degree of vinyl acetate (VAc) and ricinoloazoline maleinate (OXA), this is due to the fact that St can copolymerize easily with HEMA and MMA but not with VAc and OXA (Vainio et al 1996) (Xie et al 1999).

### *1.3.3 Reactive extrusion*

Reactive extrusion, as the term suggests, involves the synthesis of materials by melt phase reaction in an extruder (Moad 1999). It is one of the most extensively used technologies to produce and functionalize polymers. Figure 1.2 shows a typical reactive extruder and the process: The initial components are fed into the extruder through a feed hopper. Various liquid or gaseous reagents can be injected at specific points in the reaction sequence along the extruder barrel. The reactive mixture is conveyed through the extruder, and the reaction is driven to the desired degree of completion. At the end of the barrel, any volatile by-products will be removed by vacuum through vent port, and the molten polymeric



product is pumped out through a die and subsequently quenched, solidified and pelletized (Raquez et al 2008) (Azizi et al 2004) (Hu et al 1996).



**Figure 1.2** Schematic representation of an extruder reactor

Extruder is a versatile mixing equipment with consistent product quality. It has been used to resolve heat and mass transfer problems that arise when dramatic viscosity of the reaction medium increases within a magnitude order of  $10^5$  in batch polymerization processes (Tzoganakis 1989). The increased viscosity in a batch reactor would make the materials become uncontrollable in terms of mixing and heat transfer, while the capability of the extruder to create new thin surface layers continuously can increase the degree of mixing and minimize temperature gradients within the polymer being processed (Raquez et al 2008). Another advantage of extruder lies in that the residence time can be controlled via several processing parameters, such as screw speed and differences in screw design. Generally, the total residence time in the extruder is in the range of 2-5 min, which is much lower compared with that in a batch reactor, therefore significantly reducing the cost of facilities and avoiding the long exposure time to high temperatures of the reactants. Finally, extruder provides

opportunities for adding or removing reagents and/or additives such as processing aids and stabilizers during the process (Moad 2010). As mentioned in the 1.3.2, there are several practicable approaches to prepare grafted copolymer, and the most widespread one is the melt-state grafting implemented by reactive extrusion. Although chain degradation and crosslinking of the polymer substrates are unavoidable, synthesis of grafted copolymer by reactive extrusion has many advantages compared to alternative technologies, for instance, solvent free melt process, control over reaction time, continuous processing and integration of other extrusion streams along with the polymerization process (Raquez et al 2006).

#### **1.4 Research Objectives**

Although free radical grafting of MA has become a common pathway for modification of polyolefins, only recently has it been grafted onto biodegradable polyesters, such as Poly(butylene adipate-co-terephthalate) (PBAT), PLA and PCL. The MA-based copolymer can significantly improve interfacial adhesion, and thereby result in good mechanical properties of the composites. Carlson et al (Carlson et al 1999) firstly reported the preparation of maleic anhydride grafted PLA (PLA-g-MA) and the morphology study showed that PLA-g-MA improved the adhesion in starch filled composites. Petersson et al (Petersson et al 2006) reported improved phase interaction and mechanical properties by the use of PLA-g-MA as compatibilizer in layered-silicate nanocomposites. Plackett (Plackett 2004) showed enhanced adhesion has been reached in the PLA/wood fiber system with the addition of PLA-g-MA.

However, there is very little literature examining the compatibilization effect of PLA-g-MA on the properties of soy protein and PLA composites. In order to investigate that, the objective of this research is to prepare compatible PLA/SPC composites with excellent mechanical properties. PLA-g-MA was prepared and used as compatibilizer in the PLA/SPC composites. Specifically, two major aims of this research are included:

aim #1. Functionalize PLA by the melt free radical grafting of MA onto its backbone.

aim #2. Investigate the compatibilization effect of PLA-g-MA on morphological structure and mechanical, physical properties of the PLA/SPC composites.

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## Chapter 2 Preparation and Characterization of Maleic Anhydride

### Functionalized Polylactide

#### ABSTRACT

In this study, free radical melt grafting of maleic anhydride (MA) onto Polylactide (PLA) was carried out using Lupersol 101 as free radical initiator in a co-rotating twin-screw extruder. An electron-donating monomer styrene (St) was added in the grafting reaction. The amount of grafted MA was determined by means of direct titration. The effects of MA/St molar ratio, initiator concentration, monomer concentration, processing temperature and screw speed on the grafting reaction were investigated. Nuclear Magnetic Resonance and Fourier Transform Infrared Spectroscopy analysis confirmed the grafting reaction of MA on the PLA substrate. It was found that the presence of St in the reactive processing could remarkably enhance grafting degree of MA. Proposed grafting mechanism and possible side reactions were also discussed in details.

**Keywords:** *Free radical grafting, Maleic anhydride, Polylactide, Maleation*



## 2.1 Introduction

In recent years, substantial efforts have been directed towards chemical modifications of existing polymers in order to obtain functional and/or engineered new materials (Lambla 1993). Among these modification methods, free radical grafting polymerization has been investigated most extensively. Generally, free radical grafting reaction can be realized either in a solution process or in a melt process. In the solution process, the polymer is dissolved in a suitable solvent at elevated temperatures, and then monomer is added together with initiator (Li et al 2002). On the other hand, the melt process usually takes place in the batch mixer or screw extruder, which allows the free radical grafting reaction to occur without solvents (Hu et al 1997).

The free radical grafting of maleic anhydride (MA) onto polyolefins have been extensively studied, and the reaction scheme has been well known. Polyolefins have been widely used as plastics in industry owing to its low cost, growing commercial applications and ready availability. However, their low polarity and nonfunctional characteristics limit their application in composites. MA-grafted polyolefins are often used to compatibilize the nonpolar polyolefins with common minerals such as glass fibers, talc and mica (Huneault et al 2007). MA was also grafted onto cellulose acetate butyrate (CAB) in order to improve interaction between CA and organoclay to produce exfoliated and/or intercalated clays in (Park et al 2004). MA is a common monomer for grafting reactions because it is difficult to homopolymerize in free radical grafting polymerization (Chen et al 2003). Nevertheless, the free-radical reactivity of MA is low, primarily due to its structural symmetry and deficiency

of electron density around the double bond (Malaika 1997). Therefore, it is conceivable that the presence of a co-monomer, such as Styrene (St), which is capable of donating electrons could activate MA by rendering its structure unsymmetrical and its  $\pi$  bond of radical-anion character. Besides that, St can interact with MA through charge transfer complexes and copolymerize with MA alternatively in certain conditions (Li et al 2001).

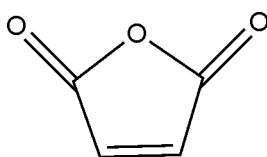
Recently, there is an increased interest in developing biobased materials to resolve environmental pollution problem and increase the use of natural and renewable resources (Petersson et al 2006). Many studies have been carried out on biobased materials such as polyhydroxyalkanoate (PHA) and poly(lactic acid) (PLA). The grafting of MA onto PLA was first reported by Carlson et al. (Carlson et al 1999) and Mani et al. (Mani et al 1999). The maleation reaction was carried out in a twin-screw extruder using 2 wt% of MA and up to 0.5% of a peroxide initiator. The achieved grafting degree of MA was around 0.5 wt%. With the addition of MA-grafted PLA, improved interfacial adhesion between granular starch and PLA was achieved, which was revealed through microscopy (Carlson et al 1999). Later, Zhang et al. (Zhang et al 2004) prepared the PLA-g-MA copolymer and showed that the tensile strength and elongation at break of starch/PLA composites were improved by the presence of this grafted copolymer. Huneault et al. (Huneault and Li 2007) investigated the effects of PLA-g-MA as a compatibilizer in PLA/thermoplastic starch (TPS) blends and showed that much finer dispersed phase was obtained in the blends comprising PLA-g-MA.

Surprisingly, there is very little literature using St as co-monomer in preparation of biobased grafting copolymer, for example, PLA-g-MA. In this study, free radical grafting MA

onto PLA was conducted in the molten state with the addition of St as co-monomer in order to increase the grafting degree of MA. The major aim was to examine the influence of various polymerization conditions, including MA/St molar ratio, initiator concentration, monomer concentration, temperature and screw speed on the grafting degree of MA. The grafted copolymer was characterized by several analytical techniques including titration, FT-IR and  $^1\text{H}$  NMR.

## 2.2 Experimental

**Materials.** The PLA used in this study was NatureWorks 2002D. This PLA had a density of  $1.24\text{ g/cm}^3$ , and a glass transition and melting temperature of 60 and  $150\text{ }^\circ\text{C}$  (DSC analysis), respectively. Maleic anhydride (MA) (95%) (Figure 2.1) and 2,5-Dimethyl-2,5-di-(tert-butylperoxy) hexane (L101) were purchased from Sigma-Aldrich Chemical Company. All chemicals in this study were used as received without further purification.



**Figure 2.1** Structure of maleic anhydride (MA)

**Preparation of grafted copolymer.** MA, St and L101 were firstly dissolved in 20mL dehydrated acetone, and then mixed thoroughly with PLA grains in a zip-lock plastic bag. After the acetone was evaporated completely, the mixture was compounded using a co-rotating twin-screw extruder (Leistritz ZSE-18HP) equipped with a volumetric feeder and a strand die.

The diameter of the screw was 18-mm with a length-to-diameter ratio (L/D) of 40. The heating temperatures and screw speed were adjusted in each series based on the different investigation factors. The barrel of the extruder had seven heating zones. For most of the series (except the one investigating the effect of temperature), from the feed throat to the die, the temperatures were set at 140, 160, 180, 180, 180, 180, and 165 °C, respectively. The die temperature was 145 °C. A vacuum pump was connected to the vent at the sixth heating zone on the barrel to remove vapors generated in the process. The extruded strands were cooled in a water bath and subsequently pelletized. Pellets were dried in a convection oven at 80 °C for 12 h for further analysis.

**Characterization of grafted PLA.** The grafting degree was determined by a direct titration method, with a slight modification of a procedure proposed by Nabar et al. (Nabar et al 2005). Pellets obtained from extrusion were dried at 80 °C under vacuum for 12 h to evaporate any unreacted MA. Then a sample of 2.5 g grafted PLA was dissolved in 40 mL chloroform, and 0.75 mL hydrochloric solution in water (1 M) was added to hydrolyze the anhydride groups into carboxylic acid at room temperature. The solution was stirred vigorously for 30 min. Then, the grafted sample in the solution was further purified by dropwise precipitating into excess acetone (400 mL) to remove any homo- and copolymers of MA and styrene. The filtered precipitates were then washed by acetone and distilled water several times and dried at 85 °C in a vacuum for 24 h.

To measure the grafting degree, the purified PLA-g-MA (0.4g) was dissolved in 20 mL chloroform, and the solution was titrated to a phenolphthalein end point using potassium

hydroxide in methanol (0.04 M). The grafted sample was completely soluble and did not precipitate during titration. The grafting degree was calculated using the following equation. Each sample was tested in triplicate and average values were reported.

$$\% \text{MA | grafted} = \frac{N_{\text{KOH}} V_{\text{KOH}}}{2W_{\text{sample}}} \times 98.06 \times 100$$

where  $V_{\text{KOH}}$  and  $N_{\text{KOH}}$  are the volume (liters) and the normality (moles per equivalent) of the KOH solution, respectively.  $W_{\text{sample}}$  is the mass (in grams) of the maleated sample.

**Nuclear Magnetic Resonance (NMR).**  $^1\text{H}$  NMR spectra was recorded with a Bruker 500 MHz spectrometer at room temperature in deuterated chloroform ( $\text{CDCl}_3$ ). Spectra of the neat polymer and grafted copolymer were recorded separately.

**Fourier Transform Infrared Spectroscopy (FTIR).** The FTIR spectra of neat PLA and PLA-g-MA were scanned from 400 to 4000  $\text{cm}^{-1}$  with 32 repeated scans at a resolution of 2  $\text{cm}^{-1}$  using a Thermo Nicolet Nexus 670 spectrometer. Thin films of all samples were pressed into thin films at 160  $^{\circ}\text{C}$  between two Teflon sheets. All samples were oven-dried under vacuum to eliminate effects of residual solvent and moistures.

## 2.3 Results and Discussion

### 2.3.1 Characterization of the grafted copolymer

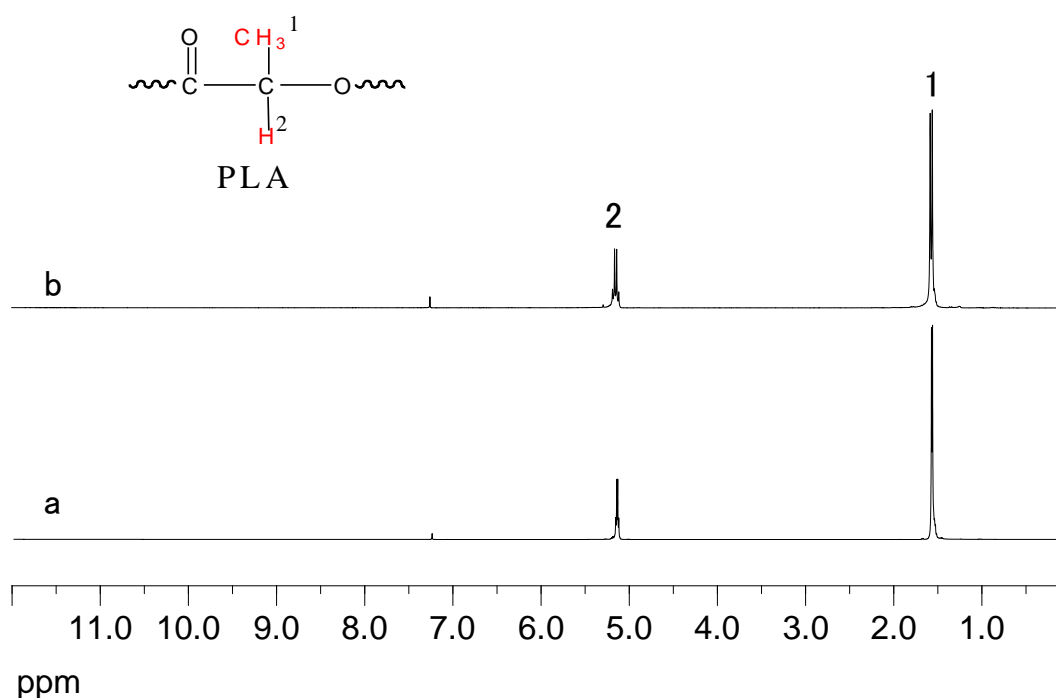
#### 2.3.1.1 NMR

Due to the low concentration of succinyl anhydride bound to the PLA chain,  $^{13}\text{C}$  NMR yielded no information concerning the MA. Consequently, analysis of the maleated samples

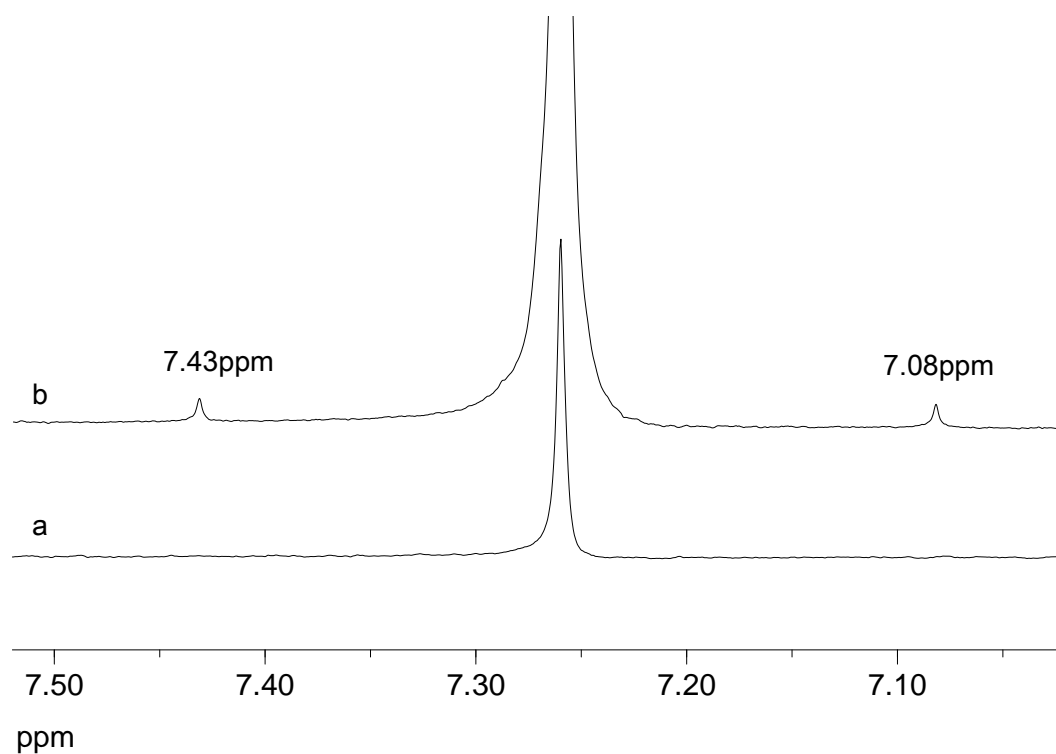
had to be based on the proton spectra. Figure 2.2 (A) presents the  $^1\text{H}$  NMR spectra of neat PLA (a) and grafted PLA with highest grafting degree (b). There are three major resonances with chemical shifts of about 1.5 ppm, 5.2 ppm and 7.2 ppm. The resonances at 1.5 ppm and 5.2 ppm are assigned to the methyl proton and methine proton of PLA, respectively. The resonance at 7.2 ppm is attributed to the solvent deuterated chloroform.

