## PRODUCTION AND CHARACTERIZATION OF THERMOPLASTIC CASSAVA STARCH, FUNCTIONALIZED POLY(LACTIC ACID), AND THEIR REACTIVE COMPATIBILIZED BLENDS

By

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#### ABSTRACT

## PRODUCTION AND CHARACTERIZATION OF THERMOPLASTIC CASSAVA STARCH, FUNCTIONALIZED POLY(LACTIC ACID), AND THEIR REACTIVE COMPATIBILIZED BLENDS

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Cassava starch was blended with glycerol using a co-rotating twin-screw extruder (TSE). Thermoplastic cassava starch (TPCS) at a ratio of 70/30 by weight of cassava/glycerol was selected and further blended with other polymers. TPCS sheets made from compression molding had low tensile strength ( $0.45 \pm 0.05$  MPa) and Young's modulus ( $1.24 \pm 0.58$  MPa), but moderate elongation at break ( $83.0 \pm 0.18.6\%$ ), medium level of oxygen permeability, and high water vapor permeability with a very high rate of water absorption.

TPCS was blended with poly(lactic acid) (PLA) at various ratios by using a TSE. The blend resins exhibited good properties such as increased thermal stability ( $T_{max}$ ) and crystallinity of PLA, and improved water sensitivity and processability of TPCS. PLA and TPCS exhibited a high interfacial tension between the two phases of 7.9 mJ·m<sup>-2</sup>, indicating the formation of an incompatible, immiscible blend. SEM micrographs showed a non-homogeneous distribution of TPCS droplets in the PLA continuous phase. TEM micrographs of the blend films made by cast-film extrusion showed coalescence of the TPCS droplets in the PLA continuous phase of the blend, indicating that the compatibility between the polymer pair needs to be improved.

A response surface methodology (RSM) design was used to analyze the effects of maleic anhydride (MA) and 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (Luperox or L101) contents, and TSE screw speed on the degree of grafted MA and number average molecular weight ( $M_n$ ) of functionalized PLA (PLA-g-MA), a reactive compatibilizer. PLA-g-MA made by reactive extrusion had an array of colors depending on the content of L101 and MA used. New FTIR peaks suggested that MA was grafted onto the PLA backbone and oligomeric MA may occur. Increasing L101 increased the degree of grafting and decreased  $M_n$ , but the  $M_n$  of the PLA-g-MA's produced with a high amount of L101 was stable during storage. MA exhibited an optimum concentration for maximizing the degree of grafted MA, and increasing MA content retarded the reduction of  $M_n$  during processing. However, the  $M_n$  of PLA-g-MA during storage decreased more rapidly with a high content of MA. TSE screw speed had an impact on the  $M_n$  with the maximum value predicted at 20 rpm.

PLA-g-MA compounds differing in  $M_n$  and/or grafted MA content were used as reactive polymers with TPCS (to produce binary blends) and as reactive compatibilizers (to produce ternary blends of PLA/TPCS/PLA-g-MA) with TPCS content of 30 wt% using a TSE. As a result of maleation, PLA-g-MA had a higher grafted MA content with a lower  $M_n$ , and higher *PI*. The interaction of anhydride groups from PLA-g-MA and hydroxyl groups from TPCS was found by FTIR. The reactive binary blends exhibited a change in thermal stability, decrease of  $T_{cc}$ , the presence of double melting peaks, and an increase of the  $T_gs$  of glycerol and starch. The higher the grafted MA content and/or the higher  $M_n$  of the PLA-g-MA used, the better were the distribution and smaller the TPCS domains obtained in the blends. The highest elongation at break was achieved when 30 wt% TPCS was blended with 70 wt% of PLA having 0.1 wt% of grafted MA and  $M_n$  of PLA-g-MA with a 45 kDa. Finally, the optimum PLA-g-MA was determined by using the results from PLA-g-MA RSM design and the reactive blending. Copyright by SUKEEWAN DETYOTHIN 2012 To my parents, my sisters, the people of Thailand, and everyone who is part of the knowledge and contribution in this work

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## LIST OF SYMBOLS AND ABBREVIATIONS

•	=	Free radical
+, 1	=	High coded level in RSM CCD
-, -1	=	Low coded level in RSM CCD
0	=	Mid coded level in RSM CCD
α	=	<ul><li>(1) Exponent of the Mark-Houwink equation</li><li>(2) Distance from the center point to the star point in CCD</li></ul>
$\beta_0$	=	Intercept in the second-order RSM model
$\beta_1, \beta_2, \beta_3$	=	Linear main effect of maleic anhydride, Luperox 101, and screw speed of counter-rotating conical twin screw extruder in the second-order RSM model, respectively
$\beta_{11}, \beta_{22}, \beta_{33}$	=	Quadratic main effect of maleic anhydride, Luperox 101, and screw speed of counter-rotating conical TSE, in the second-order RSM model, respectively
$\beta_{12},\beta_{13},\beta_{23}$	=	Interaction effect of maleic anhydride and Luperox 101, maleic anhydride and screw speed of counter-rotating conical TSE, and Luperox 101 and screw speed of counter-rotating conical TSE in the second-order RSM model, respectively
$\lambda_{21}$	=	Spreading coefficient of polymer 2 over polymer 1
$\phi$	=	Weight fraction
$\gamma_{1}, \gamma_{2}$	=	Surface tension of polymer 1, and polymer 2, respectively
$\gamma_{12}$	=	Interfacial tension between polymer 1 and 2
$\gamma^d$	=	Non-polar or dispersion component
$\gamma^p$	=	Polar component

<i>W</i> <sub>12</sub>	=	Work of adhesion between two polymers
$\psi(p)$	=	Universal function of viscosity ratio
A, a	=	Coded level of $+\alpha$ , and $-\alpha$ in RSM CCD, respectively
a*	=	Axis extending from negative (green) to positive (red) in the CIELAB
AC	=	Acetyl triethyl citrate
ANOVA	=	Analysis of variance
ASTM	=	the American Society for Testing and Materials
ATR	=	Attenuated total reflectance
b*	=	Axis extending from blue (negative) to yellow (positive) in the CIELAB
°C	=	Degree Celsius
сс	=	Cubic centimeter
CCD	=	Central composite design
CIELAB	=	A color space dfined by the Commission Internationale de l'Eclairage
cm	=	Centimeter
СОР	=	Carbon dioxide (CO <sub>2</sub> ) permeability
$\Delta C_p$	=	Heat capacity
d	=	<ul><li>(1) Day</li><li>(2) Particle size of a dispersed phase</li></ul>
DCP	=	Dicumyl peroxide
DEM	=	Diethylmaleate
dL	=	Deciliter
DOE	=	Design of experiments
DS	=	Degree of substitution

DSC	=	Differential scanning calorimetry
DTG	=	Derivative thermogravimetry
E	=	Storage or elastic modulus
<i>E</i> ″′	=	Loss or viscous modulus
EVOH	=	Ethylene/vinyl alcohol
$E\{Y\}$	=	Estimate response of interested parameter in the second-order RSM model
FTIR	=	Fourier transform infrared
G	=	Shear rate
g	=	Gram
$\Delta G_m$	=	The Gibbs, free energy of mixing of two polymers
GM	=	The geometric mean
GPa	=	Gigapascal
GPC	=	Gel permeation chromatography
GTPS	=	Glycerol plasticized starch
h	=	Hour
$\Delta H_{cc}$	=	Enthalpy of cold crystallization
HDPE	=	High density polyethylene
HDT	=	Heat deflection or distortion temperature
$H_{f}$	=	Heat of fusion or enthalpy of fusion
HM	=	The harmonic mean
$\Delta H_m$	=	Heat of mixing or the enthalpy of a system or enthalpy of mixing

in	=	Inch
IV	=	Intrinsic viscosity
J	=	Joules
Κ	=	Mark-Houwink constant
k	=	Degradation fractor
kDa	=	Kilodalton
КОН	=	Potassium hydroxide
L*	=	Lightness in the CIELAB
L101	=	Luperox 101, Lupersol 101, or 2,5-bis( <i>tert</i> -butylperoxy) -2,5-dimethylhexane
L/D	=	Length to diameter ratio of the extruder screw
LDPE	=	Low density polyethylene
LW	=	Lifschitz-van der Waals
LLDPE	=	Linear low density polyethylene
М	=	Molarity
m	=	Meter
MA	=	Maleic anhydride
MC	=	Moisture content
MFI	=	Melt flow index
min	=	Minutes
mm	=	Milimeter
M <sub>n</sub>	=	Number average molecular weight
MPa	=	Megapascal
MSW	=	Municipal solid waste

MTPS	=	Maleated thermoplastic starch			
$M_{\mathcal{V}}$	=	Viscosity average molecular weight			
$M_{W}$	=	Weight average molecular weight			
MWD	=	Molecular weight distribution			
N	=	Normality			
$\eta_d$	=	Viscosity of the dispersed phase			
$\eta_m$	=	Viscosity of the matrix phase			
O.D.	=	Optical density			
OP	=	Oxygen permeability			
OPP	=	Oriented polypropylene			
р	=	Viscosity ratio			
PA	=	Polyamide			
PBAT	=	Poly(butylenes adipate-co-terephthalate)			
PBSA	=	Polybutylene succinate adipate			
PC	=	Polycarbonate			
PCL	=	Poly( <i>ɛ</i> -caprolactone)			
PDLA	=	Poly(D-lactide) PDLLA			
PDLLA	=	Poly(D,L-lactide)			
PDXL	=	Polydioxolane			
PE	=	Polyethylene			
PEA	=	Polyesteramide			
PEG	=	Polyethylene glycol			

PET	=	Polyethylene terephthalate
PGA	=	Polyglycolic acid
РНА	=	Poly(hydroxyalkanoate)
PHB	=	$Poly(\beta-hydroxybutyrate)$
PHB/V	=	Poly(hydroxybutyrate-co-valerate)
phr	=	Parts per hundred parts
PI	=	Polydispersion index
PMA	=	Polymaleic anhydride
PLA	=	Poly(lactic acid)
PLA-g-MA	=	PLA grafted MA, functionalized PLA, or maleated PLA
PLLA	=	Poly(L-lactide)
РР	=	Polypropylene
PPC	=	Polypropylene carbonate
PPG	=	Polypropylene glycol
PS	=	<ul><li>(1) Polystyrene</li><li>(2) PLA/starch blend</li></ul>
psi	=	Pounds per square inch
PSMA	=	Compatibilized one-step PLA/TPS blend with MA as compatibilizer
PSMATPS	=	Compatibilized two-step PLA/MTPS blends
PTFE	=	Poly(tetrafluoroethylene)
PVAc/VA	=	Poly(vinyl acetate-co-vinyl alcohol)
PVC	=	Polyvinyl chloride
PVDC	=	Polyvinylidene chloride
PVOH	=	Polyvinyl alcohol

R•	=	Alkyl radical
$R^2$	=	Coefficient of determination
RH	=	<ul><li>(1) Relative humidity</li><li>(2) Polymer backbone</li></ul>
RO•	=	Alkoxy radical
ROH	=	Alkyl alcohol
ROOH	=	Hydroperoxide
rpm	=	Revolutions per minute
RSM	=	Response surface methodology
S	=	Second
SA	=	Succinic anhydride
$\Delta S_m$	=	Entropy of mixing which is related to the disorder of the system.
SEM	=	Scanning electron microscopy
Т	=	Absolute temperature
$T_{\alpha}$	=	Glass transition temperature of $\alpha$ relaxation (starch-rich domain)
$T_{eta}$	=	Glass transition temperature of $\beta$ relaxation (glycerol-rich domain)
tan <i>δ</i>	=	Damping coefficient
TC	=	Triethyl citrate
T <sub>cc</sub>	=	Cold crystallization temperature
$T_d$	=	Thermal degradation temperature
T <sub>e</sub>	=	End decomposition temperature
TEM	=	Transmission electron microscopy

$T_g$	=	Glass transition temperature
TGA	=	Thermogravimetric analysis
THF	=	Tetrahydrofuran
$T_m$	=	Melting temperature
T <sub>max</sub>	=	Temperature at the maximum rate of weight loss
T <sub>o</sub>	=	Onset decomposition temperature
TPCS	=	Thermoplastic cassava starch
TPS	=	Thermoplastic starch
TSE	=	Twin-screw extruder
μm	=	Micrometer
UV	=	Ultraviolet
V	=	Volt
V	=	Volume
VCG	=	Van Oss, Chaudhury, and Good approach
w, wt	=	Weight
WTPS	=	Water plasticized starch
WVP	=	Water vapor permeability
$X_1, X_2, X_3$	=	MA content, L101 content, and Screw speed of counter-rotating conical TSE in the secondary-order RSM model, respectively
X <sub>c</sub>	=	The degree of crystallinity

### **1.1** Introduction and motivations

The awareness and concerns of the public about using plastics derived from petrochemical resources started in the mid to late 1970s due to significant increases in oil prices. Since that time, the solutions have focused on energy efficiency and the use of regrind plastics in packaging production [1]. The second concern in environmental issues arose in the mid-1980s due to limited landfill space, increasing landfill cost, and the concern that plastics in landfills could accumulate for hundreds of years [1]. Thus, the idea of using biodegradable plastics emerged. Polyethylene (PE) was blended with around 6% of granular starches under the theory that, after starch degrades, it will leave small pores in the PE matrix increasing surface areas for microbial degradation, and accelerating the final rate of degradation [1-2].