Note that the peak signals of the monomer MA obtained from  $^1\text{H}$  NMR were very weak and had to be observed by significantly magnifying the signals (Figure 2.2 (B) (C)). The reason lies in that the grafting degree of MA was only 0.89%, which is considerably low. The backbone signal of PLA was approximately 112 times stronger than that of the MA, which resulted in difficulty in detecting MA signals. Only the spectra from 7 to 7.5 ppm and 2.8 to 4.5 ppm are magnified and shown in Figure 2.2 (B) (C)), as no changes in the spectra were noted in other regions. One peak at 7.08 ppm is observed in the Figure 2.2(B) for the grafted PLA, corresponds to the unreacted maleic anhydride, which was not completely removed from the crude polymer by precipitation (Henry et al 2008). The resonance at 7.43 ppm is detected, which should belong to the proton on the benzene ring of styrene. As can be shown from Figure 2.2(C), there was a broad group of complex resonances with four peaks centered at 4.3 ppm, which is characteristics of poly(maleic anhydride) chains and is similar to the  $^1\text{H}$  NMR spectrum of poly(maleic anhydride) as reported in the literature (Regel 1981). This result revealed that some MA was grafted onto PLA as oligomers (grafts containing more than one succinic anhydride unit). Free-radical grafting reactions are extremely complex, usually along with some side reactions, for instance, backbiting,  $\beta$ -scission and branching. Therefore, the

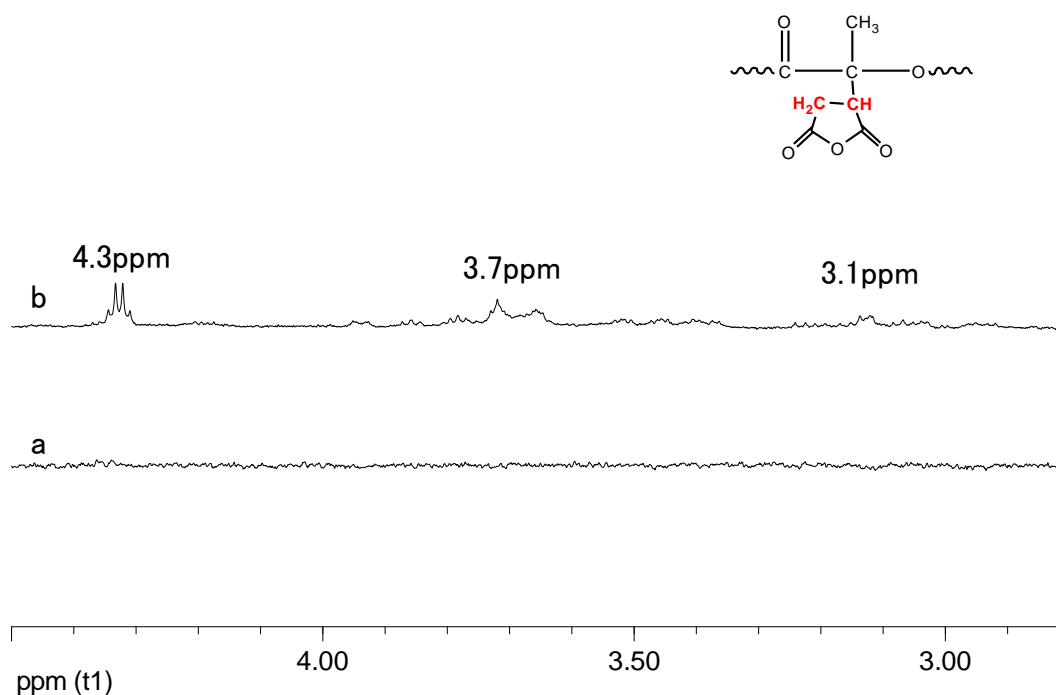
chemical shifts of MA depend mainly upon the structure of the polymer substrate, and the NMR characterization of protons in MA would vary slightly in different polymer backbones. Li et al. (Li et al 2002) used syndiotactic polystyrene (sPS) as polymer substrate, and proposed that the resonances at 2.8-3.2 and 3.5-4.0 ppm are attributed to the methine protons and the methylene protons of the succinic anhydride ring, respectively. In our PLA system, The weak chemical shifts at about 3.0-3.2 and 3.6-3.8 ppm might be assigned to the methine protons and methylene protons of the succinic anhydride rings, respectively, which suggests that grafts also consisted of a single succinic anhydride ring (Russell et al 1988).



(A)



(B)



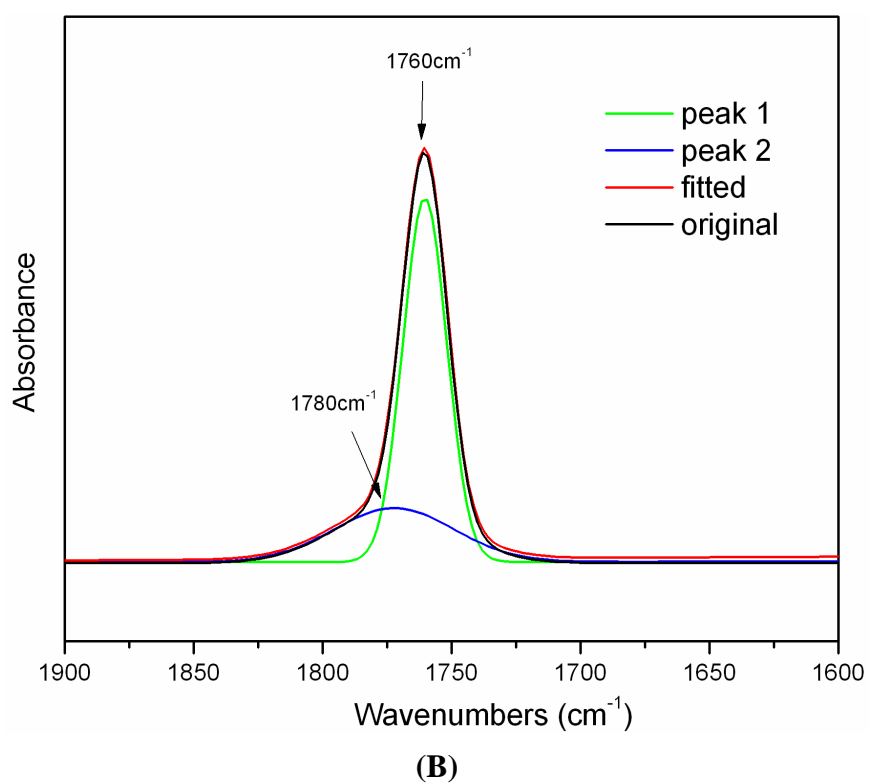
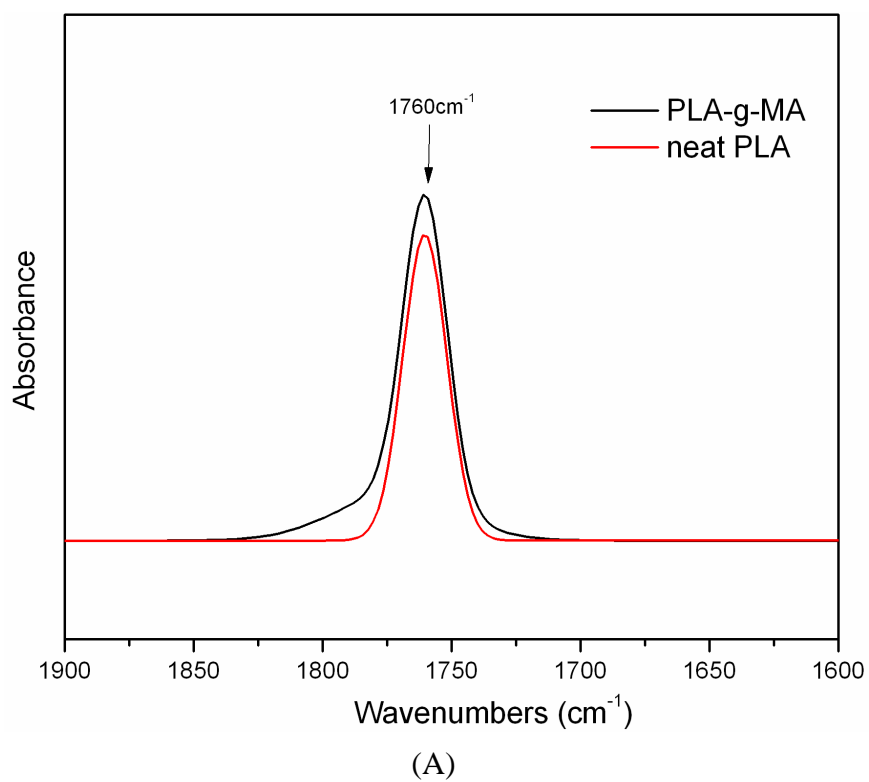
(C)

**Figure 2.2**  $^1\text{H}$  NMR spectra of neat and grafted PLA: (a) neat PLA, (b) MA grafted PLA (the grafting degree is 0.89%): (A) is whole spectra with chemical shift 0-12 ppm; (B) is magnified spectrum from (A) with chemical shift 7-7.5 ppm; (C) is magnified spectrum from (A) with chemical shift 2.8-4.5 ppm.



### 2.3.1.2 FT-IR

The FT-IR analysis is an analytical tool frequently used to characterize maleation reaction. To that end, purified samples were ground with KBr and pressed into discs for FT-IR analysis. Figure 2.3 (A) shows the absorbance spectra of neat PLA and PLA-g-MA in the range of 1600-1900  $\text{cm}^{-1}$ . For the PLA-g-MA sample, the MA concentration and grafting degree is 6wt% and 0.89%, respectively. Neat PLA had a strong absorption band at 1760  $\text{cm}^{-1}$  (C=O stretching). In comparison, The PLA-g-MA exhibited a very similar spectrum to that of the neat PLA. According to John et al (John et al 1997), cyclic anhydrides should exhibit an intensive absorption band near 1780  $\text{cm}^{-1}$  and a weak band near 1850  $\text{cm}^{-1}$  due to the symmetric and asymmetric stretching of C=O. In our MA grafted PLA system, however, these two peaks were somewhat overlapped with the neighboring C=O stretching peak of PLA, which is much stronger. In order to separate the overlapped peaks into specific spectral bands, deconvolution technique is used on the spectrum of PLA-g-MA, as shown in the Figure 2.3 (B). Beside the strong absorption band at 1760 $\text{cm}^{-1}$  (peak 1), A small shoulder at 1780  $\text{cm}^{-1}$  (peak 2) was obtained on the deconvolved spectrum, which should be assigned to the symmetric stretching of C=O. However, the intensity of the absorbance at 1850  $\text{cm}^{-1}$  (asymmetric stretching of C=O) is very weak, which was not observed even in the deconvolved spectrum. Overall, the FT-IR results confirmed that MA was grafted onto PLA successfully.

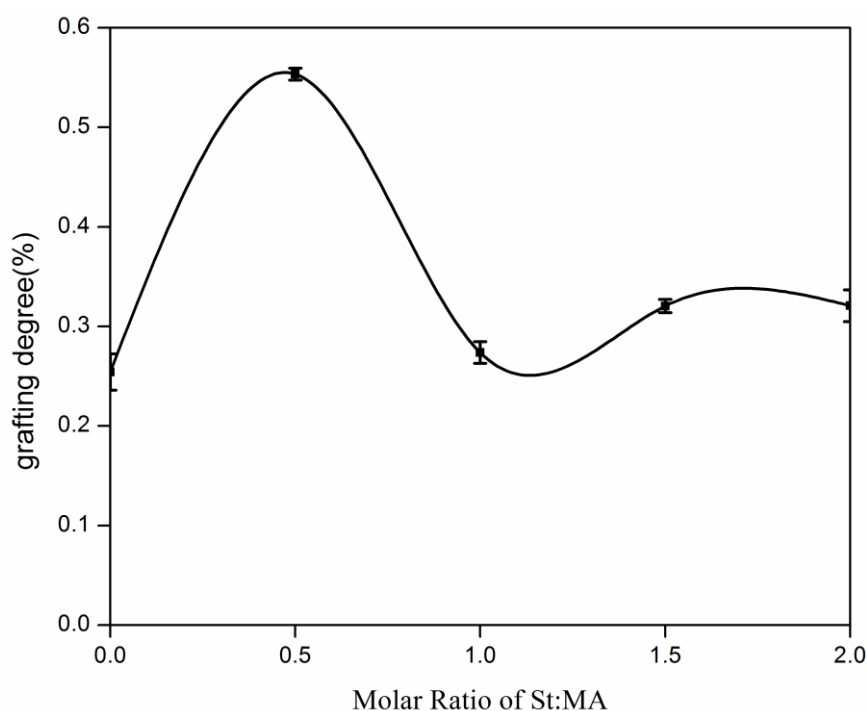


**Figure 2.3** FT-IR absorption spectra of (A) neat PLA and PLA-g-MA; (B) deconvoluted spectrum from PLA-g-MA.

### 2.3.2 *Parameters affect grafting degree*

#### 2.3.2.1 Effect of MA/St ratio

The grafting degree of the MA was measured by the titration method as mentioned in the experimental section. Figure 2.4 shows the effect of St as a co-monomer on the grafting degree of MA. With the addition of St, the grafting degree of the sample increased compared to the sample without St regardless of the St concentration, which substantiated that using a co-monomer (St) in the free-radical grafting of MA onto PLA enhanced grafting yield. Cartier and Hu (Cartier et al 1998) concluded that the fundamental basis of the co-monomer concept was the reactivity ratio of free radical copolymerization. Adding a co-monomer will be beneficial for improving the monomer grafting yield only if this co-monomer reacts with the macroradical more rapidly than the monomer and the resulting macroradical is capable of copolymerizing with the grafting monomer (Cartier and Hu 1998). For the MA grafted PLA system, the optimum molar ratio of MA/St which resulted in maximum grafting degree turned out to be 1/0.5, which was not consistent with the results reported by other researchers, which stated that the optimum molar ratio of MA/St is 1/1 (Li et al 2001). The reason may owing to the lower reactivity of the St-based macroradicals than the PLA macroradicals. It is well accepted that St reacts with macroradicals more rapidly than MA. When the MA/St ratio is 1/0.5, the free MA monomers are more easily to react with PLA macroradicals, and thus higher grafting degree can be obtained compared to the situation when MA/St ratio is 1/1. To investigate the effects of other parameters on the grafting degree, MA/St molar ratio was fixed at 1:0.5 for all the formulations in the following discussions unless mentioned.