However, the degradation rate of PE did not change and did not provide any advantage for applications such as disposable packaging and agricultural mulch. Therefore, auto-oxidative additives were introduced into granular starch/PE blends to improve the rate of degradation. However, the basic degradation mechanisms of PE were still unchanged – *biodeterioration (i.e.* fracture and loss of polymer strength without a significant change in molecular structure) not *biodegradation* (break-down of molecular structure into carbon dioxide, biomass, and water or methane by naturally occurring microorganisms in a specific time) [1-2]. Therefore, the demand for granular starch/PE blends decreased, and 'biodegradable starch-based plastics' were removed from the market, tainting the image of these polymers for consumers. However, the development of truly biodegradable plastics continued.

At this same time, the solution to the problems of plastic waste accumulation turned to recycling with the increasing of *curbside recycling programs*, especially for plastic bottles [1]. In the mid-1990s, recycling approaches were expanded and programs such as use of *the producer responsibility principle* in the European Union were created. Concurrently, truly biodegradable plastics were returned to market along with an increase in composting of biodegradable packages [1].

In recent years, data from the Environmental Protection Agency (EPA) revealed that the average U.S. landfill size has increased albeit the number of landfills in the USA decreased from 6,326 in 1990 to 1,908 in 2010 [3-4]. Total municipal solid waste (MSW) generation increased from 208.3 to 249.9 million tons from 1990 to 2010 [4]. Containers and packaging were the largest component of the MSW categorized by product category, at about 30 wt% in 2010 [4]. Among the container and packaging waste, plastics took the second place (18.1%) after paper and paperboard (49.8%) [3]. The total percentage of MSW recycling increased from 29.5% in 2002 to 34.1% in 2010 and *curbside recycling programs* increased from 8,875 in 2002 to approximately 9,000 in 2010 [4]. However, only 13.5% of plastic containers and packaging (mostly from soft drink, milk and water bottles) were recycled [4].

Therefore, additional approaches, such as using biodegradable plastics, are sought to enforce the reduction of using petroleum-based plastic packaging that ends in landfills, especially in food packaging applications where recycling is difficult or prohibited due to contamination. Under the crucial driving forces of environmental benefits, political conditions, and the limitations and rising prices of petroleum resources, world production of biodegradable polymers is expected to increase. The prices of biodegradable polymers should be comparable with the prices of conventional polymers due to the soaring price of petroleum resources, post disposal, environmental recovery costs, and mass production. Based on a study by the Freedonia Group, Inc., world bioplastic demand is expected to increase from around 300,000 metric tons in 2010 to 1,025,000 metric tons in 2015 [5].

Currently depending on the sources, biodegradable polymers can be classified into two groups: *biodegradable petroleum-based polymers* – such as polybutylene succinate terephthalate, poly(*ɛ*-caprolactone) (PCL), and polyvinyl alcohol (PVOH) – and *biodegradable biobased polymers* such as poly(lactic acid) (PLA) and starch [6]. The latter group may provide advantages in terms of being perceived as environmentally friendly, having lower environmental footprint, managing sustainable carbon cycle (the rate of carbon dioxide fixation equals the rate of carbon dioxide sequestration and release), and reducing the use of petroleum [7]. *Biodegradable biobased polymers* such as starch, cellulose, casein, silk, vegetable oils, and animal fats can be directly extracted from their sources, while monomers of PLA can be derived from the synthesis or fermentation of carbohydrate feedstocks, and poly(hydroxyalkanoate) (PHA) can be produced by microorganisms [8]. Among these, starch has a high potential for being used as a raw material for biopolymers because of its natural biodegradability in a wide variety of environments, low price, and natural abundance in most regions (Americas, Asia, Europe, and Africa) [9-11].

Among the four major starches – corn, potato, wheat and cassava – cassava starch is one of the most important products grown in tropical and subtropical regions of Africa and Asia [12]. Corn or maize is mostly produced in Americas and Asia, while wheat and potatoes are mainly produced in Asia and Europe [12]. Cassava (*Manihot esculenta* Crantz) is known by different names around the world such as "tapioca" in Asia, "manioca" in Africa, and "manioc", "yucca", or "mandioca" in South America. In Europe and the USA, the term "cassava" is applied to the

roots and "tapioca" is applied to processed products including starch [13]. World cassava production is expected to increase from 212 million metric tons in 2007 to 275.1 million metric tons in 2020 [14-15]. The major producers of cassava are Nigeria (the major producer of Africa), Brazil (the major producer of South America), and Thailand (the major producers of Asia and major starch exporter of the world) [12, 15-16]. Fifty percent of cassava in Thailand is used to extract starch. Product yield is approximately 22%, half of which is exported [17].

The export price of cassava flour (cassava starch with low quantity of protein) from Thailand in 2009 was around US \$268 per ton, which was lower than the prices of potato flour (US \$1325 per ton from Netherlands) and maize flour (US \$376 per ton from the USA) [16]. The low price of cassava flour is attributed to low labor cost and advantages in production. Cassava roots can survive under severe environmental conditions, such as drought and degraded soils. It provides high yields per cultivated area and also a higher percentage of starch (dry weight) than almost any other food crop. Furthermore, planting and harvesting of cassava are very flexible, and starch extraction can be performed by simple technologies [14, 17]. This keeps costs down, and it can be grown in large amounts inexpensively.

Cassava starch also has superior properties such as high clarity, high viscosity, bland taste, high stability in acidic products, and outstanding properties for use in non-food products (pharmaceuticals and thermo-bioplastics) [17-18]. Therefore, cassava starch has a high potential to be used as raw material for starch-based biodegradable polymers in tropical and subtropical regions, and the world [19-20].

However, cassava starch has a highly hydrophilic nature, poor mechanical properties, and low processability, which limit its use in packaging applications. To overcome these drawbacks, a more feasible approach – *reactive compatibilization* or *reactive blending* – should be applied.

This technique may not only improve the properties and performance of starch based material, but also offer commercial scale-up with material cost-effectiveness [21]. In this approach, thermoplastic cassava starch (TPCS) will be reactive blended with modified biodegradable polyester made from renewable sources to produce new biodegradable materials.

### 1.2 Goal and objectives

The goal of this research was to develop biobased biodegradable polymers from TPCSbased material to meet the requirements of short-life, single-use disposable packaging applications, and offer compostability. To accomplish this goal, TPCS were blended with modified and/or native hydrophobic aliphatic biobased biodegradable polyester (PLA) to improve compatibility and enhance its mechanical property.

The objectives of this study were as follows:

- 1. Production and characterization of the physicochemical properties of TPCS
- 2. Extrusion melt-compounding of TPCS/PLA and investigation of the properties of the physical blends
- 3. Functionalization of PLA and evaluation of the effects of processing variables on functionalized PLA (PLA-g-MA)
- 4. Investigation of the effects of molecular weight and grafted MA in PLA-*g*-MA on the reactive compatibilization of TPCS/PLA blends

### 1.3 Research plan

# **1.3.1** Phase I: Production and characterization of physicochemical properties of TPCS materials

TPCS resins were produced from premixed cassava starch and glycerol at various ratios and melt-compounded using a twin-screw extruder (TSE), and then pelletized. The resins were dried and the melt flow index values were measured. Films from dried resins were fabricated by compression molding or film-extrusion technique. The physicochemical properties such as tensile, light transmission, and color were determined. The optimum TPCS materials that were suitable for blending were selected. The thermo-mechanical and barrier properties of the final TPCS sheets were also evaluated.

# **1.3.2** Phase II: Extrusion of melt-compounded TPCS/PLA and investigation of the properties of the physical blends

The TPCS resins (containing glycerol at the optimum ratio obtained from phase I) and PLA resins were dried and manually premixed at various ratios. Then, they were meltcompounded using a TSE and pelletized. The morphology, surface properties, Fourier transform infrared (FTIR) spectra, thermal properties, and molecular weight of PLA extracted from the blend resins were investigated. The blend sheets were fabricated by cast-film extrusion; and the film morphology was investigated.

# **1.3.3** Phase III: Functionalization of PLA and evaluation of the effects of processing variables on PLA-g-MA

Functionalization of PLA was conducted by using a design of experiment – Response surface methodology (RSM) – to evaluate the effects of processing variables (maleic anhydride (MA) concentration, 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (Luperox 101 or L101) concentration, and TSE screw speed) on the final properties of PLA-*g*-MA. The reactions were performed in the TSE. FTIR was used to identify grafted MA onto PLA. The properties of PLA-*g*-MA resins (*i.e.* grafted MA content and molecular weight) were determined. Data were used to analyze the significant parameters and optimized the production of PLA-*g*-MA.

# **1.3.4** Phase IV: Investigation of the effects of molecular weight and grafted MA of PLA-*g*-MA on the reactive compatibilization of TPCS/PLA blends

PLA-g-MA resins with various grafted MA content and/or molecular weight were used to investigate the effects of their molecular weight and grafted MA content on reactive compatibilization of the polymer blends. The thermal properties of the PLA-g-MA samples were evaluated. Reactive binary blends (TPCS/PLA-g-MA blends) and reactive ternary blends (TPCS/PLA-g-MA/PLA blends) were produced using TSE and then injection molding. The thermal, thermo-mechanical, morphology, FTIR-Attenuated total reflectance (ATR) spectra, and/or tensile properties were measured. The optimum PLA-g-MA sample that provided a finer morphology and better tensile properties was selected as the optimum PLA-g-MA to be produced.

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### 2.1 Introduction

The intrinsic properties of polymeric materials, such as chemical structure, mechanical, thermal, and rheological properties are crucial indicators to frame their potential production, applications, and material developments. This chapter aims to provide a literature review of the properties of cassava starch as a main raw material for the production of thermoplastic starch (TPS). It will also cover the theory, production, and properties of TPS and its drawbacks for packaging applications. As this point neat TPS materials could not satisfy packaging applications. Current approaches that have been applied to improve TPS properties and performance are reviewed; the techniques that could provide cost-effectiveness, improving processability, tailoring properties, as well as retaining biodegradability are discussed. An overview of the main commercially biodegradable polyester that could be a good candidate as a blending pair for TPS, and the production and properties of the pair are also presented.

### 2.2 Physicochemical and functional properties of cassava starch

Naturally, starches occur in the form of granules in roots, tubers and seeds (or cereal) of plants. Therefore, granule sizes, compositions, and physicochemical and functional properties of starches vary. As shown in Table 2.1, starches from tubers (potato) and roots (cassava) have lower amounts of lipid, protein, and phosphate and lower gelatinization temperature than cereal starches (wheat and maize). The low lipid content causes cassava starch to be odorless and bland in flavor, with a non-cereal taste and no after taste, which are very advantageous characteristics in delicately scented applications, such as many food and cosmetics [1-2].

	Maize	Wheat	Potato	Cassava
Туре	Cereal	Cereal	Tuber	Root
Granule size, µm	2-30	1-45	5-100	4-35
Amylose, %	28-30	26-31	21-23	15.9-22.4
Protein, %	0.35	0.4	0.06	0.1
Lipid, %	0.7	0.8	0.05	0.1
Phosphate, %	0.02	0.06	0.08	0.01
Polymorph (type of crystals)	A	A	В	А, С
Degree of crystallinity, %	27	36	28	38
Gelatinization temperature, °C	75-80	80-85	60-65	65-70

**Table 2.1** Physicochemical properties and characteristics of four major starches [2-6]. For explanation of crystal types (*A*, *B*, and *C*) see text.

Chemically, starch is a polymer of D-glucose units linked together in two different forms, alpha-1,4 links between the linear molecules, and alpha-1,6 links at the branch points. The links of D-glucose units form the macrostructure of starch as a mixture of *amylose*, a predominantly linear polymer with some slight branches, and *amylopectin*, a highly branched polymer. Determinations of the molecular weight of cassava amylose, ranging from 232 to 1,250 kDa, and cassava amylopectin, ranging from 1,880 to 4,500 kDa, vary more depending on testing methods than on different varieties [7-8]. Cassava starch has the lowest amylose and highest amylopectin content (calculated by deducting amylose content from a total of one hundred percent starch). Therefore, cassava starch paste has high clarity and transparency and shows high viscosity and low retrogradation – retrogradation is the process in which starch chains reassociate and form ordered structures [1, 9-10].

In the starch granules, even though the arrangement of amylose and amylopectin is not completely known, the packing of those molecules generates orderly growth rings composed of alternate amorphous and semicrystalline layers (growth rings) where amylopectin is recognized
to hold the framework of the semicrystalline layers (comprised of alternate crystalline and amorphous lamellae) (Figure 2.1). The crystalline lamellae are part of side chain clusters formed by linear and short chain amylopectin with degree of polymerization ranging from 15 to 18, packed and twisted to form the double helices, the basis of the crystals. The amorphous lamellae are part of the branching region of amylopectin.

Therefore, the degree of crystallinity of starch is presumably dependent on amylopectin content [3, 5, 10]. While location, conformation and the role of amylose in starch granules are unclear; it is often suggested that amylose is found mostly in the amorphous layers of the growth rings and some may be found in crystalline lamellae, associated with either amylopectin short chains or lipids [3, 10]. However, increased amylose content increases the size of crystalline lamellae without altering the combined distance of adjacent crystalline and amorphous lamellae





**Figure 2.1** Orderly growth rings (comprised of alternative amorphous and semicrystalline growth rings) within starch granule, adapted from Nowjee [11].

The crystal structures of amylose and amylopectin in starches can be divided into three groups (Figure 2.2), *A*-,*B*-, and *C*-types (a mixture of *A*- and *B*-type) found in cereal starches, tuber and high amylose starches ( $\geq$  40%), and legumes and root starches, respectively [3, 2, 10, 12]. There is a difference in geometric structure between a unit cell of *A*-crystal and that of *B*-crystal. *A*-crystal can occur in monoclinic array – a crystal having three axes of different lengths in which two of the axes are at oblique angles to each other, and the third axis is perpendicular to the plane that is made by the other two, while *B*-crystal can occur in hexagonal array – a crystal having three equal axes intersecting at angles of 60° in one plane and one axis of variable length that is perpendicular to the others. The difference in geometric structure significantly affects the amount of bound water within the crystallites and thus crystallite density [2, 10, 13-14].



**Figure 2.2** Unit cells and double helix packings of *A*-type and *B*-type crystals of starch, obtained from Eliasson and Zobel [2, 15]. The small dark dots indicate water molecules

Furthermore, the crystal structures of amylopectin are related to its weight-average chain length [14-15]. Amylopectin with short chain length (26), exhibits *A-type* whereas amylopectin with intermediate chain length (28) and long chain length (36) show *C*-, and *B-types*, respectively. The crystal structure of cassava starch was reported to be *A*- or *C-type* by different researchers [2, 5]. Another crystal structure is *V*- or *Vh-type*, an association of single amylose helices with aliphatic alcohol, fatty acids, phospholipids, certain surfactants, or iodine [5, 15]. *V*-

*type* is generally found in cereal starches because they are rich in fatty acids and phospholipids. *A-type crystals* are denser and have fewer molecules of bound water (1.22 to 1.48 g·cm<sup>-3</sup> and 8 water molecules) than those of *B-type crystals* (1.10 to 1.40 g·cm<sup>-3</sup> and 36 water molecules) [14]. The ability of starch crystals to hold water leads to a positive correlation between the water content and the crystallinity of starch films, in which crystallization is the driving force for increased water uptake [5]. But crystallite density does not have a major effect on starch melting temperature ( $T_m$ ) and melting enthalpy [14]. Crystalline amylopectin is ruptured at the lowest temperature (55 to 95 °C) compared with crystalline amylose (121 °C) and *V-type crystals* (in water temperatures of above 112 to 120 °C) [15]. Recrystallization of starch can occur after treatment or processing via retrogradation, and crystallinity increases with increased moisture content, which dramatically affects its stability (performance) during storage and use [12, 15].

## 2.3 Thermoplastic starch theory

Since the starch monomer unit contains three free hydroxyl groups (-OH) (Figure 2.3), starch granules are hydrophilic [16-17]. The strong intermolecular association due to the hydrogen bonding of hydroxyl groups and the crystallinity of starch leads to high  $T_m$ , which is higher than the degradation temperature ( $T_d$ ) [17]. The glass transition temperature ( $T_g$ ) and  $T_d$ of cassava starch are around 230 and 220 °C, respectively [18].



Figure 2.3 Structure of starch monomer unit

Therefore, by its nature, starch is not a typical thermoplastic polymeric material. However, starch is completely soluble when heated in water or treated with alkaline aqueous solutions. This phenomenon is called gelatinization [16]. At low water contents (5 to 20 wt%), under high pressure and mechanical shear force, and with addition of plasticizer with moderate temperature (90 to 160 °C), *the starch granules*, crystalline regions, and hydrogen bonding in starch are disrupted. Starch can be melted and will flow and behave like a plastic material [19-20]. This process mainly aimed at mixing and heating starch and plasticizer can be performed by using an extruder, intensive batch mixer, or hot cylinder [16, 21]. Optimum conditions are needed to minimize chain degradation. Among these techniques, extrusion provides more advantages besides creating pressure and high shear. The technique of forming extrudates into pellets is similar to that for conventional synthetic polymers [16]. A co-rotaing, twin-screw extruder (TSE) is preferable for this processing because its self-wiping feature helps prevent caking and burning of cooked starch [22]

Organic liquid plasticizers with high boiling point and low molecular weight are necessary for the transformation process. Plasticizers get in between the polymer chains and act as lubricants increasing flexibility and movement and decreasing  $T_g$  and  $T_m$  of the polymer, leading to more processability [23]. To be effective, the chemical structures of plasticizers must be similar to those of polymers [24]. For starch, polyols, hydrophilic plasticizers containing hydroxyl groups, such as glycol, sorbitol, sugars, and glycerol, are generally used, with glycerol as the most popular plasticizer [5, 19, 24]. Wang *et al.* reviewed that a small amount of natural plasticizer, water, is needed since it is the most effective plasticizer in facilitating chain movement [25]. Without water, the permeation of glycerol in dry starch chains and complete plasticization of starch are limited. The addition of 20 to 40% glycerol plus the intrinsic moisture content of starch provides the optimum content for completely plasticized starch [21, 26]. With a smaller amount of glycerol, starch is very difficult to process, and its chain degradation increases, especially in the amylopectin fraction. With a larger amount of glycerol, the  $T_g$  of transformed products possibly decreases below room temperature, resulting in the increasing of recrystallization and brittleness during storage. Meanwhile, the transformed product is more sensitive to water due to a high number of available hydroxyl groups from glycerol. Simultaneously, glycerol tends to migrate from materials due to their weak interaction and the low molecular weight and high diffusion of glycerol [5, 16, 24, 26-27].

The properties of transformed products are dependent on the amount of plasticizers. Averous *et al.* reported that product transformed from wheat starch with 10% glycerol was stiff and brittle, but with 18 to 35% it was soft and flexible with high impact strength [20]. The transformed product is known as *thermoplastic starch* (TPS), which can be processed by using conventional synthetic polymeric techniques, such as injection molding and extrusion blow molding [21, 26]. TPS is an amorphous material but when it cools down it can recrystallize.

### 2.4 **Properties of TPS polymers**

The properties of TPS polymers after fabricating into films and articles were investigated by many authors.

#### 2.4.1 Mechanical properties

Besides glycerol, the mechanical properties of TPS materials are dependent on amylose content. With high amylose content, TPS materials are strong and stiff [28]. However, TPS materials are classified as brittle and weak materials due to low tensile strength, modulus of elasticity, elongation, impact strength and flowability. Swanson *et al.* and Soest *et al.* reported that the mechanical properties of TPS depend on its water content (plasticizer) [16, 29]. The modulus of elasticity and the tensile strength decreased when water content increased. The maximum elongation at break was obtained when the water content was about 13 to 15%. At 15% moisture content, for example, TPS material exhibited tensile strength of 20 to 30 MPa and elongation at break of 10 to 15%. These mechanical properties may be suitable for making some molded articles but are inappropriate for film applications.

Pushpadass *et al.* investigated the effects of plasticizers on the properties of thermoplastic corn starch films that were fabricated using a TSE connected with a sheeting die and a film take-off unit [30]. Corn starch was dried, and then the moisture content was adjusted to 20%, and it was mixed with 25% glycerol (based on starch). Stearic acid (0.25 to 0.75%), sucrose (2 to 10%), or urea (2 to 10%) was used as a secondary plasticizer. Films fabricated at 110 and 120 °C exhibited 0.9 to 3.2 MPa tensile strength, 4.5 to 70.2 MPa Young's modulus, and 36.5 to 56.2 % tensile strain at break. Films made of sucrose exhibited the highest stiffness, whereas films made from urea were the most flexible.

The mechanical properties of TPS material depend on the relative humidity of the environment. Galdeano *et al.* reported that increasing relative humidity from 11 to 90% reduced the stress at break of extruded thermoplastic oat starch sheets (plasticized with 20 wt% glycerol, 25 wt% sorbitol, or 16 wt% urea) from a range of 8.5 to 14 MPa to 0.5 to 2.0 MPa, but increased the strain at break from a range of 2 to 55 to 75% [31]. The hygroscopic property of starch and hydrophilic plasticizers accounted for the disruption of polymer-polymer and polymer-plasticizer interactions by substituting polymer-water and plasticizer-water interaction, leading to reduction of polymer stiffness. Absorbed water in the TPS materials also facilitated the mobility of starch chains, resulting in increasing the elongation of TPS sheets.

## 2.4.2 Water barrier properties

Compared to hydrophobic polymers, such as low density polyethylene (LDPE) which has water vapor permeability (WVP) around  $5.5 \times 10^{-16} \text{ kg} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$ , thermoplastic corn starch films (containing water and glycerol as the main plasticizers, and urea, stearic acid, or sucrose as a second plasticizer) exhibited WVP in the range of  $3.0 \times 10^{-12}$  to  $5.0 \times 10^{-12} \text{ kg} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$  [23, 30]. The poor moisture barrier of hydrophilic TPS materials is affected by the high polarity of their hydroxyl groups, which makes them sensitive to environment humidity, leading to changes in their performance properties [32]. Mali *et al.* reported that the WVP of corn, cassava, and yam starch films did not depend on starch molecular profiles [33]. The WVP of starch materials increased with increasing plasticizer contents or concentrations (molar basis) due to the increasing of extensibility and free volume between the molecular chains of starch polymers, which facilitated the higher solubility and diffusion of water vapor in starch films [16, 28, 30-31, 34].

### 2.4.3 Gas barrier properties

Weber classified the oxygen (O<sub>2</sub>) permeability (OP) of TPS biodegradable polymers and conventional mineral-oil-based polymers into three groups: high, medium, and low [35]. LDPE and Ecoflex<sup>TM</sup> (poly(butylenes adipate-*co*-terephthalate or PBAT) showed high OP (in a range of 9.3 x  $10^{-18}$  to 9.3 x  $10^{-16}$  kg·m·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>); chitosan plasticized, polyvinylidene chloride (PVDC), and ethylene/vinyl alcohol (EVOH) exhibited low OP (in a range of 9.3 x  $10^{-22}$  to 9.3 x  $10^{-20}$  kg·m·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>). Among the polymers, which had medium OP (2.9 x  $10^{-20}$  to 9.3 x  $10^{-18}$  kg·m·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>), TPS, nylon 6 (PA6), PHA, and PLA ranked from the lowest to the highest [35].

TPS materials also exhibited moderate carbon dioxide (CO<sub>2</sub>) permeability (COP) [36]. However, since CO<sub>2</sub> is a polar molecule, which dissolves and/or diffuses easily in polar materials, the COP of TPS and other polymers is higher than OP [5, 32, 37]. Forssell *et al.* reported that the diffusion of O<sub>2</sub>, CO<sub>2</sub>, and nitrogen (N<sub>2</sub>) through various types of TPS films (*e.g.* potato, rice and wheat) increased with increasing temperature, water, and plasticizer content (*e.g.* glycerol, sorbitol, and sugars) [38]. At 20 °C and 50% RH, the structure of starch polymers (amylose and amylopectin) did not affect OP [38]. In addition, potato amylose and waxy maize amylopectin films exhibited excellent oxygen barrier properties that were comparable to EVOH film. Films (< 15% MC) exhibited good oxygen barrier properties, and their oxygen barrier properties were lost when films had moisture content above 20%. The increase of gas transmission rate to O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> in cm<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup> of corn starch films with glycerol content was investigated by Arvanitoyannis *et al.* [39]. With 95% corn starch and 5% water, the O<sub>2</sub>, N<sub>2</sub>, and CO<sub>2</sub> transmission rate of a corn starch film were  $3.7 \times 10^{-17}$ ,  $5.2 \times 10^{-18}$ , and  $2.5 \times 10^{-16}$  cm<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>, respectively. The transmission rate of the gases increased to 7.4 x  $10^{-13}$ ,  $8.4 \times 10^{-14}$ , and  $1.6 \times 10^{-12}$  cm<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>, respectively with film made of 68% corn starch, 5% water, and 27% glycerol [39]. Dole *et al.* found that at 0% RH, the carbon dioxide solubility of control film made of potato starch and 20 wt% water (dry basis) was slightly higher than that of film plasticized with 12 wt% glycerol – 0.08 and 0.03% (dry basis), respectively [40]. However, at 50% RH, glycerol-plasticized film showed the higher solubility of carbon dioxide (5.9%) than the control film (5.5%) [40].