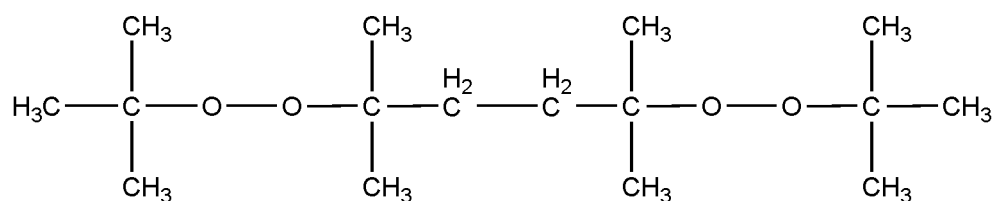


**Figure 2.4** Effect of St concentration on grafting degree at 180 °C with a constant concentration of MA (2 wt%).

#### 2.3.2.2 Effect of Initiator Concentration

Initiator is indispensable component for melt free radical grafting process. The type and amount of the initiator are among the most important parameters in grafting reaction (Li et al 2003). L101 is a difunctional di-tertiary alkyl peroxide (Figure 2.5). In this research, L101 was chosen as initiator due to several reasons: low toxicity, high hydrogen abstraction ability, appropriate half-time (according to the manufacturer, its half-time is 1 minute at 180 °C and 13 seconds at 200 °C), and low volatility. In addition to satisfying the above criteria, L101 was selected as an initiator because of its known ability to induce successful grafting of MA on a variety of polymer substrates as reported in the literature (Robert 1999) (Bettini et al 1999). L101 is also recognized by the Food and Drug Administration (FDA) as a food additive (Code of Regulations; Title 21 “Food and Drugs” part 170 under “Food Additives”) (Carlson et al

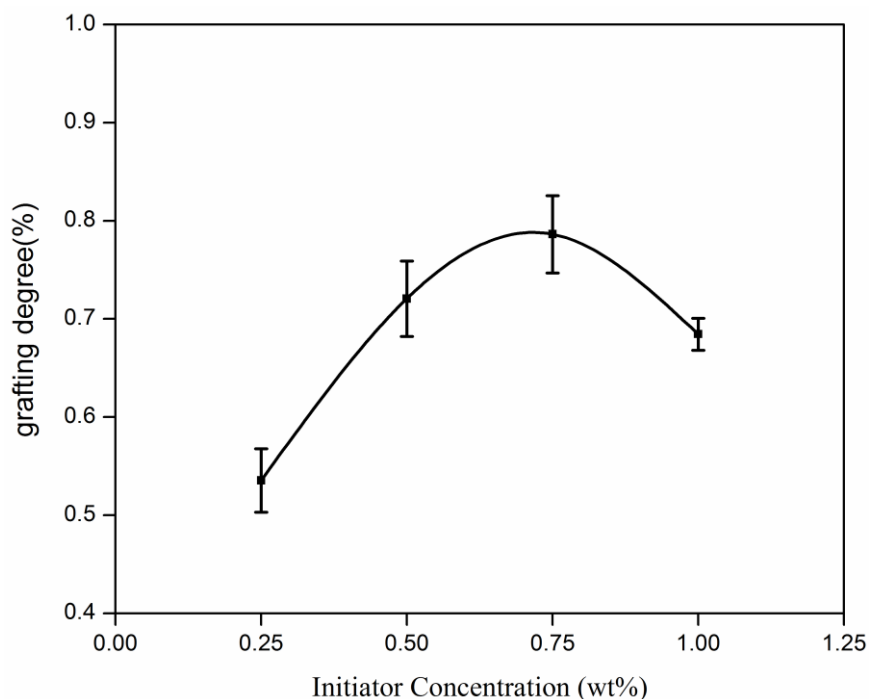
1998).



**Figure 2.5** Structure of 2,5-dimethyl-2, 5-di-(tert-butylperoxy) hexane (L101)

The grafting degree of the grafting reactions performed with different initiator concentrations are shown in Figure 2.6. Grafting degree of MA first increased and then decreased with the increasing initiator concentration. The maximum grafting degree was achieved when the initiator concentration was 0.75 wt%. This phenomenon can be explained as follows. In general, initiators have two-side effects on the free radical grafting reaction. On the one hand, as more initiators are added and decompose under high reaction temperature, more macroradicals can be produced which will increase the probability that the macroradicals and MA collides each other. The increased probability along with the higher chain transfer to the polymer backbone leads to the increase in grafting degree. On the other hand, excessively high initiator concentration would also adversely affect the grafting degree. Chain scission could more easily occur and become prominent under this condition, which in turn decrease the molecular weight of the polymer. With further addition of initiators, crosslinking may take place and processing of the grafting copolymers in the extruder would become a great challenge (K. J. Ganzeveld et al 1992). Besides, the termination rate of free radicals is faster at higher free radical concentrations (Bettini et al 1999), thus the free radical grafting reaction will be terminated earlier and the corresponding grafting degree is lower when the initiator is

excessive.

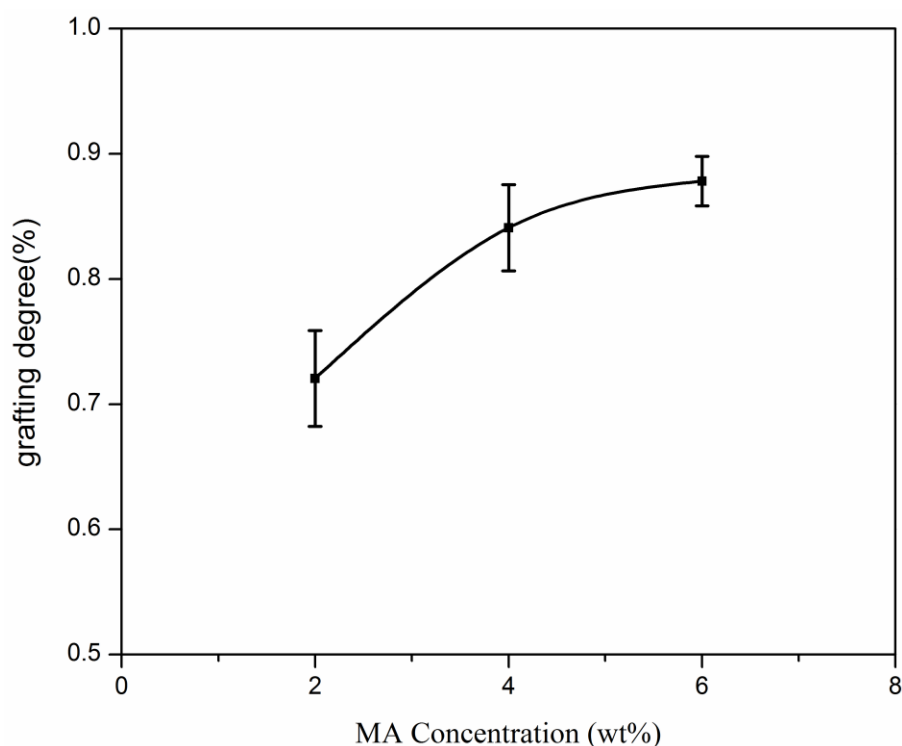


**Figure 2.6** Effect of initiator concentration on grafting degree at 180 °C with a constant concentration of MA (2 wt%).

### 2.3.2.3 Effect of Monomer Concentration

A set of experiments were conducted to investigate the influence of MA concentration on grafting degree. As exhibited in Figure 2.7, the grafting degree increased with increasing MA concentration, although the rising trend leveled off gradually. It is well-recognized that MA is a good monomer candidate for grafting reaction, because its homopolymerization is very difficult to take place due to its symmetrical chemical structure. Therefore, MA tended to attach to the PLA backbone, and the grafting degree mainly depended on the possibility that macroradicals collided with MA. Since the initiator concentration was constant in this series of experiments, any variations in grafting degree were thus due to the difference in MA concentration. Increasing the MA concentration would enhance the chances of macroradicals

reacting with MA, hence the grafting degree increased. Since the available sites on the PLA backbone are limited, the reactions between MA and macroradicals will reach a balance along with the increasing MA concentration. Consequently, the variation trend of the grafting degree slowed down. Moreover, Based on this level off tendency and other researcher's results (Chen et al 2003) (Gildo an et al 2004), It is believed that the grafting degree would decrease with addition of excessive MA monomer. In this case, excessive MA would collide with primary radicals which facilitate the occurs of cage effect and other side reactions.



**Figure 2.7** Effect of monomer concentration on grafting degree at 180 °C with a constant concentration of initiator (0.5 wt%).

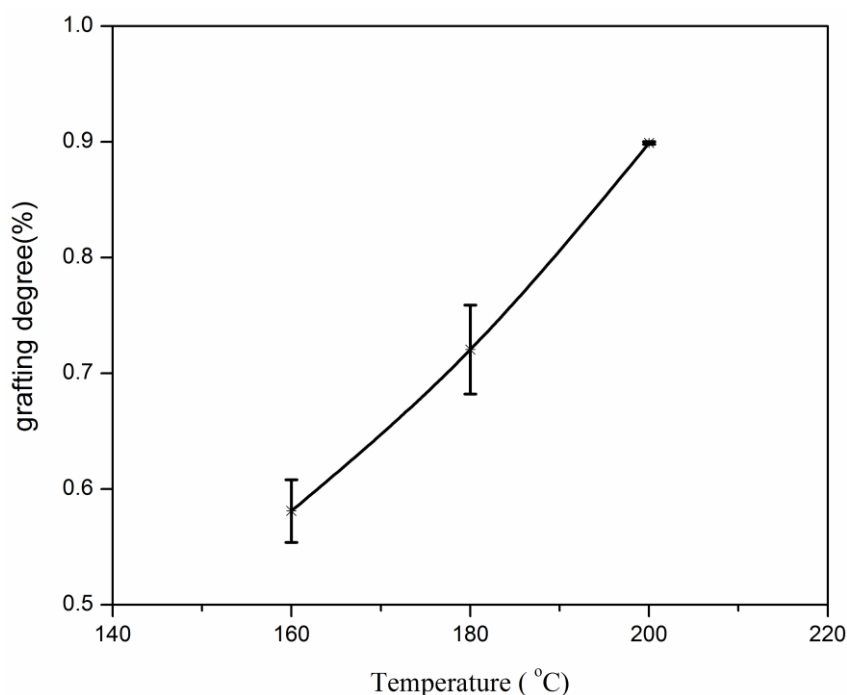
#### 2.3.2.4 Effect of Extrusion Temperature

Free radical grafting of MA onto PLA was investigated under various temperatures, ranging from 160 to 200 °C, as is depicted in Figure 2.8. The grafting degree increased continuously as the reaction temperature increased, which indicated that high temperature was favorable to free radical grafting polymerization. Initiators decomposed more completely and rapidly at higher temperature, and thus helped produce more macroradicals which gave rise to higher grafting degree (Mani et al 1999). Also, since most grafting reactions in the bulk are diffusion controlled, the increase in temperature enhanced the diffusion by reducing viscosity of the medium, which resulted in a higher grafting degree.

Nevertheless, it is worth noting that high temperature does not necessarily lead to high grafting yielding. Each initiator has an optimum temperature range in which it functions most efficiently to obtain the maximum grafting degree (K. J. Ganzeveld and Janssen 1992). The half-time ( $t_{1/2}$ ) of the L101 is supposed to be quite different, ranging from a few minutes to a few seconds in the temperature range we chose. For instance, the  $t_{1/2}$  of L101 is around 100s when the reaction temperature is 180 °C. Generally, a good free radical initiator should have a half-time which is about one-fifth of the reaction time so that once the reaction is over, the free radical initiator is also exhausted (Cartier et al 1998). Therefore, the appropriate reaction temperature strongly depends on reaction time, which is as a function of various parameters. In addition, Polymer backbone tend more easily to undergo chain scission or branching under higher temperature. These side reactions are not advantageous for polymer backbones to attach



monomers, since most of the free radical reactions may take place on the side chains produced by these side reactions.

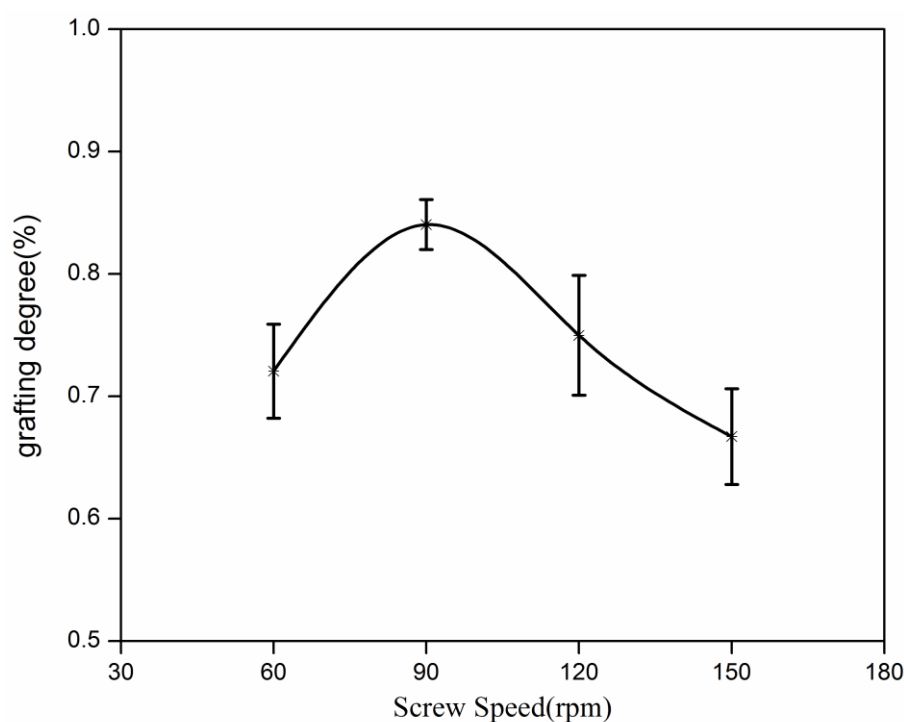


**Figure 2.8** Effect of temperature on grafting degree with a constant initiator concentration (0.5 wt%) and MA concentration (2 wt%).

#### 2.3.2.5 Effect of Screw Speed

For grafting reaction taken place in extruder, the grafting yield of monomer is strongly dependent upon the screw speed of the reactors. Figure 2.9 demonstrates the effect of screw speed on the grafting degree of MA. It is observed that an optimum screw speed appeared at 90 rpm, where the grafting degree peaked. This tendency was consistent with the results reported in other literature (John et al 1997). It is well accepted that increasing screw speed would result in increase in the mechanical shear stress of the extruder. High shear stress leads to an enhancement in mixing efficiency in the extruder, and thus the dispersion of monomer and initiator is more uniform, which is crucial and beneficial for increasing grafting degree. Also, chain scission, branching and crosslinking reaction can be eliminated to the largest extent at higher screw speed due to considerably shorter residence time corresponding to it.

However, high screw speed can also adversely affect the grafting degree, since the residence time of the extruder decreases when screw speed increases. The reaction time available in the extruder becomes the limiting factor, therefore the percentage of grafting decreases (K. J. Ganzeveld and Janssen 1992). Overall, the screw speed is an important parameter to affect grafting yield, and the optimum screw speed varies in different grafting system.

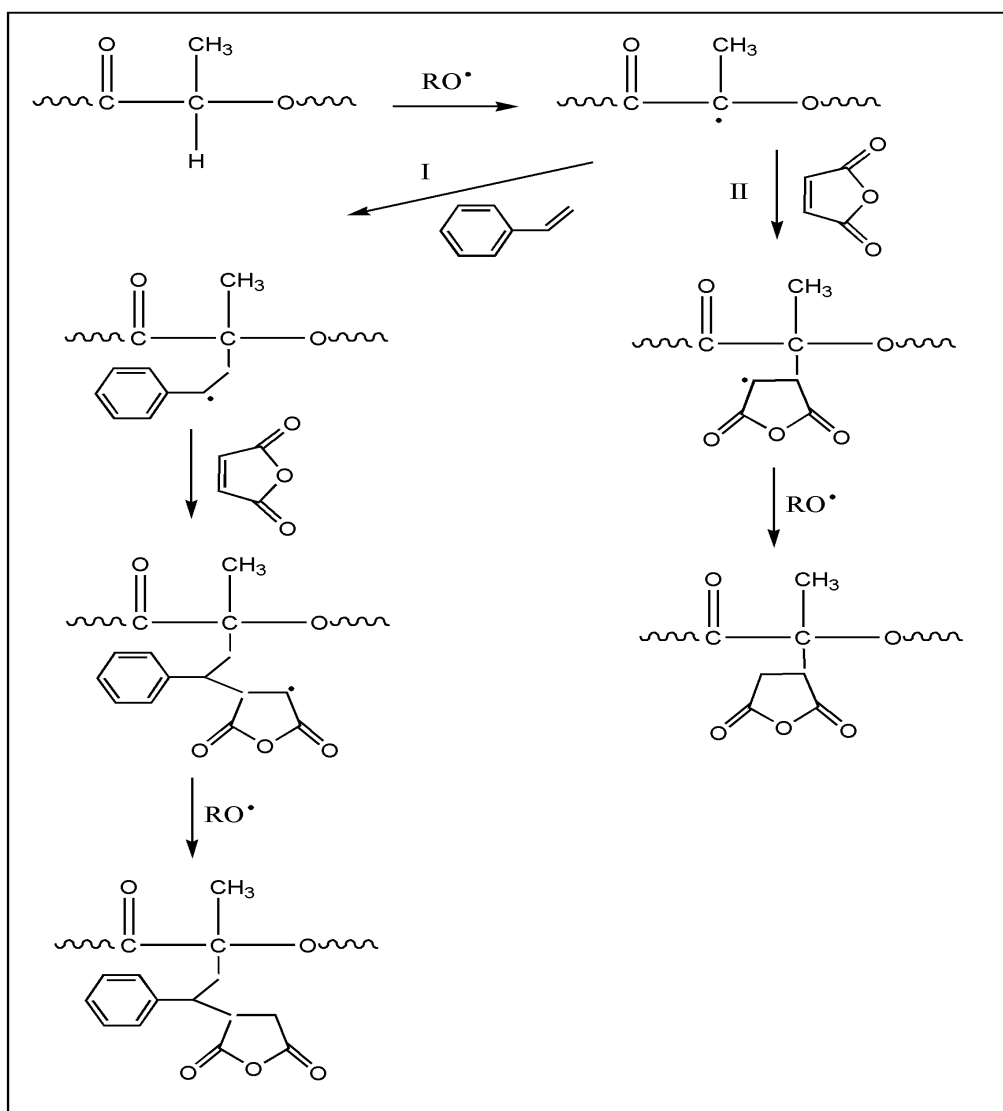


**Figure 2.9** Effect of screw speed on grafting degree with a constant initiator concentration (0.5 wt%) and MA concentration (2 wt%).

### 2.3.3 Proposed Reaction Mechanism

The general mechanism of melt free-radical grafting reaction has been well accepted. For our MA grafted PLA system with the addition of St as co-monomer, the possible reaction mechanism is summarized as follows. The first step is the decomposition of initiators under

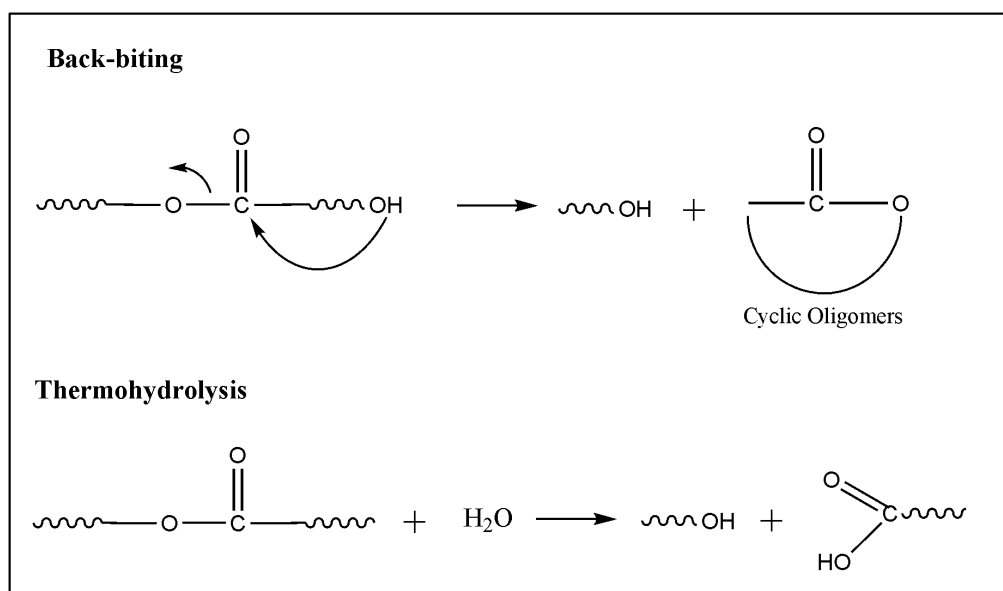
considerable high temperature, during which two free radicals are produced. Then, melt free-radical grafting reaction starts with the formation of macroradicals by a so-called hydrogen abstraction from the  $\alpha$ -carbon atom relative to the carbonyl group (Carlson et al 1999). Malincolino et al. (Avella et al 1997) first reported hydrogen abstraction on the PLA backbone in the case of radical polymerization of butyl acrylate. These macroradicals can further participate in grafting reaction as can be shown in Scheme 2.1. Since co-monomer St is present, the grafting reactions can then develop in two ways. One way begins with St reacting with PLA macroradicals and then the St-based macroradicals copolymerize with MA. Charge transfer complex (CTC) might be formed during this process because of interaction between St and MA. The existence of CTC has been known for a long time and used to explain the formation of alternating copolymers of St and MA in bulk or solution copolymerization (Li et al 2001). Another pathway is that some free MA monomers can react directly with the PLA macroradicals. In either cases, the grafted macroradicals can then react with additional MA monomers or undergo chain transfer with a hydrogen atom on its chain or another PLA chain to form a new macroradical. This process continues until grafting is terminated by recombination (Fowlks 2009). Further,  $\beta$ -scission can take place on the main chain of the copolymer.



**Scheme 2.1** Proposed reaction mechanism for grafting of maleic anhydride onto PLA

Side reactions are common in free radical reaction, and the probability of each side reaction highly depends on the nature of the macroradicals and the polymer backbone. For MA grafted PLA system, two possible side reactions: chain scission and branching/crosslinking can occur in the PLA substrate (Carlson et al 1998). Excessive chain scission leads to lower molecular weight and poor performance of the polymer. For PLA, chain scission is caused by either back-biting or thermohydrolysis, As shown in Scheme 2.2

(Carlson et al 1999). Branching and crosslinking can also take place because the present of free radicals.



**Scheme 2.2** Chain scission of PLA

Homopolymerization of MA is also considered as a significant reaction by some researchers when grafting MA onto polymer substrates (Gaylord et al 1983) (Gaylord et al 1989). There should exist a competition between homopolymerization of MA and grafting of MA if the former reaction can take place. Recently, however, Russell (Russell 1995) discussed a thermodynamic argument based on the ceiling temperature of poly(MA) in which the formation and grafting of poly(MA) during maleation in the melt (at temperatures greater than 160 °C) would not occur. Moreover, calculation of reaction ratios provided evidence that at high reaction temperatures, the reaction favors hydrogen abstraction by primary radicals rather than homopolymerization of MA (Fowlks 2009). Thus, Conflicting opinions still exist and further experimental evidence is needed to validate the reactivity of homopolymerization

of MA. In this present work for grafting MA onto PLA, analyses were conducted based on the assumption that homopolymerization would not occur under the experimental conditions.

## **2.4 Conclusions**

In this study, styrene-assist melt free radical grafting MA onto PLA was investigated. Titration results showed that styrene act as an electron donor and a good co-monomer, which could greatly increase the grafting degree of MA.  $^1\text{H}$  NMR and FT-IR spectra confirmed that the MA was successfully grafted onto PLA chains by melt free radical graft polymerization. The effects of various processing parameters on grafting degree, such as MA/St ratio, monomer concentration, initiator concentration, reaction temperature, and screw speed were also investigated. It is evidenced from experimental results that optimal reaction process depends on the interaction of these primary variables, all of which can be controlled externally to obtain the grafted copolymer with relatively high grafting degree. Moreover, molecular weight analysis revealed that side reactions such as chain degradation occurred. Reaction mechanism has also been proposed according to literatures and experimental analysis.

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## **Chapter 3 Effects of Compatibilization on the Physicomechanical and Morphological Properties of PLA/SPC Composites**

### **ABSTRACT**

In this study, Polylactide (PLA)/soy protein concentrate (SPC) composites with and without compatibilizer were melt-compounded in a co-rotating twin-screw extruder. The effects of Maleic anhydride (MA) grafted PLA (PLA-g-MA) on the morphological, tensile and dynamic mechanical properties of PLA/SPC composites were studied. Tensile strength of the composites containing 4 phr PLA-g-MA increased by 19% compared to that of the uncompatibilized PLA/SPC composites. Differential scanning calorimetry analysis indicated that SPC induced and accelerated cold crystallization of PLA in the composites, which was also affected by the presence of compatibilizer. Damping peak dropped gradually as the compatibilizer concentration increased, mainly due to the strong interactions between the PLA and SPC phases after compatibilization. Scanning electron microscopy micrographs demonstrated that the SPC granules were stretched into fine threads and became much finer under the compatibilization effect. Good interfacial adhesion between two phases is also shown in micrographs.

**Keywords:** *soy protein composites, Polylactide, compatibilizer*

### 3.1 Introduction

Biodegradable polymer materials have received extensive interests in the past decades due to following reasons: First, the expected rise in the cost of petroleum-based plastics in the future and the truth that petroleum resource is not infinite drives people to find substitutes. Second, the production of petroleum-based materials also brings a host of issues, such as high energy consumption, destruction of wildlife habitat, and volatile organic pollutants from the production process (Feng 2010).

The most common biodegradable synthetic polymers include aliphatic polyesters, such as poly(glycolic acids) (PGA), poly(lactic acid) (PLA), polycaprolactone (PCL), polyhydroxybutyrate (PHB) and poly (hydroxybutyrate-co-hydroxyvalerate) (PHBV) (Ke et al 2000). Among these biopolymers, PLA, which is derived from renewable resources such as corn, is the most promising bio-based materials commercially available in the market. PLA has been studied extensively for tissue engineering and drug delivery systems since the 1980s, and is the most widely used biodegradable polymers in human medicine (Huang 1989). PLA has good biodegradability and mechanical properties, which have made it attractive for disposable and biodegradable plastics. Amorphous PLA is a highly transparent and rigid material, making it a promising candidate for the fabrication of biaxially oriented films, thermoformed containers and stretch-blown bottles. Since the residual monomers of PLA are naturally occurring and non-toxic chemicals, it can also be used in food-contacting articles (Huneault et al 2007).

However, the price of PLA is still high compared with many petroleum-based

commodity plastics, which limits its application in industry. Also, the rate of biodegradation of PLA is relatively low. Blending PLA with some natural polymers such as starch, soy protein could substantially reduce the total cost, and at the same time increase the degradation rate of the composites. Soy protein (SP) is abundantly available from annual renewable resource. It has been considered recently as an alternative to petroleum polymer in the manufacture of adhesives, plastics, and various binders (Zhong et al 2001). Sun et al. (Sun et al 1999) compression molded the 7S-riched and 11S-riched SP containing 10% extra water into uniform plastics. Zhang et al. (Zhang et al 2001) melt compounded soy protein isolate (SPI) in the presences of sufficient water and glycerol by extrusion, and subsequently extruded the compounded SP pellets into smooth sheets. The SPI sheets show considerably high yield strength. All these studies demonstrated the plastic nature of soy protein due to the fact that SP gellates in the presence of certain levels of water and is subsequently plasticized (Feng 2010). However, PLA and SP composites are thermodynamically immiscible. SP is highly hydrophilic but PLA hydrophobic, The interfaces of simple PLA/SP blends are bounded weakly, resulting in inferior physical properties (Zhong and Sun 2001). Therefore, Compatibilization is urgently needed in PLA/SP composites to improve interfacial adhesion between the two components. Methylene diphenyl diisocyanate (MDI) is highly reactive, which can form urethane linkages with hydroxyl groups. It has been widely used as compatibilizer in natural polymer and PLA blends (Fang et al 2009) (Liu et al 2010) (Mungara et al 2002) (Wang et al 2001). However, MDI is considered an environmentally hazardous material, which make it unsuitable for food packaging or related applications

(Zhang et al 2004). Recently, a more promising interfacial modification route was adopted. This route includes grafting a reactive moiety onto the polymer matrix, and then having this moiety react in some way with the natural polymers (Huneault and Li 2007). PLA-g-MA has been widely used as compatibilizers in PLA blends with starch (Orozco et al 2009) (Zhang and Sun 2004), talc (Fowlks et al 2010), silicate (Petersson et al 2006). However, no studies have been performed related to using PLA-g-MA as a compatibilizer in PLA/SP composites.

In this work, a series of PLA/SPC composites were prepared by extrusion and the test specimens were prepared by injection molding. The water content in the pre-compounded SPC was fixed at 15% and the SPC loading level 30%. The project aims at investigating the effects of PLA-g-MA as a compatibilizer in PLA/SPC composites. The amount of PLA-g-MA was varied between 1 and 4%, and the composites were studied on the basis of mechanical, thermal and morphological properties.

### 3.2 Experimental

**Materials.** SPC (Arcon S) was provided by Archer Daniels Midland Company (Decatur, IL), and contained ca. 72% protein (on dry weight basis), 20% carbohydrate, 3% fat, 6 wt% moisture and a small amount of minerals as received. NatureWorks PLA (2002D) was used for the blends. MA grafted PLA (PLA-g-MA) was prepared by reactive extrusion using L101 as initiator, and the residual MA was removed under high vacuum at 85 °C. The degree of grafting was determined by titration method.

**Preparations of PLA/SPC Composites.** SP was first formulated and contained the following ingredients by weight: SPC (100 parts, dry weight), glycerol (10 parts), water (15 parts) and sodium sulfite (0.5 parts). The formulated SPC was mixed in a kitchen mixer, stored in sealed plastic bags, and then left overnight at room temperature to equilibrate. The mixture of formulated SPC, PLA and/or PLA-g-MA was then compounded using the same extruder as described in the chapter 2 for the preparation of PLA-g-MA. For the compatibilized composites, PLA-g-MA was incorporated based on the total weight of PLA and SPC (dry weight). The screw speed was maintained at 100 rpm for all runs, and the eight controlled temperature zones from the first heating zone to the die adaptor were set at 90, 100, 130, 145, 160, 160, 160, 155 °C, respectively. The extrudate was cooled in a water bath and subsequently granulated by a strand pelletizer. Pellets were dried in a convection oven at 80 °C for 12 h before injection molding.