#### 2.4.4 Thermal properties

As mentioned above,  $T_g$  of TPS polymers decreased with increased glycerol content. Soest *et al.* observed a decrease of  $T_g$  of thermoplastic potato starch (plasticized with water and glycerol at the ratio of 100/21/30), when its water content increased [29]. TPS materials with 5-10, 11, and 14% water had  $T_g$  around 30-60, 20-30, and 0-10 °C, respectively. Graaf *et al.* reported that  $T_g$ 's of TPS polymers depended on the amylose/amylopectin ratio of the starch [41]. Pea, potato, wheat, and waxy maize starch, which had ratios of amylose to amylopectin of 2/1, 1/4, 1/4, and 1/9, respectively, exhibited extrapolated  $T_g$  values of 75, 152, 143, and 158 °C, respectively. TPS materials of those kinds of starch plasticized with 25% glycerol exhibited  $T_g$  around 23, 29, 37, and 41 °C [41]. As a result, TPS materials exhibit a wide range of  $T_{g's}$ 

compared to other polymers (Table 2.2).

	<i>Tg</i> , °C	<i>T<sub>m</sub></i> , °C	<i>T</i> <sub><i>d</i></sub> , °C	Crystallinity, %
LDPE	-120	105 to 115	430 to 480	40 to 60
High density polyethylene (HDPE)	-120	128 to 138	430 to 480	70 to 90
PCL	-60	59 to 64	230 to 335	32 to 51
Polybutylene succinate adipate (PBSA)	-45	93 to 95	333 to 445	20 to 35
PBAT (40/60 to 60/40)	-10 to -37	107 to 162	307 to 430	7.5 to 25.0
Poly( $\beta$ -hydroxybutyrate) (PHB)	0 to 5	140 to 180	170 to 200	60
poly(hydroxybutyrate- <i>co</i> -valerate) (PHB/V)	0 to 30	100 to 190	195 to 200	56
TPS	25 to 80	110 to 115	$\geq$ 300	0 to 34
PLA	50 to 64	130 to 180	235 to 255	0 to 40
Polystyrene (PS) (atactic)	74 to 105	N/A	> 300	N/A

**Table 2.2** Thermal properties range of non-biodegradable and biodegradable polymers [3, 23, 28, 35, 42-49]

At a temperature higher than  $T_g$ , the volume relaxation and retrogradation behaviors allow the amorphous fractions of TPS materials to rearrange themselves closer and exclude water or solvents between the fractions. The intermolecular macromolecules bond together via hydrogen bonding. This leads to crystallizing amorphous fractions. Amylose and amylopectin molecules can recrystallize, but the recrystallization of amylose is faster and irreversible compared to the long-term recrystallization of amylopectin [5, 16]. The lower molecular weight amylose and short chain amylopectin tend to recrystallize faster than the higher ones. Moreover, increasing the moisture content of TPS materials enhances the movement of amorphous fractions, which leads to increased crystallinity [12, 15].

Under poor processing conditions, such as low temperature and low shear force or with an insufficient amount and/or poor ability of plasticizer, the  $T_m$  of TPS materials was observed due to incomplete gelatinization of starch granules [30-31]. Pushpadass et al. reported two  $T_{gs}$ and three  $T_m$ s for thermoplastic corn starch films (made of dried corn starch with moisture content readjusted to 20%, which was plasticized with glycerol at a ratio of 3/1, and a secondary plasticizer – stearic acid, urea, or sucrose – added), which were fabricated at 110 and 120 °C [30]. The authors concluded that the first melting temperature (61.3 to 76.6 °C) was related to swelling and relaxing of amorphous regions or to completed gelatinization of the partially melted starch granules left during extrusion, whereas the melting of amylopectin crystallites and swelling of double helices accounted for the second melting temperature (76.6 to 116.0 °C). Interestingly, the melting temperature at 112.5 to 133.0 °C was associated with the melting of amylose-lipid complexes that were formed during extrusion. Phase separation of thermoplastic starch due to separation of amylose and amylopectin or separation of plasticizer-rich and starchrich phases could account for the two  $T_{gs}$  (0.1 to 1.0 °C and 9.5 to 12.0 °C) of the extruded films.

### 2.4.5 Optical characteristics and the FTIR fingerprint

Transparency and opacity of polymers are directly related to polymer morphology [23]. They are determined by the ability of incident light that will be absorbed or scattered when passing through polymers. If polymers have a very low scattering power and a percentage of transmittance above 90%, they have transparency, and in turn, very low opacity. According to this rule, cast pea starch film was fairly transparent (83.6% transmittance at 600 nm). The film plasticized with glycerol at a ratio of 0.4 had slightly lower transmittance (79.2% at 600 nm), but had a similar transparency value (A<sub>600</sub>/mm) comparable to the neat film (1.25) [50]. However,

transparency values of cast pea starch films were very low compared to commercial traditional films, such as oriented polypropylene (OPP) (1.67), LDPE (3.05), and PVDC (4.58) [50].

Although transparency and opacity are not directly associated with chemical structure or molecular mass, Mali *et al.* investigated the relationships of starch film opacity to amylose content, molecular weight, and molecular structure of starch materials [23, 33]. Compared to corn starch and yam starch, cassava starch, which had the lowest amylose content and highest amylose molecular weight, exhibited the lowest opacity [33]. The authors attributed opacity of materials to amylose content, and molecular weight of amylose which the lower molecular weight of amylose the higher interaction of amylose chains, leading to higher film opacity. Addition of glycerol improved the transparency of cassava starch films.

To identify chemical compounds, FTIR spectroscopy is suggested as an effective tool and a widely used technique because it is a fast and highly accurate method and each compound has a specific fingerprint (IR absorption pattern) [51]. This technique can be applied to monitor and quantify the compound structure changes that may happen due to the presence of or changes in chemical interactions. However, different compounds containing certain functional groups will absorb at the same wavelength. Therefore, as hydroxyl-containing hydrocarbons, starch and plasticizers such as water and glycerol exhibit highly similar IR spectra (Table 2.3) [52]. Thus, chemical interaction between starch and plasticizer (hydrogen bonding) was observed from changes of IR spectra, such as band shifts and changes of peak shape (*e.g.* broadening, intensifying or weakening of peaks) [30, 53-57]. The stronger and more stable the hydrogen bonds between starch and plasticizer, the greater were shift of peaks to lower frequency (wavenumber) and the more changes of peak shape [30, 53].

24

Wavenumber, cm <sup>-1</sup>			Vibration mode	
Native starch	Glycerol	WTPS	GTPS	-
3500-3200	3400-3200	3500-3200	3500-3300	O-H stretching of free, intramolecular and intermolecular bound of hydroxyl group on water, glycerol, and starch molecules
3000-2800	2938, 2880-2860	2920-2850, 1740	2920	Symmetric and asymmetric C-H stretching of CH <sub>2</sub> on starch and glycerol molecules
1650-1628	1650-1630	1645		O-H bending of bound water in starch glycerol
1500-1200	1500-1200			Overlapping of C-H and C-OH bending
1160-1110	1158-1100		1150, 1124, 1106	C-O and C-C stretching
1084-1070 1047-1044	1085-1008		1084-1077 1047	C-O stretching of C-O-H and C-O-C Crystalline regions of starch
1022-1010			1022-1013	Amorphous regions of starch
995-991			1000-990	C-OH bending of OH at $C_6$ of anhydroglucose ring of starch
928				C-OH and CH <sub>2</sub> bending
915				C-O and C-C stretching (asymmetric of ring vibration)
		1200-800		C-O-C, C-O, C-O-H, C-C, and C-H

**Table 2.3** IR spectra of native starch, glycerol, and water or glycerol plasticized starch (WTPS or GTPS) [24, 30-31, 53, 55-56, 58-65]

Shi *et al.* investigated the changes in chemical structure of thermoplastic corn starch plasticized with glycerol during aging at 37 °C and 50  $\pm$  5% RH [56]. After plasticization and processing, peaks of thermoplastic corn starch at 3413 cm<sup>-1</sup> shifted downward to lower frequency with an increase of its peak height compared to native starch. The changes in the peaks were due to the increase in glycerol content which not only enhanced the interaction between hydroxyl groups but also disrupted hydrogen bonds between starch molecules. The peak at 1106 cm<sup>-1</sup> was more prominent while the peak at 2920 cm<sup>-1</sup> changed from a single peak

to double peaks due to the difference of O-H stretching between starch and glycerol molecules. With higher glycerol content, the peak at 1047 cm<sup>-1</sup> was reduced but the peaks at 1022 and 944 cm<sup>-1</sup> increased. These behaviors indicated the loss of crystalline regions and the increasing of amorphous regions and the water sensitivity of TPS material. During aging, the peak around 3413 cm<sup>-1</sup> broadened because of the reduction of interaction and phase separation between starch and glycerol.

Barone and Medynets monitored the amount of glycerol in the extrudates of thermoplastic levan polymers by using FTIR [52]. The peak at 1220 cm<sup>-1</sup> was used as an internal standard and its intensity identified in relation to glycerol concentration. By this means, the author reported no loss of glycerol during extrusion.

# 2.4.6 Rheological properties

The shear viscosity of TPS, which depends on the shear rate and polymer processing temperature, decreases as the shear rate increases (shear thinning, a non-Newtonian behavior) [66, 67]. In addition, in accordance with to its hydrophilic nature, the melt viscosity of TPS depends on moisture content. Willett *et al.* investigated the melt viscosity of thermoplastic corn starch pellets as a function of moisture content (15, 20, and 30%) and processing temperature (110 to 180 °C) using a Brabender PL 2000 torque rheometer for measurement [66]. As the processing temperature and moisture content increased, the thermal activation of melt flow and molecular weight degradation increased, resulting in decreasing the melt viscosity of the TPS. The melt viscosity behavior of TPS also became more Newtonian, the viscosity constant over the shear rate range. However, there was no significant temperature effect on the melt viscosity of TPS containing 15% MC. Under processing temperature at 160 °C and 10 to 1000 s<sup>-1</sup> shear rate,

the TPSs with 15 and 20% MC had melt viscosity in the range of around 9000 to 850 and 2800 to 280 Pa $\cdot$ s, respectively, while LDPE (MFI of 1.8 g $\cdot$ 10 min<sup>-1</sup> at 190 °C) exhibited a melt viscosity (around 6200 to 370 Pa $\cdot$ s) between these TPS values.

It is also known that high molecular weight increases melt viscosity due to increased polymer entanglement [23]. Thuwall *et al.* reported that the melt viscosity of high amylose thermoplastic potato starch (86% amylose) was approximately 36 times higher than that of normal thermoplastic potato starch (21% amylose) over the range of the measured shear rates (5 to  $2500 \text{ s}^{-1}$ ) [68]. The higher tendency of shear thinning behavior with higher molecular weight was not obtained in the capillary measurement.

Addition of plasticizers leads to lowering melt viscosity of TPS. Rodriguez-Gonzalez *et al.* and Huneault and Li examined the decreasing of the melt viscosity of thermoplastic wheat starch measured by an on-line rheometer [69, 70]. At a processing temperature of 150 °C and 130 s<sup>-1</sup> shear rate, TPS40 (comtaining 48% starch, 32% glycerol, and 20% water) had a relative melt viscosity 20% lower than that of TPS36 (48.5% starch, 27.5% glycerol, and 24% water) [69]. At a processing temperature of 180 °C and 10 to 200 s<sup>-1</sup>, TPS30 (containing 30 wt% glycerol) exhibited a melt viscosity around 50% higher than that of TPS36 at a constant shear rate [70].

#### 2.4.7 Biodegradability and compostability

The composting time of biodegradable materials as determined by the approximate duration in which materials were disintegrated into fractions < 10 mm (in final compost), based on intermediate levels of technology as observed in actively aerated and mechanically turned hall compost, was reviewed by Weber [35]. The rank of composting times of biodegradable materials

in the order of lowest to highest was TPS (less than a month), PHB/V, PCL, PLA, aliphatic (co)polyester, papers, polyester-amides, and wood (4 to 6 months) [35]. The biodegradability and compostability of materials depend on the environment (*e.g.* temperature, moisture, oxygen, and pH) and chemical properties of polymers (*e.g.* hydrolysable functional groups, degree of crystallinity, and molecular weight) [35, 71]. Since the first common step of biodegradation and composting is hydrolysis, the composting rate depends on water vapor transmittance and water resistance of materials, which affects diffusion of water through materials. The highly hydrophilic nature of TPS materials enhances hydrolysis, thus increases composting and biodegradation.

## 2.5 Drawbacks of TPS in packaging applications

The poor mechanical properties of TPS materials as well as their low processability resulting from high viscosities and poor melt properties limit their application in packaging areas [72]. Furthermore, the performance properties of TPS products are unstable during storage and use due to water sensitivity and relaxation and retrogradation behaviors. Increasing the water content of TPS materials due to the absorption of environmental humidity decreases its  $T_g$  and increases movement of the amorphous fractions. This behavior allows permeants to be soluble and diffuse through TPS materials; on the other hand, macromolecules may rearrange themselves to pack together in an orderly way. These phenomena alter  $T_g$ , mechanical and gas barrier properties of TPS materials during their shelf life [16, 38]. The hydrophilic natures of TPS molded products make them swell during exposure to heat and water. Distortion and shrinkage of TPS molded objects were observed when materials with high moisture content were processed [16, 73].

During storage, low molecular weight plasticizers, such as glycerol, can leach out from TPS materials [70, 74]. As mentioned, the recrystallization of TPS materials occurs at environmental temperatures above their  $T_g$ s. These phenomena affect product performance stability during storage and use since the brittleness (increase of tensile strength and decrease of elongation) and shrinkage of TPS materials increase [41]. Product performance instability of TPS materials was found even under controlled storage conditions and remarkably increased in high humidity conditions [75].

# 2.6 Current approaches for improving TPS performance properties

Several approaches have been applied to overcome the drawbacks of TPS properties (water sensitivity, poor mechanical properties, brittleness, and shrinkage). Correcting these problems can also improve mechanical properties, stability, and processability to meet packaging application requirements as well as retain biodegradability.

## 2.6.1 TPS composites

To obtain specific characteristics and properties, TPS is mixed with one or more distinct components, which differ in compositions or forms on a macroscale [76-77]. By this means, 'TPS composites' have synergistic properties, which could not be obtained by using each component separately [76-77]. Currently, two main types of materials, fibers (or microfibrils) and nanomaterials, are widely studied [78-79]

#### 2.6.1.1 Reinforcement with natural fibers

Addition of natural fibers in TPS materials increases the mechanical properties, such as tensile strength and modulus of elasticity, but decreases elongation [26, 80-81]. The similarity of chemical structures facilitates good adhesion and good compatibility between the starch matrix

and cellulose fibers. The hydrophilic nature and water sorption of reinforced TPS decreases due to addition of less hydrophilic materials (natural fibers) and glycerin which increases water uptake was absorbed by fibers [26].  $T_g$  of reinforced TPS increases due to the strong interaction of fibers and plasticizer, which reduces the segmental movement of starch chains [26, 82]. Ma *et al.* observed the increase of thermal stability of reinforced TPS which was because the fiber reduced a mass loss of plasticizer [81].

Reinforcement by cellulose fibers in thermoplastic wheat starch was investigated by Averous et al. [82]. The composites were formulated to obtain Young's modulus in the range of 700 to 900 MPa, which was suitable for making thermoformed trays. Trays (0.6 to 0.7 mm thickness) from composite materials, which had 730 MPa Young's modulus, 14.5 MPa maximum strength, and 4% strain at break were fabricated under lower thermoform temperature (78 °C) and time, compared to those using polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polypropylene (PP). However, there were small defects/deformations at angles and deep parts of composite trays due to a decrease in flow properties because of the high viscosity of the fibers. The brittleness of composite trays did not increase significantly during two months storage at room temperature. Teixeira et al. investigated properties of TPS film containing intrinsic fibers, cassava bagasse [83]. Films of thermoplastic cassava bagasse starch - 72.7% starch (containing 5% amylose), 17.3% fiber, and 10% moisture - showed a strong adhesion between starch and its fibers. Compared to films of thermoplastic cassava starch (TPCS) - 90% starch, (containing 18.2% amylose), 0% fiber and 10% moisture – films of thermoplastic cassava bagasse starch tended to recrystallize during aging due to its shorter chain amylose besides exhibiting low ductility and elongation, high fragility, and no significant difference in water absorption [83].

Gaspar *et al.* studied the effects of reinforcement by natural fibers (cellulose, zein, and hemicellulose) and blending of PCL with thermoplastic corn starch on reducing water absorption [84]. The composites were prepared from 70% corn starch and 30% glycerol added with 10 wt% natural fibers or blended with 10 wt% PCL. Zein/TPS composite and hemicellulose/TPS composite exhibited the highest tensile strength and highest Young's modulus, while cellulose/TPS composite and TPS/PCL blend showed the lowest of these properties. TPS had percentages of elongation (around 1.2%), of water uptake, and of enzymatic hydrolysis higher than all composites. The higher tensile strength and lower water uptake of zein/and hemicellulose/TPS composites were due to perfect compatibility of additives and amylose, which formed structures closely and excluded water.

Amounts of natural fiber used are limited to around 7 to 15% to obtain optimum mechanical properties and processability [80-81, 84]. With higher amounts of natural fibers (> 20%), fibers tend to agglomerate, dispersion of fibers in matrix decreases, starch degradation increases due to increasing of melt viscosity, especially in amylopectin fractions, and finally, reinforced TPS tends to recrystallize [21, 26,81]. However, the drawbacks can be minimized by using a wet state fiber, soaking fibers in wetting agents, such as epoxidized soybean oil and epoxidized fatty acids [21, 85]. The wetting agents served as compatibilizers to increase the compatibility between cellulose fibers and starch matrix and improve the melt flow rate of composites. Narayan *et al.* investigated shock absorbance and processability of thermoplastic starch ester, degree of substitution (DS) – the average number of substituted hydroxyl groups per anhydroglucose unit – at 2.1, reinforced with natural fibers [85]. The mechanical properties and processability of TPS composites were improved when cellulose microfibers (average length 75 to 750 microns, L/D ratios between 6 and 30) 20 to 30% in a wet state (wet in 1% to 10% by wt

of wetting agents, such as epoxidized soybean oil) were added. With 68% of starch acetate, 12% triacetin and 20% cellulose fiber, the composite had 6.0 kpsi tensile strength, 3.2% elongation at break, 420 kpsi tensile modulus, 10.4 kpsi flextural strength, and 0.24 ft<sup>-1</sup> Notched Izod impact strength. Those properties were comparable to general purpose PS.

### 2.6.1.2 TPS nanocomposites

Adding nanomaterials [fibers, particles, or platelets (layer)] into polymers could offer markedly enhanced physico-chemical properties for polymer nanocomposites compared to pure polymers and conventional (microscale) composites [86-88]. This advantage is because the dispersion of nanometer size offers an extremely high surface-to-volume ratio (750 m<sup>2</sup>·g<sup>-1</sup>) resulting in the creation of highly-reactive, stronger interchain forces between the nanomaterial and the polymer phases. In addition to the size of the nanomaterials, the properties of nanocomposites depend on the degree of mixing between the nanomaterial and the polymer matrix [87-89].

Montmorillonite (MMT) is a natural clay mineral that is widely used due to its availability and low price [88]. Five percent of Na-MMT increased tensile strength and elongation at break of thermoplastic corn starch (containing 30 wt% glycerol and 20 wt% water) around 20 and 30%, respectively compared to pristine TPS. With eight percent activated MMT, the tensile strength, Young's modulus, and tensile strain of thermoplastic corn starch plasticized by urea and ethanolamine increased by 270, 380, and 25%, respectively. In addition, activated MMT improved water resistance and thermal stability of the TPS composite. There was a report that clay-based compounds acted as processing aids by decreasing viscosity of TPS during

extrusion. It also prevented loss of plasticizer during aging, leading to improvement of TPS stability [90].

### 2.6.2 Chemical modification of starch

To decrease the hydrophilic nature of TPS, the chemical structure of starch needs to be modified. This happens through homogeneous chemical modification methods of which *chemical substitution* is the most preferable. The free hydroxyl groups of starch have been replaced or substituted by ester or ether groups to obtain *starch esters* or *ethers*, respectively. The hydrophobic nature can be easily altered through derivatization, and the degree of hydrophobicity depends on DS [66, 91-92].

Properties of modified thermoplastic starch esters were investigated by many authors. Jiang *et al.* reported that thermoplastic acetylated starch showed better thermoplasticity and processability due to  $T_g$  having been decreased [19]. Films were more transparent since associations of amylopectins at their outer branches were retarded. However, the rate of biodegradability of the films decreased. Wootthikanokkhan and Santikunakorn reported better compatibility of esterifed cassava starch blended with PCL due to the increase of interfacial adhesion [93]. Blomembergen and Narayan reported that starch esters prepared under anhydrous conditions at DS 1.2 to 1.7 provided the optimum balance in mechanical properties, water resistance, processibility, and rate of biodegradation while the starch esters at higher DS showed high crystallinity and did not biodegrade [94]. Narayan *et al.* stated that the major parameters in developing starch esters as biodegradable material are a high percentage of amylose (at least 50% although,  $\geq$  70% is more preferable) and DS of starch at 1.5 to 2.5 to maintain water resistance, biodegradability, and thermoplasticity [85]. However, plasticized or neat starch esters were brittle materials with poor mechanical properties; materials could be molded or extruded

into articles but did not meet requirements for commercial application. The addition of cellulose microfibers (L/D ratios between 6 and 30) up to 30% into starch acetates (DS 2.1) improved processability and provided better properties than general purpose PS.

Bien *et al.* investigated the properties of materials made of hydrophobic  $\alpha$ -hydroxy thermoplastic starch, which did not dissolve in water [92]. The ribbons of modified TPS were made by using a co-rotating TSE at 130 to 160 °C, without adding plasticizer. With molar substitution at 1.6, materials exhibited melt flow index (MFI) and modulus of elasticity in tension comparable to LDPE but they had lower elasticity. However, the water permeability and oxygen permeability of the materials were 500 and 40 times, respectively, higher than those of LDPE. Kim *et al.* reported that the modification of starch by hydroxyalkylation improved the flexibility and clarity of films [95]. The degree of crystallinity, water uptake, and  $T_g$  of films decreased with an increase of DS. Plantic Technologies Ltd. reported that hydroxypropylation of high amylose corn starch (more than 70% amylose) retarded retrogradation and recrystallization, and enhanced the thermoplastic behavior of modified plasticized starch [96].

However, this technique increases product cost due to integration of additional steps, such as material modification and product purification to remove a variety of undesirable and toxic by-products. The other limitations are changes of mechanical properties due to a reduction of modified TPS molecular weight, and inferior mechanical properties, which could not satisfy material application requirements [77, 90]

# 2.6.3 TPS-based multilayers

Multilayer materials where TPS is as an inside or center layer and waxes or hydrophobic biodegradable polyesters are outside or surface layers were introduced to improve moisture-resistance of starch based products [79, 90]. Multilayer materials can be produced by

compression molding, coating, or with a widely used technique – coextrusion [79]. However, due to a large difference in intrinsic viscosity among those materials, the critical defects of coextruded products, such as wavy interfaces because of the interfacial instabilities of two material phases, encapsulation (the entrapment of more viscous material by less viscous material), or non-uniform layer distribution, exist [79, 90]. The defects lead to low quality of the multilayer products [90].

#### 2.6.4 Polymer blends

Polymer blending is an important research area in polymer science since it offers advantages than developing new polymers, not only when time and cost-effectiveness are concerned, but also when desired properties cannot be easily obtained from new polymers [97-98]. The ability to combine existing polymers into new materials broadens the opportunity to improve their processability, develop finished product properties to meet specific applications, and/or reduce material cost.

## 2.6.4.1 Basic concepts

Generally, polymer blends can be categorized into two groups: miscible and immiscible blends [97].

The Gibbs, free energy of mixing of two polymers  $(\Delta G_m)$  is expressed as

$$\Delta G_m = \Delta H_m - T \Delta S_m \tag{1}$$

where  $\Delta H_m$  is the heat of mixing or the enthalpy of a system

*T* is the absolute temperature

 $\Delta S_m$  is the entropy of mixing which is related to the disorder of the system.

The entropy of mixing of two polymers is very small, so  $\Delta G_m$  can be approximated as

$$\Delta G_m \approx \Delta H_m$$

Similarly to processes or reactions that take place spontaneously, miscibility of polymer blends occurs when the heat of mixing is exothermic, leading to negative free energy of mixing (the system shifts to a lower free energy state) [97-98]. Miscibility of polymer blends does not usually happen; besides, some miscible blends are "metastable" where the level of miscibility depends on component fractions and temperature [98]. To obtain exothermic heating of mixing, strong attractive forces between polymers (ranging from strong covalent and ionic bonding to nonbonding weak interactions, such as hydrogen bonding, ion-dipole, dipole-dipole, and donoracceptor, etc.) are required [97-98]. The mixing in miscible polymer blends is considered when the molecular dimensional scale yielding of a single-phase material is achieved, resulting in the properties of a single phase material such as a single  $T_g$  [98]. Furthermore, the blend properties, especially the mechanical properties, are related to the composition-weighted average of the properties of each component. An important example of a commercial miscible polymer blend is poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and PS [98]. The property profile of the blends is intermediate between the composition-weighted averages over the entire composition range. An increase of PPO improves  $T_g$ , heat distortion temperature (HDT), impact resistance, and flammability resistance; and increases tensile properties [98].