**Injection Molding.** Standard tensile bars (ASTM D638, Type III) were prepared by a Sumitomo injection molding machine (SE 50D). The barrel zone temperatures were set at 150, 160, 170 and 165 °C from the feeding section to the nozzle. Mold temperature was set at 40 °C and cooling time was ca. 40 s. All samples were conditioned for one week at  $23 \pm 2^\circ\text{C}$  and  $50 \pm 5\%$  RH prior to mechanical test and characterization.

**Tensile test.** Tensile tests were performed on an 8.9-KN, screw-driven universal testing machine (Instron 4466) equipped with a 10-KN electronic load cell and mechanical grips. The tests were conducted at a crosshead speed of 5 mm/min with strains measured using a

50-mm extensometer (MTS 634.12E-24). All tests were carried out according to the ASTM D638. Five replicates were tested for each sample to obtain an average value.

**Microscopy.** Field emission scanning electron microscopy (FE SEM, Quanta 200F) was applied to investigate the microstructure of the PLA/SPC composites. Tensile fracture surfaces and microtomed smooth surfaces of the composites were examined after sputter coating.

**Fourier Transform Infrared Spectroscopy (FTIR).** Composites samples were extracted in a Soxhlet extractor (chloroform as the solvent) for 72 h to remove the free PLA. The extracted SPC particles were ground with KBr and pressed into discs for FT-IR analysis. The analysis was performed using a Thermo Nicolet Nexus 670 spectrometer. The spectra were scanned from 400 to 4000  $\text{cm}^{-1}$  with 32 repeated scans at a resolution of 2  $\text{cm}^{-1}$ .

**Dynamic Mechanical Analysis (DMA).** Dynamic mechanical properties were measured by a dynamic mechanical analyzer (DMA, Rheometrics Solids Analyzer, RSAII). DMA specimens ( $12.8 \times 3.2 \times 35 \text{ mm}^3$ ) were cut from the injection molded samples and conditioned in the same environment as tensile samples. DMA test was conducted on a single-cantilever fixture at a vibration frequency of 1Hz. All tests were conducted at amplitude of 15  $\mu\text{m}$  using a 2  $^{\circ}\text{C min}^{-1}$  temperature ramp from -10 to 150  $^{\circ}\text{C}$ .

**Differential Scanning Calorimetry (DSC).** The melting and crystallization behavior of the PLA/SPC composites were studied by DSC (Mettler Toledo 822e) using the specimens sliced from injection molded samples. About 4mg of sample was crimp sealed in 40mL aluminum pan. A sealed empty pan was used as a reference. The sample was first scanned

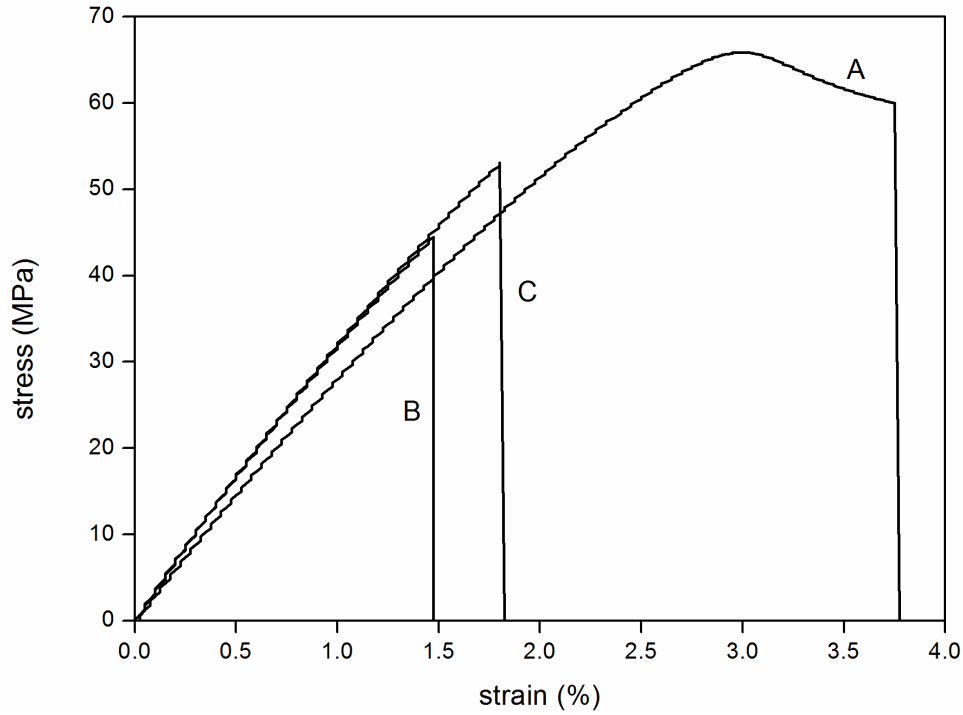
from 25 to 180 °C at the heating rate of 20 °C min<sup>-1</sup> to erase its thermal history, isothermally conditioned at 180 °C for 2 minutes, and then cooled to 0 °C at 20 °C min<sup>-1</sup>. Finally, the sample was heated again from 0 to 180 °C at 5 °C min<sup>-1</sup> to examine the glass transition temperature and crystallinity of PLA in the PLA/SPC composite. Samples were characterized in an inert environment using nitrogen. Results were obtained from the second DSC heating scan.

### **3.3 Results and Discussion**

#### *3.3.1 Tensile Mechanical Properties*

The mechanical properties of a polymer blend strongly depend on its composition, interfacial adhesion and morphological structure (Chen et al 2010). Typical stress-strain curves of neat PLA and PLA/SPC composites with or without PLA-g-MA are shown in Figure 3.1. Both PLA/SPC composites with or without compatibilizer showed brittle fracture and did not exhibit any yielding. The modulus of the composites was higher than that of neat PLA due to the incorporation of rigid SPC. In the PLA/SPC blend, the molecular mobility of PLA is restricted by rigid SPC granules, which have higher modulus than PLA. The fact that the PLA molecules were less free to stretch resulted in a high Young's modulus in the PLA/SPC composites (Wang et al 2001).





**Figure 3.1** Stress-strain curves of PLA and PLA/SPC composites (70/30 weight ratio): (A) Neat PLA, (B) PLA/SPC composites without PLA-g-MA, and (C) PLA/SPC composites with 4phr PLA-g-MA.

The mechanical properties of neat PLA and PLA/SPC composites with different PLA-g-MA concentration are summarized in Table 3.1. One-way ANOVA statistical analysis was applied to evaluate the data under the 95% confidence level. Examination of the  $p$ -value of every property showed that the addition of SPC and the PLA-g-MA concentration significantly affected the strength, modulus and elongation of the composites. Tukey multiple comparison further identified the significant differences among samples at  $\alpha=0.05$ . The samples which had the same labeling letter were not significantly different from each other. Compared to the neat PLA, the addition of 30% SPC in the composite resulted in ca. 21% increase in modulus but reduced the strength and elongation of the materials. The modulus of the composite was not statistically varied by the addition of PLA-g-MA. However, it is interesting to note that both

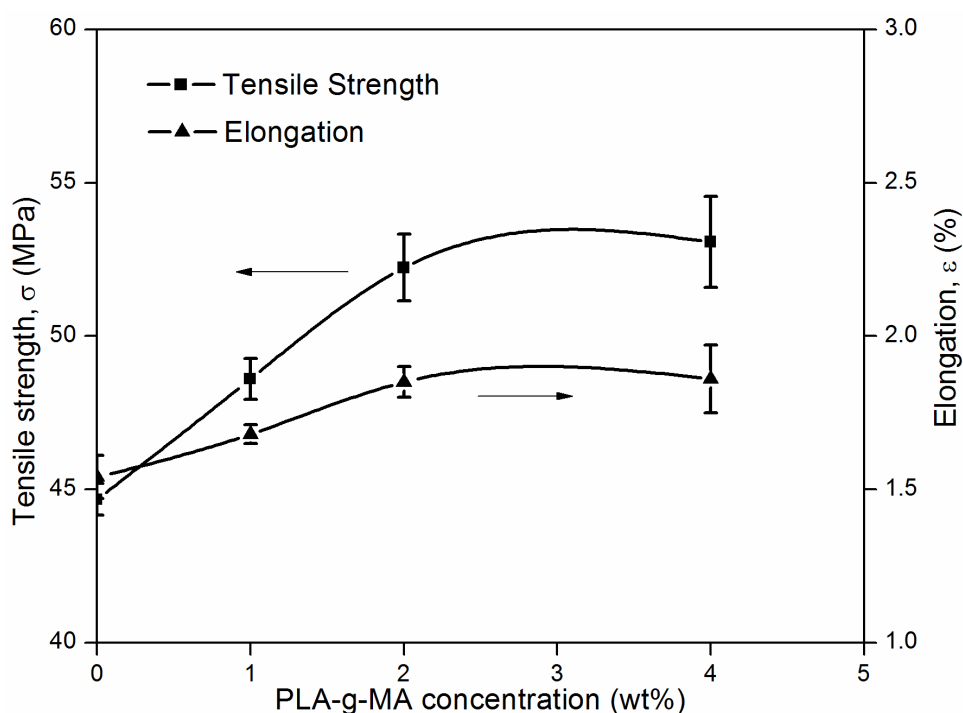
tensile strength and elongation of the composites increased as the PLA-g-MA concentration increased. For the blend with 4 phr PLA-g-MA, the tensile strength increases by about 19% and elongation by about 21% with respect to the blend without PLA-g-MA. MA grafted polymers are often used to increase the interfacial adhesion between hydrophobic synthetic polymers and various hydrophilic natural polymers (John et al 1999). The anhydride groups were likely to react with the amino groups of proteins and hydroxyl groups of carbohydrates in SPC, therefore greatly decreased the interfacial tension which played a key role in reducing the sizes of the dispersed phase (Tol et al 2004). Nevertheless, it is worth noting that the increasing trend of tensile strength and elongation level off when the PLA-g-MA concentration is above 2% as shown in Figure 3.2. It is well known that in the reactive processing, only low concentrations of block or graft copolymer are required to saturate the interface and produce optimum compatibilization (Vasile 2000). The emulsification curve in several polymer blends system displays similar characteristics, an initial significant drop in the size of the dispersed phase with the addition of copolymer followed by the obtention of an equilibrium value at high concentration of copolymer (Li et al 2002).

**Table 3.1** Mechanical Properties of PLA/SPC blend and Effect of PLA-g-MA Concentration

Composition		Tensile strength (MPa)		Modulus (GPa)		Elongation(%)	
PLA/SPC	PLA-g-MA (%) <sup>a</sup>						
100/0	0	65.05±0.62	A <sup>b</sup>	3.47±0.04	A <sup>b</sup>	3.59±0.14	A <sup>b</sup>
70/30	0	44.67±0.52	B	4.17±0.07	B	1.54±0.07	B
70/30	1	48.60±0.67	C	4.30±0.11	B	1.68±0.03	B
70/30	2	52.23±1.09	D	4.21±0.03	B	1.85±0.05	C
70/30	4	53.07±1.48	D	4.19±0.04	B	1.86±0.11	C

<sup>a</sup>PLA-g-MA is added on the basis of per hundred resin (total weight of PLA and SPC) and the grafting degree is fixed at 0.53%.

<sup>b</sup>One way ANOVA Analysis (SAS) and Tukey multiple comparison of the effects of SPC and PLA-g-MA concentration. Values with different letters mean they are significantly different from each other. The confidence level was set at 95%.

**Figure 3.2** Effect of PLA-g-MA concentration on tensile strength and elongation of the PLA/SPC composites.

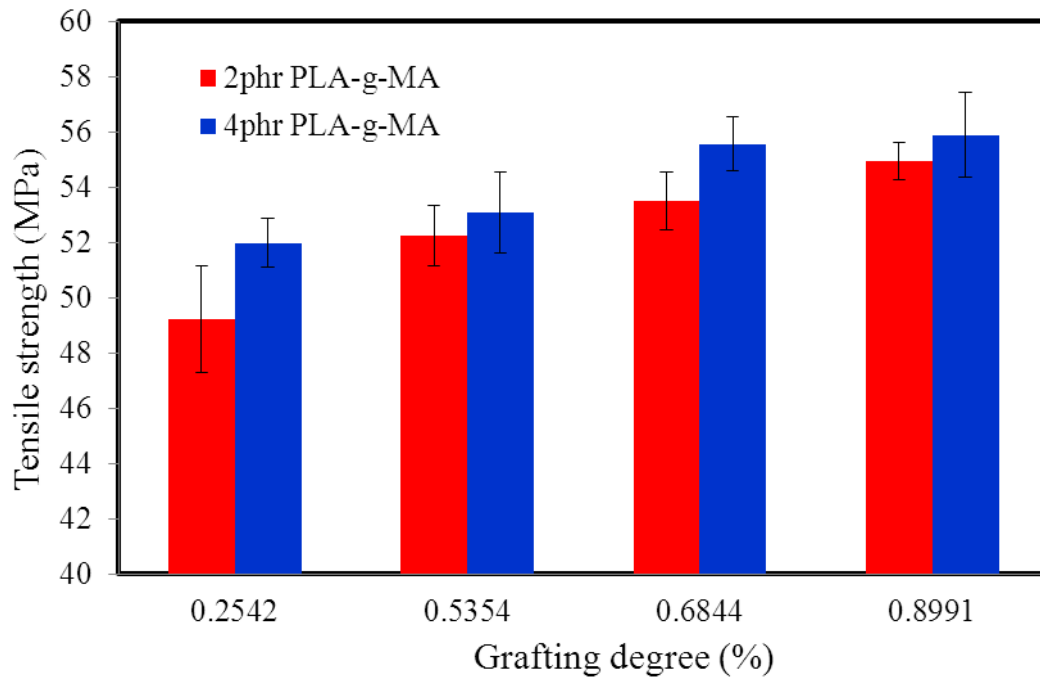
To further investigate the effects of functionalization on the mechanical properties of PLA/SPC composites, PLA-g-MA with four different grafting degree were prepared and used as compatibilizers in the PLA/SPC composites. The grafting degree of these PLA-g-MA range from 0.25% to 0.89%. PLA-g-MA compatibilizers were added at two loading levels, 2 phr and 4 phr, respectively (on the basis of the total weight of dry SPC and PLA). The mechanical properties of PLA/SPC composites (4 phr PLA-g-MA) with different PLA-g-MA grafting degree are shown in Table 3.2. The tensile strength increased gradually with the increasing grafting degree of PLA-g-MA, while elongation and modulus have only slight changes. The results further substantiated that the anhydride groups in MA can form covalent bonds with various functional groups in soy protein. With more MA attached on PLA backbone, the possibility that reactions between compatibilizer and SPC increased, and thus higher tensile strength could be achieved. Figure 3.3 indicates that the composites with 4 phr PLA-g-MA have overall higher tensile strength than the composites with 2 phr PLA-g-MA. This series of data also proved that the proposed reactions between MA and SPC took place.

**Table 3.2** Mechanical Properties of PLA/SPC composites and Effect of grafting degree of PLA-g-MA<sup>a</sup>

Composition	grafting degree (%)	Tensile strength (MPa)		Modulus (GPa)		Elongation(%)	
PLA/SPC(70:30)	0.2542	51.97±0.88	A <sup>b</sup>	3.98±0.06	A <sup>b</sup>	1.81±0.05	A <sup>b</sup>
	0.5344	53.07±1.48	A	4.19±0.04	B	1.86±0.11	AB
	0.6844	55.56±0.99	B	4.00±0.05	A	1.96±0.05	B
	0.8991	55.88±1.54	B	4.05±0.09	A	1.93±0.07	AB

<sup>a</sup>PLA-g-MA concentration is fixed at 4 phr of total weight of PLA and SPC for all formulations.