In general, mixing two or more polymers that have differences in solubility parameters, cohesive energy density, polarity, molecular structure, or large differences in molecular weight, results in a positive heat of mixing (endothermic heat of mixing), leading to immiscibility or phase separation of polymer blends [23, 98]. However, the high viscosity of polymers hinders them in forming a complete separation. In fact, the polymer present in a small amount or having

high viscosity normally disperses in a matrix of the polymer present in a large amount or with low viscosity. Thus, most polymer blends are immiscible, which can be shown by multiple  $T_{gs}$ . The properties depend on the properties of individual polymers, and the morphology and interfacial properties of polymer blends [97]. If the interfacial tension of two polymer phases (the excess energy per unit area required to create the formation of an interfacial (surface) tension between polymer 1 and 2,  $\gamma_{12}$ ) is small (approaching zero) – the dispersion of one phase (polymer) in the other phase (polymer) is easy and feasible. Thus, it is possible to obtain a fine dispersion, a large interfacial thickness, and a strong interface and also provide good properties obtained from properties of each component [97-101]. This type of immiscible polymer blend is "compatible" [97, 99]. In contrast, if the interfacial tension of two polymer phases is high (*e.g.* 1.5 to 15 mJ·m<sup>-2</sup>), the size of the dispersed phase will be large, interfacial thickness will decrease, and the interface will be weak, leading to inferior properties [97, 99]. This immiscible polymer blend is "incompatible" [99].

Besides the interfacial tension, the work of adhesion between two polymers ( $W_{12}$ , the reversible work per unit of interface area required to separate two bulk phases) can be used to indicate the compatibility of the polymers [98, 101-102]:

$$W_{12} = \gamma_1 + \gamma_2 - \gamma_{12} \tag{2}$$

where  $\gamma_1$  and  $\gamma_2$  are the surface tension of polymer 1 and 2, respectively.

If the polymers have high affinity, the work adhesion will increase and the interfacial tension will decrease, leading to better compatibility; in turn, it also improves the performance properties of the polymer blend. A negative value of work adhesion indicates that the separation of the two polymers is dominant and will occur spontaneously, whereas the spreading coefficient  $(\lambda_{21})$  assesses the spreading of polymer 2 over polymer 1 [98, 101].

$$\lambda_{21} = \gamma_1 - \gamma_2 - \gamma_{12} \tag{3}$$

A positive value of spreading coefficient reveals the ability of polymer 2 to spread over polymer 1 and vice versa, whereas a negative spreading coefficient due to  $\gamma_{12} > |\gamma_1 - \gamma_2|$  indicates that there is no spreading between the two polymers [98]. The spreading concept can be applied to identify whether a third polymer can improve compatibility of polymer blends, where:

$$\lambda_{31} = \gamma_{12} - \gamma_{32} - \gamma_{13} \tag{4}$$

 $\gamma_{12}$ ,  $\gamma_{32}$ ,  $\gamma_{13}$  are the interfacial tensions of polymer between polymer 1 and 2, polymer 3 and 2, and polymer 1 and 3, respectively.

 $\lambda_{31}$  is the spreading coefficient of the polymer 3 over polymer 1

## 2.6.4.2 TPS/biodegradable polyester blends

For TPS, blending this hydrophilic polymer with hydrophobic biodegradable polyesters should have a high potential to not only to improve the properties and balance material cost to meet consumer needs, but also to meet a commercial production. Biodegradable polyesters should minimize inferior TPS properties, while TPS should improve biodegradability and processability, and reduce material cost of biodegradable polyesters [81, 84, 91, 103-104]. Furthermore, tailoring blend properties to meet specific applications should be achieved simultaneously. Examples of commercial biodegradable polyesters that may have potential to be used as a polymer pair with TPS to accomplish biodegradability-property-cost features are PHB, PHB/V, PLA, PCL, polyesteramide (PEA), PBSA, PHA, PBAT, poly(vinyl acetate-*co*-vinyl

alcohol) (PVAc/VA), polyglycolic acid (PGA), and polypropylene carbonate (PPC) [53, 8, 103, 105-106].

The two common techniques for blending natural polymers, such as starch, are solvent and melt mixing [78, 98]. The first technique is normally used when the amount of the polymers is limited, when polymers or compounds cannot be processed at high temperature due to thermal degradation, or when the phase behavior needs to be evaluated quickly. Types of solvent and solvent-removal conditions have strong impacts on phase behavior and phase boundary (immiscibility-miscibility) of polymer blends. Melt mixing is the technique that is emphasized in this review because it is an economical, practical, one-stage continuous, and solvent-free process; besides, products are in a ready-to-use form (compression molded or injection molded articles) or a ready-to-transform form (resins) [98, 107]. The disadvantage of this technique is that it may induce thermal degradation of polymer blends, leading to changes in their properties and performance. In addition, a polymer pair that has a large difference in melting temperature and viscosity may be difficult to process [107].

Averous and Fringant reported that blending of thermoplastic wheat starch with 10 to 40% PEA, PBSA, PBAT, or PCL decreased shrinkage and improved the dimensional stability of injection molded articles [106]. The PEA/TPS blend showed the lowest dimensional shrinkage. The hydrophobic nature of the injection molded articles increased even with blends containing 10% polyester, since polyester rich materials formed thin skin at the surface of the injection molded articles during the injection molding process. Even though the effect of blending on tensile properties was not really clear, it was shown that the PBAT/TPS and PEA/TPS blends had higher elongation than TPS, and PBSA/TPS, and PCL/TPS blends had the lowest elongation. The elongation of the blends correlated well with data from scanning electron microscopy

(SEM), which showed that thermoplastic wheat starch was more compatible with PBAT and PEA than with PBSA and PCL.

Sriroth and Sangseethong reported increasing water resistance and brittleness of PLA/TPCS sheets (500 µm thickness) when PLA content was increased [103]. The 50/50 (by wt) TPCS/PLA sheet, TPCS sheet, and PLA sheet exhibited tensile strength around 12, 3, and 65 MPa; elastic modulus around 8, 0.5, and 22 MPa; elongation at break around 5, 78, and 4%; and approximate water solubility of 10, 26, and 1%, respectively. Averous *et al.* reported that the brittleness of thermoformed trays made from thermoplastic wheat starch/PCL blend increased during a few weeks of storage at ambient conditions [82].

However, phase instability of the TPS/biodegradable polyesters after injection molding was reported. The migration of the polyester phase to the surface of articles with the TPS phase inside was due to a large difference in the viscosity of the molten polymers [90]. Kalambur and Rizvi claimed that the properties of TPS/polyester blends were significantly inferior and phase separation occurred when the amount of starch used was over 25% [108]. The results above also show that there are some beneficial properties obtained from immiscible TPS/polyester blends [91, 106]. As mentioned before, the inferior properties of thermodynamically immiscible blends are due to lack of interfacial adhesion at the interfaces. The unstable thermodynamics of immiscible blends causes phase instability [97]. This slowly happens when the mixing process stops: interfacial tension is only one driving force of the system, which promotes coalescence of the dispersed phase when there is proximity. To overcome these drawbacks "compatibilization" is needed.

## 2.7 Compatibilization

Compatibilization is the process or technique of modification of the morphology (representing the ultimate balance of the drop breakup and coalescence rates at the end of processes (*i.e.* mixing, fabrication)) and interfaces of immiscible polymer blends [97, 99]. In the melt mixing process, the particle size of a dispersed phase (*d*) is a direct function of the interfacial tension ( $\gamma_{12}$ ) and also the viscosity ratio (*p*) [98].

$$G\eta_m d / \gamma_{12} = \psi(p) \tag{5}$$

where G is shear rate

p is the ratio of  $\eta_d/\eta_m$  which are the viscosity of the dispersed phase and the matrix

phase, respectively

 $\psi(p)$  is a universal function of p

Thus, to minimize the particle size, and in turn, improve the dispersion, the interfacial tension should be small and the viscosity of polymer 1 should be similar to polymer 2 [98].

The degree of compatibility and the properties of immiscible polymer blends are improved via compatibilization due to the reduction of the interfacial tensions of the two immiscible phases. This generates smaller dispersed globules, increases the interfacial adhesion of two immiscible phases, stabilizes the morphology due to preventing the coalescence of disperse globules by steric stabilization (hindrance) effects, and facilitates the stress (energy) transfer between the two phases. The more the ability to transmit stress across the interface is (achieved from smaller globules and greater area of phase boundary), the better are the mechanical properties of the polymer blends [97-98, 107, 109].

According to Baker *et al.*, Robeson, and Utracki, there are many different means to categorize compatibilization strategies for immiscible polymer blends [97-98, 110]. In conclusion, there are two main approaches: non-reactive compatibilization and reactive compatibilization. The classical approach, non-reactive compatibilization, can be achieved by adding proper compatibilizing agents (compatibilizers) with good interfacial adhesion with both immiscible polymers and interfacial tension that will allow the compatibilizers to locate at the interfaces of the immiscible blends [97-98]. The compatibilizers commonly used are block or graft copolymers and low molecular weight coupling agents.

However, this approach is limited because specific agents that are required for particular immiscible polymer pairs may be unobtainable or costly [99]. A large amount of the agents may be needed to saturate the interfaces, leading to changes in the desired phase components [97-98]. Besides, the molecular weight and architecture of block copolymers must be considered. The lower the molecular weight, the higher is the ability to diffuse into interfaces. However, the ability to stabilize the morphology is weak [99]. A higher molecular weight of the block copolymer makes it an ineffective compatibilizer due to poor diffusion and a low critical micelle concentration.

The latter approach, reactive compatibilization or *in situ* compatibilization or reactive blending, is more attractive and cost-effective [97]. Under the *in situ* concept, block or graft copolymers (compatibilizers) can be generated through covalent or ionic bonding during the melt blending of reactive (functionalized) polymers. Thus, there are two chemical reactions involved in the one-step melt blending process: functionalization and interfacial reactions [97].

Functionalization is performed to create the reactive polymers. There are three main preparation methods for reactive compatibilization: polymerization through terminal, backbone, and side chain groups; copolymerization of monomers containing the desired reactive groups; and chemical modification of existing polymers using free radical grafting, substitution, terminal modification, *etc.* [97]. The first method is normally applied with polymers containing inherent reactive (functional) groups, such as condensation polymers (*e.g.* polycarbonate (PC), polyamides (PA)s, or polyesters), which contain reactive groups in the backbone and at the chain ends, and addition polymers (*e.g.* poly(acrylic acid), polyacrylates, PVAc), which contain reactive groups in their side chains. For the second and the last methods, functional groups, such as anhydride, hydroxyl, isocyanate, and epoxide must be added to generate the reactive polymers. Both methods can be applied to either condensation or addition polymers whereas grafting is mainly applied to addition polymers. Among these methods, grafting is the most practical and cost-effective and has been widely used [97].

In summary, functionalization by grafting is achieved by mixing the functional groups, such as maleic anhydride (MA) and suitable initiators, such as peroxide, with the non-reactive polymers, such as PP. MAs are grafted along PP chains. Consequently, the reactive polymer (PP grafted with MA, PP-g-MA) can form graft copolymer with another reactive polymer, for example: PP-g-MA/PA6 blend [97-99]. Another option is introducing a third reactive polymer, which is miscible with the non-reactive polymer of the immiscible polymer pair, to form graft copolymers with the reactive polymer of the immiscible polymer pair. If both polymers of the immiscible polymer pair contain only non-reactive groups (most hydrocarbon polymers), functionalization or reactivity of both polymers is required.

Once the *in situ* graft copolymers are formed, these reactive compatibilizers will perform their functions at interfaces of the immiscible blend phases similarly to non-reactive compatibilizers; except the reactive graft copolymers are generated directly at the interfaces of the immiscible polymer blends [97, 99]. Grafting reactions also increase the viscosity of the mixture or the level of stress when the deformation rate in the mixing machine is kept constant [99]. As a consequence, the particle sizes of the dispersed phased are significantly reduced, and the morphology of the compatibilized blends is more stable and predictable.

As far as cost-effectiveness, commercial scale-up, and practical process are concerned, or when there are limitations on processing in a batch reactor due to high viscosity or low solubility of chemical substances, reactive compatibilization of immiscible polymer blends by meltblending using an extruder as a continuous flow reactor (termed "reactive extrusion") is preferable [77, 97-98]. However, under the restrictive conditions of reactive extrusions (limited time frame, high temperature and shear force) the functional groups used have to be stable and exhibit fast kinetics under those circumstances [97, 99]. Currently, only a few types of chemical compatibilization reactions are feasible in reactive extrusion blending [97].

## 2.8 Reactive extrusion

Reactive extrusion is a one-stage continuous process that integrates a chemical process (*e.g.* polymerization, copolymerization, or chemical modification) and the extrusion process (including melting, blending, structuring, devolatilization, and shaping) and is performed in an extruder [77, 111]. It has been considered as one of the most practical and cost-effective methods for developing new polymer materials by tailoring existing polymers [77, 97]. It also offers benefits in terms of increasing the degree of mixing, reducing thermal degradation due to the shorter processing time, the ability to process materials with high viscosity, and feasibility for mass production. The economic savings due to a solvent-free and continuous one-stage process allow cost-competitiveness of new products. Finally, polymers are produced in a ready-to-use form.

The reactive extrusion process involves introducing reactive agents at optimum points in the reaction sequence, mixing, removing any volatile by-products, shaping or forming products, quenching, solidifying, and pelletizing products [77, 97]. By using reactive extrusion, the reactive blending can be performed in either a one-step or a two-step process. The first process combines functionalization and reactive compatibilization steps in one extruder. For two-step reactive blending, the reactive polymers are generated in one extruder, and then grafting copolymers and blending are performed in a second (final) extrusion step [97]. Whereas the one-step process (single pass extrusion) is more economical, the two-step process is easier to control [97, 99].

A TSE is normally used for reactive blending and polymerization, such as grafting [97]. It can be categorized by the rotational direction (co-rotating and counter-rotating) or intermeshing type (non-intermeshing and intermeshing) where intermeshing screws afford better mixing [23, 97]. Among these, intermeshed co-rotating TSEs are widely used for many continuous reactive extrusion processes [77, 97]. They provide high speeds, strong shearing forces, high outputs, and constant mixing. The other advantages of this type of extruder are the self-wiping effect (reducing material stagnation during processing) and a broad range of mixing capacity.

## 2.9 Compatibilized TPS/polyester blends

For starch-based blends, polyethylene glycol (PEG) is generally one of the agents used as a compatibilizer [104]. Ke and Sun studied the effects of PEG and various plasticizers on the thermal and mechanical properties of dried corn starch/PLA blends (40 to 60 wt%) [112]. Five to twenty-five percent of six plasticizers – two small molecular citrate esters: acetyl triethyl citrate (AC) and triethyl citrate (TC), two low molecular weight polyethers: PEG and polypropylene glycol (PPG), and two polyhydric alcohols: glycerol and sorbitol, were used and compared with the control group (blending without adding plasticizers). AC, TC, and PEG showed good miscibility with PLA, while sorbitol and especially glycerol exhibited good miscibility with starches because dried corn starch granules were completely destructurized. AC, TC, and PEG are highly efficient in decreasing  $T_g$  of the blends, whereas TC and AC are very effective in decreasing  $T_m$  of the blends. Sorbitol and PPG slightly affected the thermal properties of the blends. When the tensile properties were compared to the control tensile strength of 35.8 MPa, Young's modulus of 1.06 GPa, and elongation at break of 4.39%, almost all of the plasticized blends exhibited lower tensile strength and Young's modulus and higher elongation at break. Nonetheless, all the blends were brittle. The tensile strength, Young's modulus, and elongation at break were in a range of approximately 7 MPa (from 25% PEG or PPG) to 36 MPa (20 or 25% sorbitol), 200 MPa (25% AC) to 1.2 GPa (5% AC) and 3% (5% glycerol or PPG) to 17.5% (25% TC), respectively [112].

Noomhorm and Tokiwa reported that using 10 wt% low molecular weight polydioxolane (PDXL) could eliminate phase separation between PCL and TPCS [104]. The tensile strength and elongation of the blends decreased when TPCS content increased. With 50% TPCS, those two properties were around 4.5 MPa and 0%, respectively. Huneault and Li reported that among the reactive compatibilizers, such as maleic anhydride (MA), acrylic acid, oxazoline and glycedyl methacrylate, MA grafting is mostly used to reactivate non-reactive polymers due to its low toxicity and lack of homopolymerization under grafting conditions [70].

The important drawback of blending native TPS with polyesters is the degradation of the polyesters due to hydrolysis from the intrinsic moisture of native starch during blending at high temperature [25, 53, 70, 105]. Hydrolysis resulted in decreasing mechanical properties of the

blends. Wang *et al.* reported that at the ratio by weight of plasticizer to PLA and dried native corn starch (dried at 135 °C for 2 h) 40/140/100, formamide was slightly more effective than glycerol. The blend plasticized with formamide exhibited 31 MPa tensile strength and 4.2% elongation at break, whereas the blends plasticized with glycerol showed 21 MPa and 2.1%, respectively. However, the mechanical properties of the blends were not useful for applications [25]. Ma *et al.* stated that 1% succinic anhydride (SA) improved interfacial adhesion and decreased the residual dried corn starch granules in the TPS/PPC blends. Therefore, the thermal stability of the blends improved, and the storage modulus, mechanical properties and  $T_g$  of the blends increased. At a ratio of TPS/PPC 50/50, 1% of SA slightly increased tensile strength from 14 MPa to around 17 MPa and elongation at break from around 55 to 70% [53].

Another approach is blending biodegradable polyesters with modified starch. Bloembergen and Narayan investigated the properties of films made from starch esters blended with polyesters [94]. Blends of high amylose corn starch esters with PHB/V, triacetin and boron nitride at a ratio of 40/40/20/1 and blends of high amylose corn starch esters with PCL and triacetin at a ratio of 38/53/9 were cast-extruded into films. The films were translucent, flexible and moisture resistant. Wootthikanokkhan and Santikunakorn studied the effects of propionyl content on the properties of esterified cassava starch blended with PCL at a ratio of 30/70 wt% [93]. The water resistance of starch ester, the compatibility of starch ester with PCL, and the tensile strength of the blends increased with propionyl content. Esterified cassava starch/PCL blends had higher modulus than TPCS/PCL blends. Elongation at break and the rate of biodegradation of esterified cassava starch/PCL blends decreased with propionyl content. However, with 16% propionyl content, the blends showed the highest elongation at break, highest modulus, and tensile stress at yield (1024%, 134.5 MPa and 11.9 MPa, respectively), whereas the mechanical properties of TPCS/PCL blends were 1011%, 92 MPa and 7.8 MPa, respectively [93]. The authors claimed that an increase of tensile properties of the modified starch blends should be contributed to better compatibility of two immiscible phases. The tensile properties of the blends did not affected by thermal degradation of PCL since the number-average molecular weight of PCL in the blends did not decrease.

Narayan *et al.* investigated the physical properties of blown films made of native or chemically modified thermoplastic corn starch, using maleic acid modifier, and grafted with Ecoflex<sup>TM</sup> or cross-linked Ecoflex<sup>TM</sup>, using a free radical initiator, at a ratio of 30 to 70 (starch to polyester) [113]. All of the blends showed break elongation comparable to Ecoflex<sup>TM</sup>, but lower tensile strength and lower modulus. Chemically modified TPS/Ecoflex<sup>TM</sup> graft copolymer and chemically modified TPS/cross-linked Ecoflex<sup>TM</sup> had tensile strength comparable to LDPE. An addition of 4 wt% clay to chemically modified TPS/Ecoflex<sup>TM</sup> graft copolymer improved mechanical properties – tensile strength and break elongation – which were higher than those of LDPE.

## 2.10 PLA

As one of a few polymers produced from renewable resources, PLA is distinct from any commercially available biodegradable petroleum-based polyesters wherever ecosystem and environmental issues are concerned. In addition, the inherent properties of PLA, such as very low or no toxicity and high mechanical performance (comparable to those of conventional polymers) also provide the opportunity for PLA to be used in many applications, such as
packaging and fiber [22, 78]. In the USA, PLA was the largest produced biobased polymer in 2007 [114].

PLA is a linear aliphatic polyester (Figure 2.4). The monomeric unit of PLA is lactic acid, which exists in two main optical configurations (enantiomers): L or D. Lactic acid can be produced by chemical synthesis or mainly by carbohydrate fermentation from aerobic bacteria of the genus *Lactobacillus* [79, 115]. The second means (using carbohydrate sources derived from agriculture and food by-products, such as starch and sugar from corn, sugar beets, potato, and cassava) offers low cost production [22, 116]. Besides, by using specific bacterial strains, the ability to select and control the lactic acid enantiomers being produced is more preferable [42]. High molecular weight PLA (> 100 kDa) is produced by two distinct processes: step-growth (condensation) polymerization and ring-opening polymerization [3]. The first process is *condensation* of lactic acids, a chemical reaction in which small molecules, such as water or methanol are eliminated during the combination reaction of the monomers [23]. By this means, high molecular weight PLA can be produced either from combining low molecular weight PLA prepolymer (1 to 5 kDa) with chain coupling agents and adjuvants or from condensation with eliminating water by azeotropic distillation [3, 115].

Ring-opening polymerization is the most preferable process. NatureWorks LLC uses this process to produce a range of PLA via polymerization of low molecular weight PLA prepolymer, which is then catalytically depolymerized and converted into lactide under low pressure [3, 115, 117]. Lactide is the cyclic dimer of lactic acid existing in three forms; L,L-lactide, L,D-lactide, and D,D-lactide. Finally, after vacuum distillation, the purified lactide undergoes ring-opening polymerization into poly(L-lactide, D-lactide, or D,L-lactide) (PLLA, PDLA, and PDLLA,

respectively). PLA obtained by ring-opening polymerization had higher  $T_m$  (178 °C) than PLA produced by direct condenstation polymerization, which had  $T_m$  of 163 °C [22].



Poly(lactic acid)

**Figure 2.4** Chemical structure of lactide monomers (L,L-lactide, *Meso* or D,L-lactide and D,D-lactide) and poly(lactic acid)

Properties of PLA are significantly affected by the ratio of enantiomers of lactic acid monomer, L,L-lactide, *Meso* or L,D-lactide, and D,D-lactide [23, 74, 35, 115]. PDLA and PLLA homopolymers, high D-lactide copolymer, or high L-lactide copolymer with a D-lactic acid content of < 8% (*e.g.* PLA containing > 93% L-lactide) can be semicrystalline if they undergo a nucleation, annealing, or stretching process [42, 115, 118]. The integration of different lactide enantiomers decreases the degree of crystallinity; as a result, PDLLA is amorphous [3, 42, 115]. Auras *et al.* reported that PLA has  $T_g$ ,  $T_m$ , and  $T_d$  ranging from 50 to 80 °C, 130 to 180 °C, and 300 to 400 °C, respectively [115]. Selke reported that grease and oil resistance, and odor and flavor barrier properties of PLA are comparable to PET, whereas its gloss, clarity, thermal stability and processibility are comparable to PS [42].

The sealing temperature of PLA is lower than PE and PP. PLA film exhibits lower oxygen, carbon dioxide, and water vapor barrier properties than PET [116]. Compared to starchbased materials, PLA showed better moisture barrier but lower gas barrier properties [119]. PLA is a stiff and brittle material with high tensile strength, very high Young's modulus but very low elongation at break in a range of 44 to 66 MPa, 3.75 to 4.15 GPa and 4.0 to 7.0 %, respectively [115]. Tensile strength of PLA increases with L-lactide content [54, 103, 105]. As an aliphatic hydrophobic biobased polyester, PLA is an inherently biodegradable material. However, the degradation of PLA is mainly triggered by hydrolysis and affected by temperature. Therefore, the degradation may take several months after moisture catalyzes the degradation reaction, especially for unmodified PLA whose decomposing takes place after one year in seawater [42, 115].

Commercial PLA is copolymers of PLLA and PDLLA [120]. PLA properties can be improved or modified by changing the content and distribution of D, L, and D,L units by copolymerization [3]. Blends of PDLA and PLLA homopolymers showed better mechanical properties, better thermal stability, and higher hydrolysis resistance than those of each homopolymer [42, 78]. Generally Regarded as Safe (GRAS) status and a variety of PLA formulations make it suitable for many packaging applications [42, 74]. However, the low HDT of PLA (55 to 65 °C) limits its applications at high temperature, such as packaging for hot filled products [78, 116, 118]. The service temperatures of PLA at a range of -20 to 45 °C are preferable for packaging applications, such as cups for soft drinks, trays for fruit and vegetables,

and packages for refrigerated and frozen foods [118]. Besides, packaging applications of PLA are also limited by its poor flexibility, low strain at break, and high modulus [3, 121-122].

As a hygroscopic material, PLA is sensitive to air humidity [123]. If a small amount of water exists during melt processing of PLA, it leads to hydrolysis, resulting in a reduction in molecular weight of the polymer [116, 123]. As a result, the processing properties of polymers, such as melt viscosity and crystallization rate are changed which makes it very difficult to process and fulfill end product quality. To minimize this problem, PLA should be kept under conditions that are designed to minimize moisture uptake, such as < 50 °C, sealed container, and low humidity [116, 123-124]. In addition, PLA resins should have moisture content  $\leq$  250 ppm before melt processing to improve viscosity and PLA stability at high temperatures [124]. To prevent sticking, softening and blocking of polymers in the dryer, crystallized and amorphous PLAs should be dried at 65 to 90 °C and 43 to 55 °C, respectively [123]. If possible, any ingredients that may contribute moisture should be dried. Furthermore, melt processing temperatures of PLA should be  $\leq$  240 °C to avoid excessive thermal degradation leading to inferior properties and performance of end products [124].