<sup>b</sup>One way ANOVA Analysis (SAS) and Tukey multiple comparison of the effects of grafting degree of PLA-g-MA.



**Figure 3.3** Tensile strength of the PLA/SPC composites comprising PLA-g-MA with different grafting degree

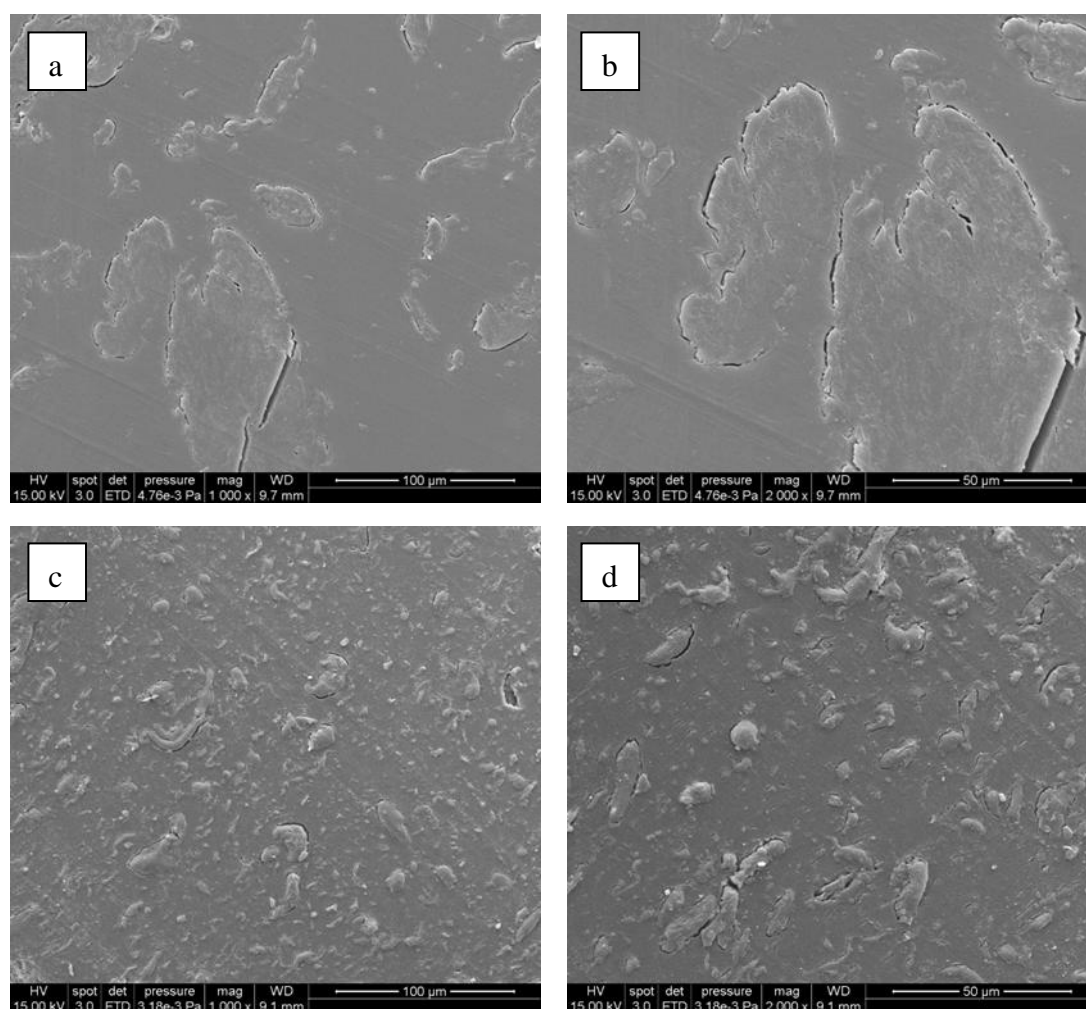
### 3.3.2 Morphology

Mechanical properties of composite are highly associated with its morphology and microstructure. Figure 3.4 shows the microtomed surfaces of the PLA/SPC composites with and without compatibilizer. In the sample without PLA-g-MA (Figure 3.4 a & b), the SPC

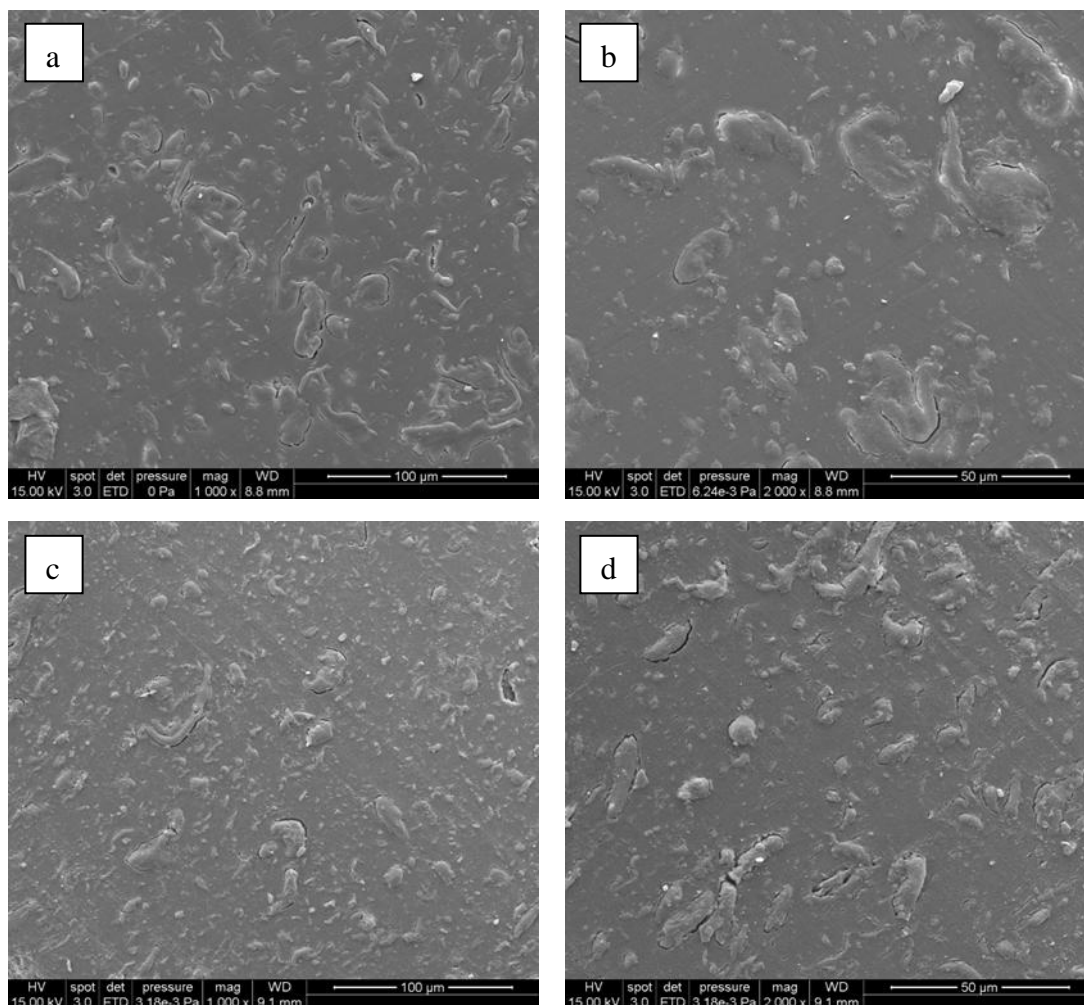
granules were relatively large and unevenly distributed. With the presence of 4 phr PLA-g-MA, however, the SPC granules became much finer and more evenly dispersed within the matrix ( Figure 3.4 c&d). Besides, the shape of the SPC phase changed from round particles of natural soy protein into threads with the addition of PLA-g-MA (Liu et al 2010). Therefore, stress transfer from the matrix to the filler could be improved since the length/diameter ratio of SPC granules increased, and the mechanical properties were also improved as already discussed in the previous section 3.3.1. Figure 3.5 shows the effects of grafting degree on SPC domain size and phase structure of the composites. By increasing the grafting degree from 0.25 to 0.89%, the SPC changed from large granules to small particles in micron sizes and the phase structure of the composites changed from coarse to fine.

According to Wu (Wu 1982), for a particulate-filled composite made with a coupling agent or grafted compatibilizer, the wetting and bonding at the interface significantly influenced the properties of the composites. The formation of an interfacial molecular contact by wetting is the prerequisite for adhesive bond. Because of the wetting, the molecules diffuse across the interface and react chemically to establish covalent bonds across the interface (Wang et al 2002). The molecular diffusion is usually accelerated by reducing the surface tension, which may be achieved by the addition of compatibilizer and subsequent establishment of chemically-stable covalent bonds. MA grafted polymers are often used as compatibilizer to stabilize the morphology between hydrophobic synthetic polymers and various hydrophilic natural polymers (John and Bhattacharya 1999). The reaction between anhydride groups of MA grafted PLA and amino groups of SPC would decrease the

interfacial tension. Therefore, the breakup of SPC suppressed the coalescence, and the SPC granules were smaller than that in the simple PLA/SPC composites. Also, it is worth noting that the reaction rate in melt state is greatly reduced by the steric hindrance of large molecules and restricted diffusion. For the reactions to occur efficiently in a short time, maximum contact surface between reacting component, fast and selective reaction are very important. Several factors besides stress concentration determine the reformation and failure of the composites.



**Figure 3.4** SEM micrographs showing the effect of PLA-g-MA on the phase morphology of PLA/SPC (70/30 w/w) blends. a&b: without PLA-g-MA; c&d: containing 4 wt% PLA-g-MA on the basis of the total PLA/SPC weight. Left column is 1000×, right column is 2000×.

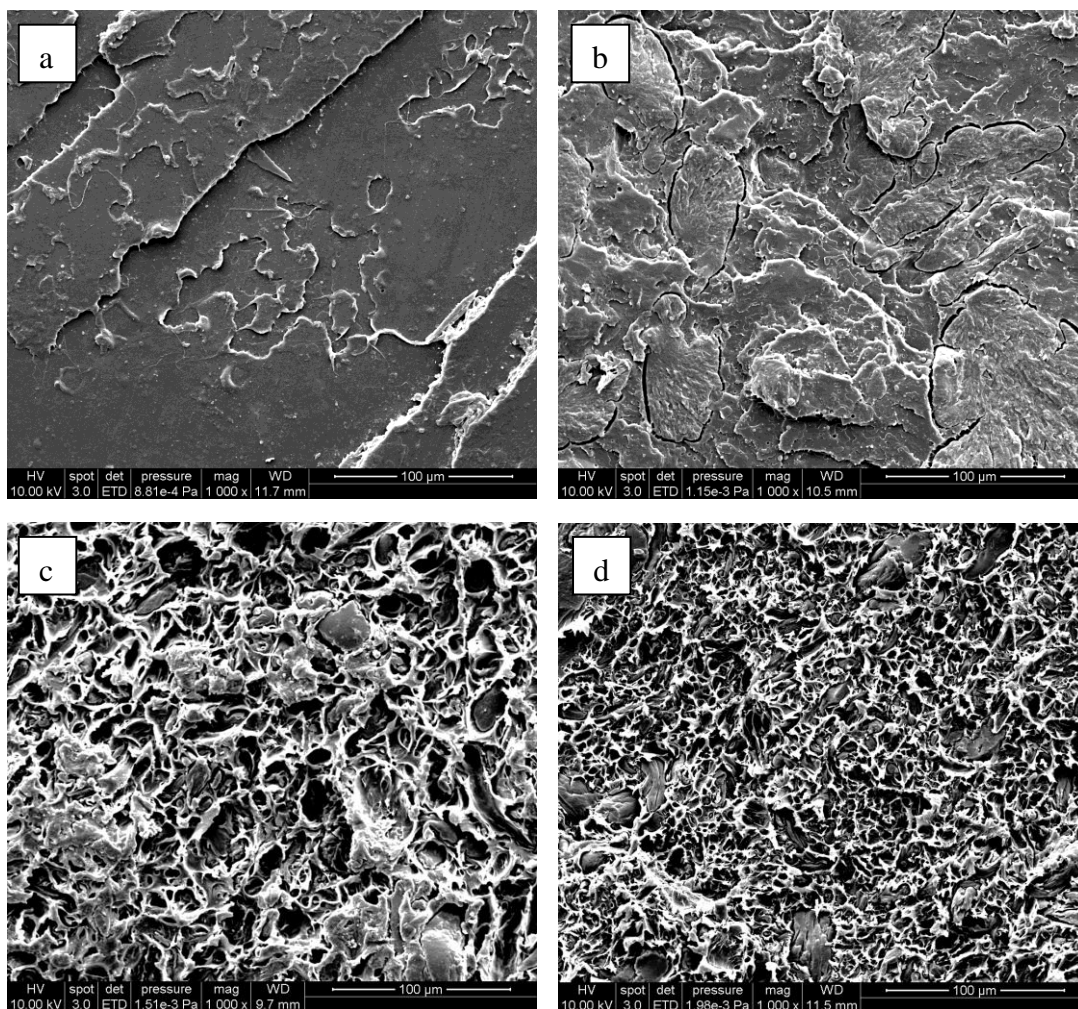


**Figure 3.5** SEM micrographs showing the effect of MA grafting degree on the phase morphology of PLA/SPC (70/30 w/w) blends. a&b: grafting degree is 0.25; c&d: grafting degree is 0.89. Left column is 1000 $\times$ , right column is 2000 $\times$ .

Figure 3.6 shows the tensile fracture surface of the neat PLA and PLA/SPC blends with varying content of compatibilizer. Neat PLA and PLA/SPC blends all exhibited brittle failure behaviors as the fractures showed little sign of plastic deformation. Without compatibilizer (Figure 3.6(b)), SPC appeared in fairly large particles, corresponding to the observation of its particles in Figure 3.4. The flat fracture surface suggests the fracture propagated through the sample straightly without detour when it encountered the SPC particles. As a result, the large SPC particles in this sample were simply broken apart in contrast the clear pullout as they were



in the compatibilized samples. This result was probably attributed to the severe stress concentration at the large SPC particles which broke the particles instead of pulling out. For the compatibilized PLA/SPC blends (Figure 3.6 (c) &(d)), pullout of the SPC particles which were much finer than that in the uncompatibilized samples can be clearly seen from the surface. The inferior strength of the blends to neat PLA was probably due to the weak interfacial adhesion which was probably true even in those blends with PLA-g-MA added. Because of the relatively weak interfacial adhesion, the PLA/SPC blends underwent debonding at the PLA/SPC interface under the stress level which was smaller than that of matrix yielding. Support for this argument can be found in the evidences that using more reactive isocyanate group-containing coupling agents, such as polymeric diphenylmethane diisocyanate (pMDI), at relatively low concentrations, could result in PLA composites with significant enhanced strength or even higher strength than that of the neat PLA (Liu et al 2010).

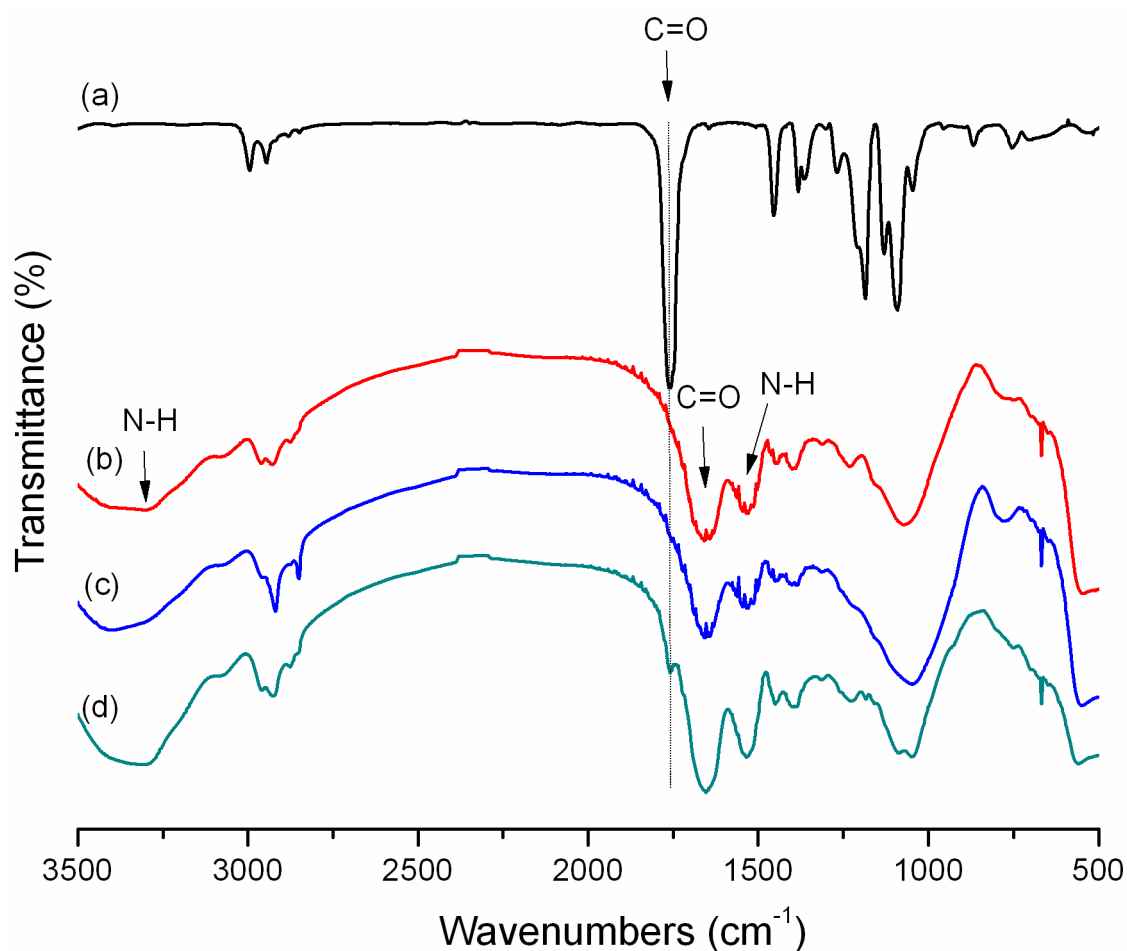


**Figure 3.6** SEM micrographs of the tensile fracture surfaces of the materials: (a) neat PLA; (b) PLA/SPC without PLA-g-MA; (c) PLA/SPC with 4phr PLA-g-MA (grafting degree=0.25%); (d) PLA/SPC with 4phr PLA-g-MA (grafting degree=0.89%).

### 3.3.3 Fourier Transform Infrared Spectroscopy

FTIR has been proven to be an effective technique to investigate interfacial bonding in polymer composites. Figure 3.7 shows the FTIR spectra of neat PLA, neat SPC, the residues of the composite with and without PLA-g-MA after solvent extraction to remove free PLA. Neat PLA had a strong absorption band at  $1760\text{ cm}^{-1}$  (C=O stretching) (Figure 3.7 (a)). Neat SPC showed strong absorption bands at  $1514$  (NH stretch, amide II),  $1658$  (C=O stretch, amide I) and  $3338\text{ cm}^{-1}$  (NH stretch) (Figure 3.7 (b) (Zhong et al 2005)). A small shoulder at  $1760\text{ cm}^{-1}$

(C=O stretching of PLA) was shown in the SPC extracted from composite with 4 phr PLA-g-MA (Figure 3.7 (d)), which was not observed in the composite without PLA-g-MA. This result substantiated the previous postulation that the grafted MA groups on the PLA backbone reacted with the amide and amine groups of SPC, which formed covalent bonding between PLA and SPC. The enhanced interaction between the PLA and SPC phases improved the compatibility between the two components and therefore increased the mechanical properties.

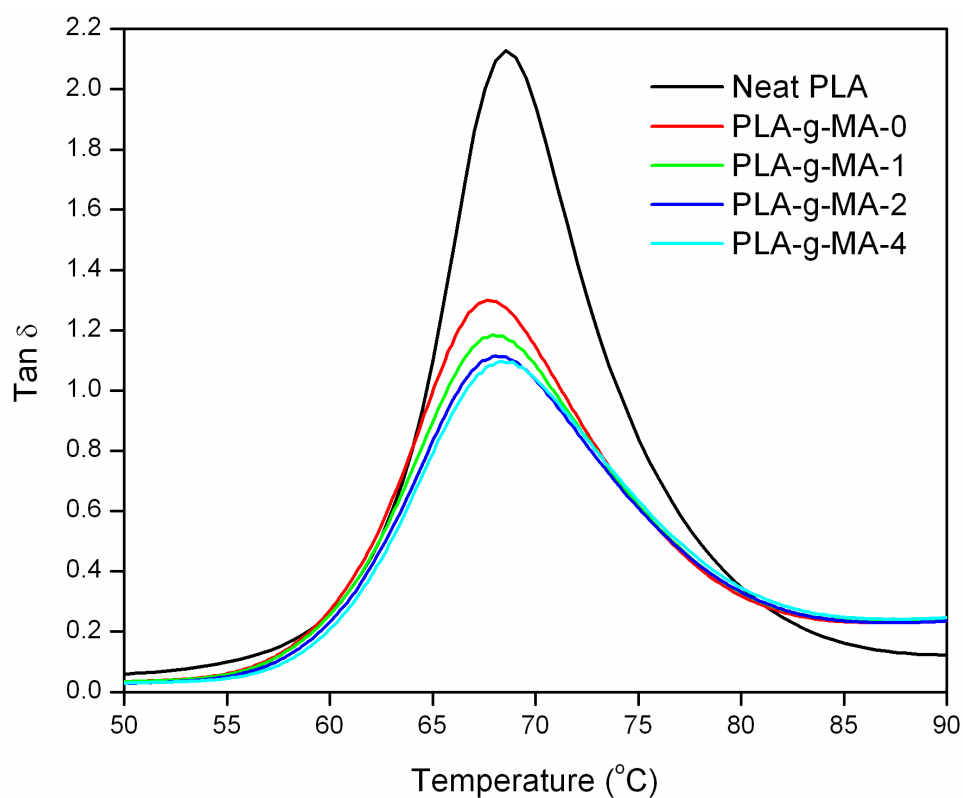


**Figure 3.7** FTIR spectra of (a) neat PLA, (b) neat SPC, (c) SPC without PLA-g-MA, (d) SPC with 4phr PLA-g-MA (grafting degree=0.89%).

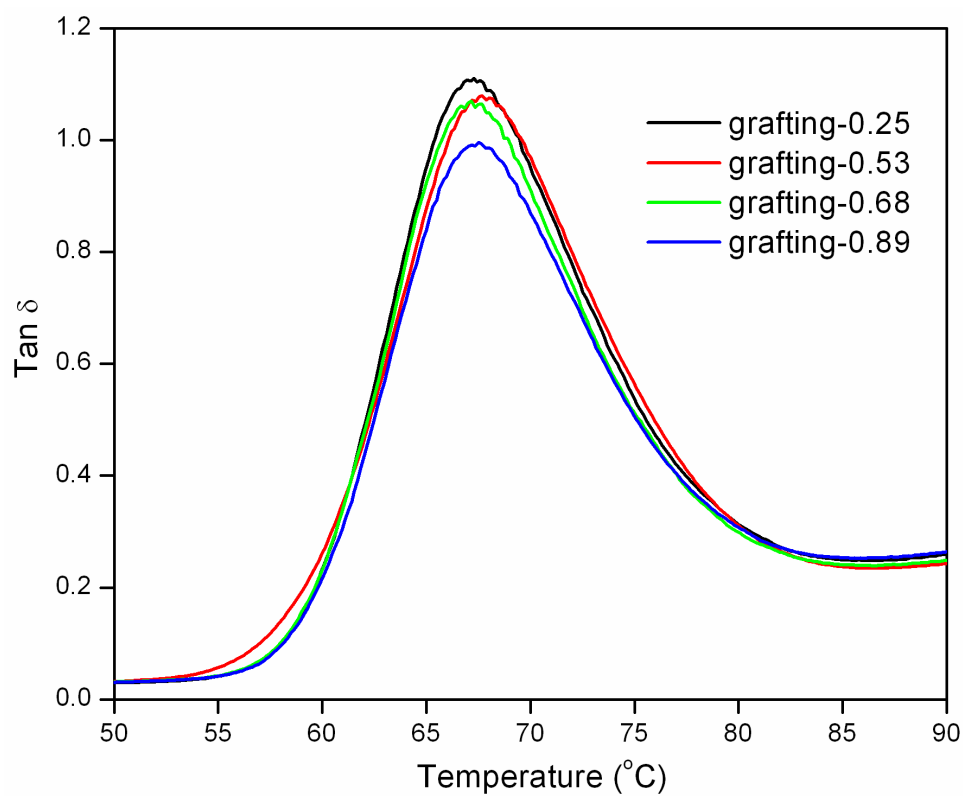
### 3.3.4 Dynamic Mechanical Properties

DMA measurements are often used to evaluate polymer stiffness under dynamic mode, molecular segment mobility, and maximum damping temperature ( $T_g$ ) (Chartoff et al 2009) .  $\tan \delta$  of neat PLA and PLA/SPC composites with different concentration of PLA-g-MA as a function of temperature are shown in Figure 3.8. Damping in the transition zone measures the imperfection in the elasticity; that is, damping reduces the snap of a material (Nielsen et al 1994). Neat PLA exhibited a sharp and high damping peak, whereas the PLA/SPC composites showed broad and low peaks. Neat PLA became very soft when the temperatures were above its  $\alpha$ -transition (peak at ca. 70 °C) (Zhang et al 2006), and hence a high damping peak was observed in the transition zone. Filler would restrict the motion of the matrix chain, thereby affecting the relaxation of the matrix chain, and resulting in a broader and lower damping peak in the transition zone. Compared to PLA/SPC composites without PLA-g-MA, composites with PLA-g-MA compatibilizer demonstrated broader and lower damping peaks, which means that the blend had improved interactions between PLA and SPC. Increasing compatibilizer concentration further reduced the height of damping peak, which may be due to the more effective contribution of SPC phase to the superior elastic modulus ( $E'$ ) in the rubbery region under condition of good interfacial adhesion (Sumita et al 1984). Moreover, the enhanced interfacial adhesion between PLA and SPC might be due to the appearance of an absorbed layer of polymer surrounding the filler surface, which restricted the molecular motion and resulted in lower damping (Wang et al 2001).

It was observed that the  $T_g$  of PLA in all the PLA/SPC composites was slightly lower than that in the neat PLA as shown in Figure 3.8. The result indicates that SPC was not soluble in PLA at all even with the addition of PLA-g-MA. Although small molecules including glycerol and water are plasticizers for SPC are not considered to plasticize PLA or miscible with PLA, they are able to decrease  $T_g$  of PLA if absorbed onto PLA (Zhang et al. 2006). However, with increasing compatibilizer concentration, the  $T_g$  of PLA in the PLA/SPC composites shifted to higher temperatures and became very close to that in the neat PLA. In general, it has been established that the shift of  $T_g$  results from the contribution of the interaction between the dispersed phase and matrix and the volume fraction of the resulting interface (Huang et al 2004). Since volume fraction was constant in all formulations, the shift of  $T_g$  was due to the better interaction between PLA and SPC with the addition of PLA-g-MA. This conclusion can be further substantiated by varying the grafting degree of PLA-g-MA, as shown in Figure 3.9. It was found that damping peak became lower and  $T_g$  shifts slightly towards higher temperatures with increasing grafting degree of PLA-g-MA.

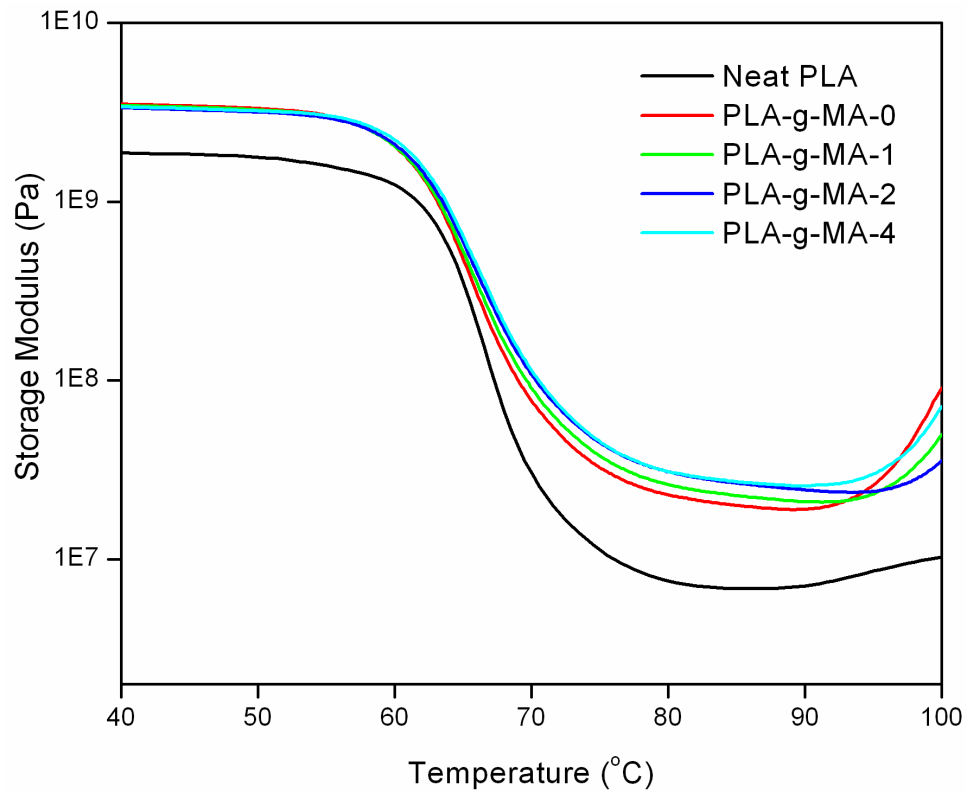


**Figure 3.8** Tan  $\delta$  versus temperature of the neat PLA and PLA/SPC composites comprising different concentration of PLA-g-MA



**Figure 3.9** Tan  $\delta$  versus temperature for PLA and PLA/SPC composites comprising compatibilizers with different grafting degree

Figure 3.10 compares the  $E'$  of neat PLA and PLA/SPC composites with and without compatibilizer. The storage modulus of all samples suddenly dropped when the glass transition temperature ( $T_g$ ) of PLA (ca. 60 °C) was reached, and then recovered to a significant degree between 85 and 100 °C due to PLA cold crystallization (Liu et al 2010). The storage moduli of selected samples at four different temperatures are summarized in Table 3.3. Neat PLA had the lowest storage modulus at all four temperatures due to the absence of reinforcing effect of SPC. The SPC acted as filler to improve stiffness. The PLA/SPC composites with 4 phr PLA-g-MA had higher storage modulus than composites without PLA-g-MA in the whole temperature range. Generally, the higher storage modulus for compatibilized blends evidences the rigidity obtained due to chemical interaction of the reactive groups in the soy protein towards the maleated polymer during the processing of the blends (John and Bhattacharya 1999). The reinforcing effect of SPC was even stronger at higher temperatures due to the accelerated cold crystallization of PLA (Liu et al 2010). For instance, storage modulus of the composites with 4 phr PLA-g-MA was 182% of that of the neat PLA at 30 °C, whereas the value was 361% at 90 °C. A similar trend was observed while changing the grafting degree of PLA-g-MA, as shown in Figure 3.11. Higher grafting degree led to higher storage modulus, although the change was small due to the fact that the PLA-g-MA concentration was fixed at 4 phr in this series.

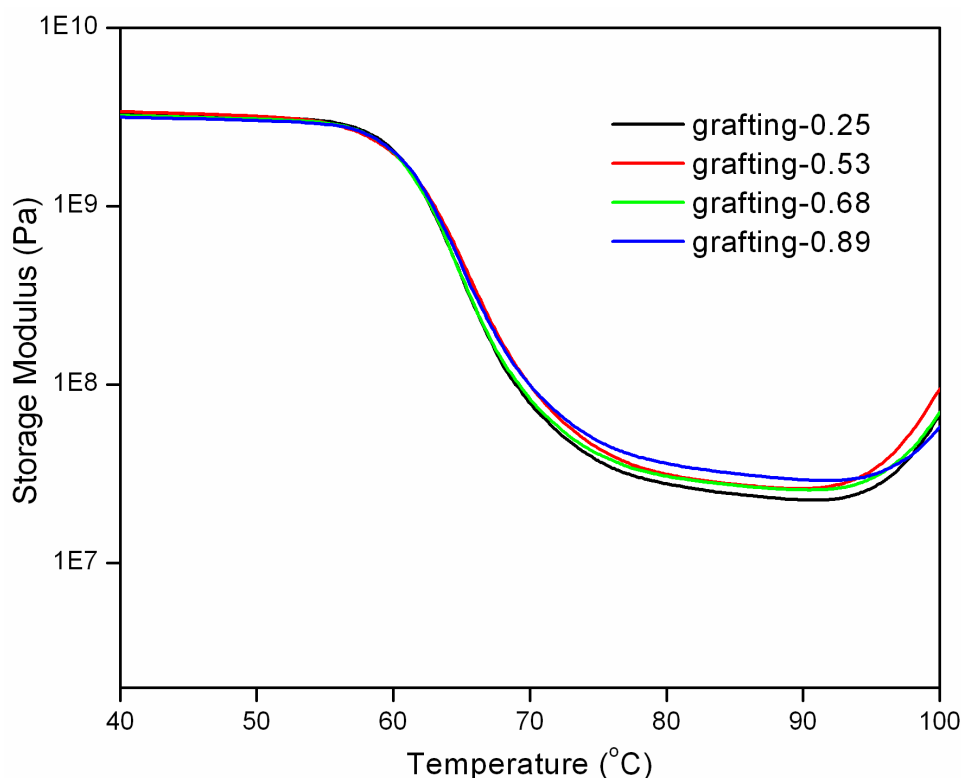


**Figure 3.10** Storage modulus versus temperature of the neat PLA and PLA/SPC composites comprising different concentration of PLA-g-MA

**Table 3.3** Storage Modulus of PLA and PLA/SPC composites at different temperature

Blend composition	Storage Modulus (Pa)			
	30°C	60°C	90°C	120°C
Neat PLA	1.93E+09	1.24E+09	7.11E+06	6.71E+07
PLA/SPC without PLA-g-MA	3.64E+09	2.03E+09	1.90E+07	2.37E+08
PLA/SPC with 4phr PLA-g-MA	3.81E+09	2.22E+09	2.57E+07	2.68E+08





**Figure 3.11** Storage modulus versus temperature of PLA and PLA/SPC composites comprising compatibilizers with different grafting degree. Concentration of compatibilizer was 4% in each blend sample.

### 3.3.5 Thermal properties (DSC)

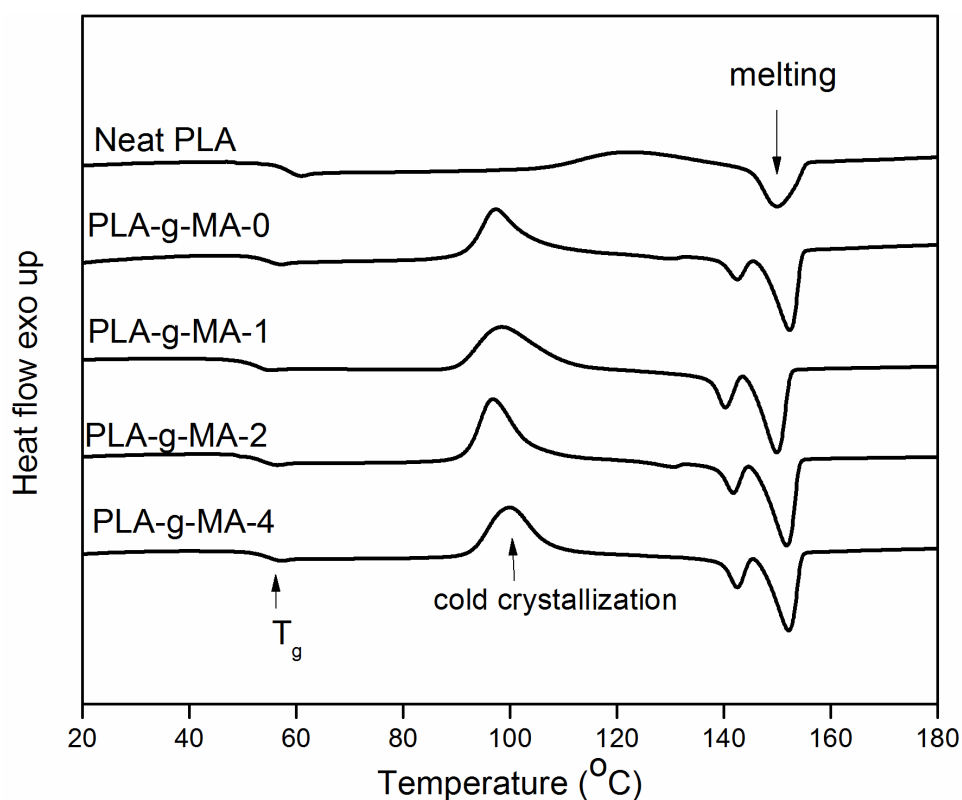
Figure 3.12 and Figure 3.13 present the DSC thermograms of neat PLA, PLA/SPC composites. Table 3.4 summarizes the DSC data, which show the glass transition and crystallization/melting behaviors of the PLA component in the composites. All of the composites samples showed three transitions, namely PLA glass transition, cold crystallization, and melting (Zhang et al 2006) (Liu et al 2010). The neat PLA had a melting temperature of about 150.1 °C and a very broad crystallization peak starting at about 110 °C and ending at about 150 °C.

$T_g$  of PLA in the composites is slightly lower than that of neat PLA, which is consistent

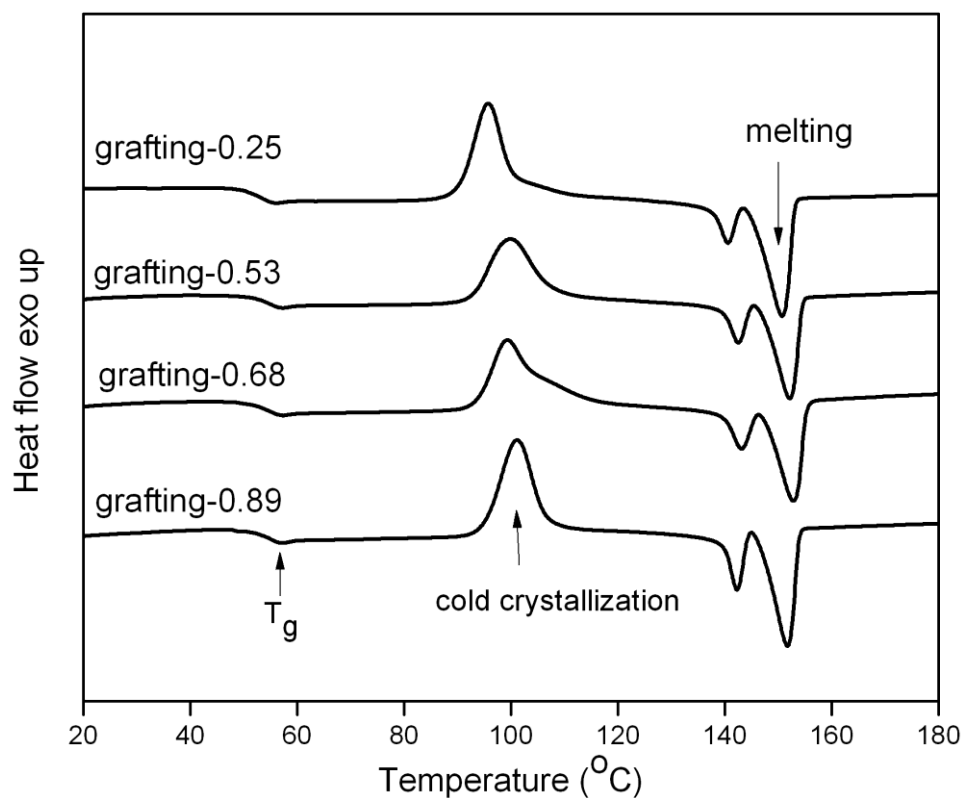
with the results observed from DMA. Compared to the cold crystallization of neat PLA, that of PLA in the composites occurred at much lower temperatures with narrower temperature range, which indicates that SPC increased the cold crystalline ability of PLA. Many polar groups of SPC were prone to induce heteronucleation and likely promoted PLA cold crystallization. As a result, the cold crystallization temperature decreased and the enthalpy of fusion ( $H_m$ ) increased for the PLA/SPC composites. Generally, fillers would induce heterogeneous nucleation at polymer phase boundaries, where the effective surface energy is lower, thus diminishing the free energy barrier and facilitating nucleation. As shown in Table 3.4, The PLA/SPC composite without PLA-g-MA displayed a cold crystallization temperature ( $T_{cc}$ ) of 97.3°C, After loading 4 phr PLA-g-MA, however,  $T_{cc}$  of the composite shifted to 99.8 °C. Such behaviors may be attributed to the restricted slippage and mobility of the PLA macromolecular segment because interactions between PLA and SPC increased in the presence of PLA-g-MA (Fang et al 2009). Reactions between PLA-g-MA and SPC increased wetting of SPC by PLA, which increased the free energy needed for nucleation and therefore decreased the nucleation effect of SPC (Vehkamäki 2006). Therefore, the  $T_{cc}$  increased with the increasing PLA-g-MA concentration. Moreover, DSC results of the composites comprising compatibilizers of different grafting degrees followed a similar trend. As the grafting degree of PLA-g-MA increased from 0.25% to 0.89%,  $T_{cc}$  increased from 95.7 °C to 101 °C.

Two melting peaks ( $T_m$ ) in all the PLA/SPC composites are observed. The lower temperature peaks (ca. 140-143 °C) and the higher temperature peaks (ca. 150-153 °C) were

due to the melting of a certain amount of previously formed PLA crystals and the melting of crystals formed through a melt-recrystallization progress, respectively (Li et al 2010). In fact, multiple melting behaviors haven been reported in many semi-crystalline polymers, such as PLA (Yasuniwa et al 2004) (Zhang et al 2006), poly(ethylene terephthalate) (Tan et al 2000) and poly(butylene terephthalate) (Yasuniwa et al 2000).



**Figure 3.12** DSC thermograms of neat PLA and PLA/SPC composites comprising different concentration of PLA-g-MA



**Figure 3.13** DSC thermograms of neat PLA and PLA/SPC composites comprising compatibilizers of different grafting degrees

**Table 3.4** Thermal behaviors of neat PLA and PLA/SPC composites determined from DSC

Sample Codes	$T_g$ (°C)	$T_{cc}$ (°C)	$T_{1m}$ (°C)	$T_{2m}$ (°C)	$H_m$ (J/g)
Neat PLA	60.6	120.5	-	150.1	12.26
PLA-g-MA-0	56.8	97.3	142.5	152.4	18.19
PLA-g-MA-1	54.5	98.3	140.3	149.9	21.46
PLA-g-MA-2	56.0	98.8	141.8	151.8	21.31
PLA-g-MA-4	56.9	99.8	142.6	152.3	18.39
grafting-0.25	55.6	95.7	140.7	150.8	23.05
grafting-0.53	56.9	99.8	142.6	152.3	18.39
grafting-0.68	56.8	99.2	143.2	152.9	18.7
grafting-0.89	57.0	101.0	142.3	151.8	23.22

### **3.4 Conclusions**

Soy protein could be used as plastics component in PLA-based composites to reduce cost and retain PLA's mechanical properties. Addition of PLA-g-MA as compatibilizer demonstrated to be an effective way to obtain PLA/SPC composites with superior properties. The tensile properties of the compatibilized PLA/SPC composites were significantly higher than that of the uncompatibilized one. The addition of PLA-g-MA as compatibilizer resulted in fine morphological structure of the composites and SPC domains. Dynamic mechanical properties of the composites were greatly affected by the phase structure. Damping peak of the PLA/SPC composites was reduced by the addition of compatibilizer, which meant better interfacial adhesion was achieved. Storage modulus was also increased with addition of compatibilizer in the whole temperature range. It is found that SPC induced the cold crystallinity of PLA while the addition of compatibilizer decreased the nucleation effect of SPC.

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## **Chapter 4 Conclusions and future work**

### **4.1 Conclusions**

In this contribution, completely biobased PLA/SPC composites are prepared by twin-screw extruder. Generally, the implementation of the research is divided into two sections: preparation of MA grafted PLA and investigation of effects of compatibilization on properties of the composites. Chapter 2 detailed MA grafting of PLA by reactive extrusion. Chapter 3 described the effects of PLA-g-MA as compatibilizer on the properties of the composites.

The results in chapter 2 showed that MA grafting of PLA can be initiated by peroxide L101 using melt free radical grafting process. PLA-g-MA is of great interest due its intrinsic ability to promote good interfacial adhesion between inorganic fillers and PLA resins. Styrene (St) was revealed to be an effective co-monomer in increasing the grafting degree of MA. Influences of reaction variables, i.e. MA/St molar ratio, initiator concentration, monomer concentration, and processing parameters such as temperature and screw speed, on grafting degree of MA were investigated in details.

The blends of SPC and polyesters are known to be completely biodegradable plastics and so as to attract many research and industrial interests. In chapter 3, an attempt was made to compatibilize the blends of PLA and SPC using the obtained PLA-g-MA. Adequate water and glycerol were added as plasticizer in the pre-formulated SPC so that SPC can undergo gelation and behave like a plastic component during mixing. The effects of PLA-g-MA on the morphological structures and properties of the PLA/SPC composites were thoroughly

investigated. PLA-g-MA was proven to be an effective compatibilizer for PLA/SPC composites. It significantly improved the interfacial adhesion between the PLA and SPC phases. With the addition of compatibilizer, the SPC phase in the composite changed from large and coarse particles to fine elongated threads. Good interfacial bonding led to high mechanical properties. The addition of compatibilizer was shown to be the prerequisite for obtain PLA/SPC composites with superior properties.

## **4.2 Future work**

Although the grafting degree of MA was successfully increased by using styrene as a co-monomer in melt grafting reaction, it was still fairly low as the highest grafting degree achieved was only ~ 0.8 wt%. The low degree of functionality of the compatibilizer probably accounted for the lower strength of the composite compared with that of the composites using polymeric diphenylmethane diisocyanate as compatibilizer. Besides, side reactions during the MA grating of PLA still need to be addressed. In future, the following investigations should be conducted.

- (1) Enhance grafting degree of MA through using PLA of low molecular weight;
- (2) Improve the properties of PLA/SPC composites using dual compatibilization.