Currently, the application of biodegradable plastics focuses on thermoformed products and biaxially-oriented film. Due to the low melt strength of PLA compared to conventional polymers; it is preferable to fabricate PLA film using cast film extrusion [124]. Fabrication of blown PLA film without using additives such as viscosity enhancers and slip additives is very difficult [116]. The instability of PLA at high temperature is also a drawback for film fabrication [22]. This problem can be solved by controlling the molecular composition of PLA and adding stabilizer or catalyst-deactivating agents. Semi-crystalline PLA containing <15 wt% D,L-lactide and the remaining weight percent of L-lactide is suitable for processing into films with desirable barrier properties [22]. However, due to the relatively slow nucleation and crystallization rates of PLA, the film ( $\leq 0.076$  mm or 0.003 in thickness) or sheet ( $\geq 0.25$  mm or 0.01 in thickness) becomes amorphous after the common quenching step [123]. Slow crystallization of PLA may happen during storage, leading to changes in its properties and performance. To improve product stability and also processability, rapid crystallization of PLA occurring within a few seconds is required [22]. Adding plasticizer (*e.g.* dioctyl adipate) and/or a nucleating agent (*e.g.* talc), drawing the film during or after film fabrication, and/or heat setting the film (holding constrained oriented film at temperatures above its  $T_g$ ) are effective tools to improve the slow nucleation and crystallization rates.

Plasticizers also play an important role in decreasing PLA's  $T_g$  and improving flexibility of films. Among biocompatible plasticizers (*e.g.* citrate esters, lactic acid monomer, glucose monoesters, partial fatty acid esters), PEG showed high efficiency for improving flexibility and impact resistance of PLA [121-122]. Nonetheless, as a hydrophilic polyether, PEG also increased the hydrolysis rate of PLA [22]. Furthermore, properties and performance of end products changed over time [122]. The other approaches to improve the low strain at break and high modulus of PLA are copolymerization of PLA with other monomers and blending PLA with other polymers [121-122]. Although a variety of mechanical properties can be obtained by using the first technique, cost-ineffectiveness of this technique is a limitation for packaging applications [122]. The latter technique, blending, offers moderate mechanical property improvement.

The high modulus of elasticity of PLA offers high stiffness and stability to thermoformed articles [118]. It also provides the ability to make PLA thermoformed packages with lower wall thicknesses and decreased weight. Furthermore, the thermal properties of PLA allow it to be thermoformed at lower temperatures (80 to 110 °C) compared to traditional thermoformed plastics: amorphous PET (100 to 120 °C), high impact PS (120 to 160 °C), and PP (150 to 165 °C). However, due to its lower thermal conductivity and  $T_g$ , the cooling step of PLA thermoformed articles in the mold is longer than for those traditional plastics [118, 120]. In addition, PLA sheet is very brittle. It can crack during trimming without preheating the sheet near 90 °C [120].

#### 2.11 Reactive blending of TPS/PLA blends

Due to the relatively high material cost and slow degradation (several months to 2 years) of PLA, blending granular starch or TPS with PLA is an effective method to improve biodegradability and cost-effectiveness and broaden packaging applications for short life, single use disposable packaging [54]. As products obtained from renewable resources and materials with reduced environmental impact, starch and PLA blends could be good candidates for biodegradable polymers [121]. Starch also offers flexibility and ductility to the blends [125]. Moreover, starch has a nucleating effect; it leads to enhancing the crystallization rate of PLA [22, 125].

Blending PLA with TPS could be more effective than blending with starch granules since granular starch reduces flowability, whereas TPS is easier to deform to smaller globules and disperse into another polymer [70, 126]. Li *et al.* reported that the better flowability of TPS in LDPE is obtained when glycerol content in TPS is greater than 28% based on total TPS weight [127]. Furthermore, a variety of properties of TPS/PLA blends can be designed by using modified TPS or TPS with various properties (*e.g.* degree of ductility) or by producing blends with different morphologies (TPS as a dispersed phase, co-continuous phase, or continuous phase in the blends) [70].

Blended PLA and TPS are immiscible due to the lack of affinity between hydroxyl and carboxyl end groups of hydrophobic PLA and the hydroxyl groups of hydrophilic TPS. The interfacial adhesion between the two phases is weak, so it leads to poor mechanical properties and brittle materials even when blended with a flexible and ductile TPS (modulus at 0.02 GPa and elongation at break 110%) as reported by Martin and Averous [128]. As mentioned earlier, the interfacial adhesion between two immiscible phases can be improved by using compatibilizers or coupling agents. For PLA/starch blends, compatibilizers containing amino, carboxylic, anhydride, or isocyanate groups could be used [3]. Those agents can react during extrusion to form block or graft copolymers and interact with functional groups of the polymers via reactive extrusion. Among compatibilizers, anhydride groups, such as those in MA and diethylmaleate (DEM) could be more effective in grafting [3, 70, 77, 129]. MA exhibits high reactivity, low toxicity, easy handling, and low potential to polymerize itself during free radical grafting conditions, while DEM exhibits better stability, a well-defined structure of its grafted groups, and also easy handling. To obtain desirable graft content with low degradation, parameters such as processing temperature, residence time, and monomer and initiator concentrations must be investigated and controlled [3, 129].

As mentioned above, the reactive blending can be performed in either a one-step or a two-step process. Wang *et al.* investigated characteristics of thermoplastic corn starch blended with PLA (molecular weight of 160 to 200 kDa and containing 12% D-isomer) in one-step reactive extrusion by using glycerol as the starch plasticizer, and MA with dicumyl peroxide (DCP) initiator as the compatibilizer and initiator [54]. Native corn starch was dried before blending to minimize hydrolysis of PLA and premixed with glycerol at a starch-to-glycerol ratio of 100/40. At 1% MA and 0.01% DCP (based on PLA content), the compatibility between the

two polymer phases increased, dispersion of TPS in PLA improved, and granule size of TPS decreased. Tensile properties of the blends, especially compatibilized blends, increased with PLA content. For example, PLA, thermoplastic dried corn starch, TPS/PLA (50/50) blend, and compatibilized TPS/PLA (50/50) blends showed tensile strength and elongation at break of around 36.2 MPa and 3.0%, 38.3 MPa and 1.8%, 13 MPa and 2.1%, and 40.5 MPa and 3.5%, respectively. However, all the materials were rigid and fragile with poor flexibility [54].

For two-step reactive blending, functionalization by grafting to generate reactive polymers can be performed onto TPS or PLA. Raquez et al. functionalized MA onto pearl corn starch [130]. Twenty percent of glycerol (by wt) was used as a starch plasticizer. Under the processing conditions (melting temperature at 153 °C, screw speed of 120 rpm, and residence time of around 7 min) the granular starch was completely disrupted. Increasing MA reduced the intrinsic viscosity and the recovery yield for the resulting maleated TPS (MTPS). The highest recovery yield for the resulting MTPS (96%) was obtained when 2.5 wt% MA (2.5MTPS; based on starch) was used. Compared to TPS (1.19 dL·g<sup>-1</sup>), 2.5MTPS had lower intrinsic viscosity  $(0.27 \text{ dL} \cdot \text{g}^{-1})$  due to reduction of its molecular weight via hydrolysis and glucosidation, reactions between the starch and the hydroxymethylene groups in glycerol. MA grafting enhanced these two reactions. The authors concluded that reduction of the melt viscosity could improve the processability of MTPS. In addition, the preferable esterification reaction of starch at the C<sub>6</sub> position with MA provided a free carboxylic group. It promoted an acid-catalyzed transesterification reaction of MTPS and biodegradable aliphatic-aromatic copolyester during melt-blending, thus improving interfacial adhesion between the two phases, and in turn, improving the properties of the immiscible blends.

Jang *et al.* studied thermal properties, morphology, and biodegradability of a compatibilized one-step PLA/TPS blend with MA as compatibilizer (PSMA), compatibilized two-step PLA/MTPS blends (PSMATPS), and PLA/starch blends (PS) [105]. Reactive blending increased the degree of crystallinity, decreased the reduction of PLA molecular weight, and improved the interfacial morphology and the biodegradability of compatiblized blends: PSMA and PSMATPS. At the ratio of PLA to starch or modified starch (70 to 30 wt%), PSMA, PSMATPS, and PS had a degree of crystallinity of 36, 14 to 24, and 9%, respectively, and the PLA molecular weight of these blends was 86, 122 to 126, and 66 kDa, respectively. PSMA showed good interfacial morphology without cavities at the interface between PLA and granular starch, and its biodegradability was also higher than that of PS.

Carlson *et al.* performed a free-radical-initiated grafting of MA onto PLA backbone by using reactive extrusion [131]. Lupersol 101 (L 101) was used as an initiator. The reactions were performed at 180 and 200 °C. The results showed that increasing reaction temperature increased the percentage of MA-grafted PLA and MFI, but decreased PLA molecular weight. With 2 wt% MA and 0.5% L 101 and by grafting at 180 °C, researchers obtained 0.653% maleation, 83.4 g·10 min<sup>-1</sup> of MFI, and 92.5 kDa of PLA. Those features obtained from grafting at 200 °C were 0.672%, 134.9 g·10 min<sup>-1</sup>, and 90.2 kDa, respectively, whereas pure PLA resins exhibited MFI of 12.8 g·10 min<sup>-1</sup> and molecular weight of 134.5 kDa. The onset and maximum decomposition temperatures of MA-grafted PLA (309 and 315 °C) obtained from grafting at 180 and 200 °C were similar, but slightly lower than those of pure PLA resins, which were 320 and 321 °C, respectively. Blending MA-grafted PLA with corn starch also improved the interfacial adhesion between the two phases.

Huneault and Li reported the properties of compatibilized thermoplastic wheat starch/PLA blends processed in a twin-screw extruder in the one-step process or two-step process [70]. Glycerol was used to plasticize the starch, and MA with peroxide initiator was used as a compatibilizer. With 36 to 39% glycerol content, 2% MA, 0.25% peroxide and 27 to 60% TPS in the blends, grafting and blending especially in the one-step process improved the interfacial adhesion between the two phases, increased the uniform dispersion of TPS into the PLA matrix, and decreased the size of the dispersed phase (TPS). Tensile strength, tensile modulus, and elongation at break decreased with TPS content while grafting did not affect tensile modulus but slightly increased tensile strength. However, grafting, especially in the twostep process, increased elongation at break from 5 to 200% (27% TPS/PLA) and from 10 to 180% (60% TPS) [70]. The crystallization rate of PLA in PLA/TPS blends was also investigated by Li and Huneault [125]. Compatibilized blends with 10 to 15 wt% TPS content were prepared from the two-step process, and 20 wt% MA-grafted PLA was used as compatibilizer [125]. After injection molding compatibilized blends and controls (uncompatibilized blends) into dog-bone specimens, specimens were kept for 4 weeks before investigating the crystallization behavior of PLA. The crystallization rate of PLA increased with TPS content and was enhanced when compatibilization was applied.

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# CHAPTER 3: PRODUCTION AND CHARACTERIZATION OF PHYSICOCHEMICAL PROPERTIES OF TPCS MATERIALS

## 3.1 Introduction

In this study, cassava starch (10.5 to 11.5% MC) was used without drying or adding extra water because a small amount of the natural and most effective plasticizer, water, is essential for facilitating the penetration of glycerol in starch molecules and completely plasticizing starch [1]. With higher water contents (> 16%), TPS films and sheets may not only present with bubbles but also enhance TPS brittleness during storage due to rapidly escaped water [2-3]. To reduce brittleness and thus improve processability of starch materials, glycerol (1,2,3-propanetriol) was used as the main plasticizer due to its high compatibility with starch, effectiveness, non-toxicity, low volatility (compared to water), biobased nature, and low cost [4-6]. The small molecular weight of glycerol (92.09 Da) facilitates it getting in between the starch chains, forming hydrogen bonding via hydroxyl groups, and acting as a lubricant to facilitate large-scale motion of starch molecules and interrupt intermolecular associations (hydrogen bondings) between starch chains [6-7]. Thus, the free volume, flexibility, and extensibility of starch materials increase, resulting in improving processability, and reducing processing temperature and thermal degradation of starch polymers. The properties and performance of starch materials and also their final products (e.g. mechanical properties, permeability, water absorption, rheology, and performance stability) strongly depend on glycerol content and can be modified accordingly [6-8].

The aim of this study was to determine the optimum ratio of cassava starch and glycerol content, which was appropriate to produce thermoplastic starch sheet and has a suitable fluidity for polymer blends.

#### **3.2** Experimental

#### 3.2.1 Materials

Tapioca starch containing 10.5 to 11.5% MC as determined by 31.1.03 air oven method from the Association of Official Analytical Chemists (AOAC) 1995 and  $25 \pm 6\%$  amylose content (Erawan Marketing LTD., Bangkok, Thailand) was used [9-10]. Glycerol 99+%, food grade (Aldrich Chemical Company, Inc, Milwaukee, WI) was used as the main plasticizer.

## 3.2.2 Extrusion conditions and ratio of components for compounding TPCS resins

TPCS was prepared by premixing cassava starch with glycerol at ratios of 50/50, 60/40, 70/30, 80/20, 85/15, and 90/10 wt%. The premixes were manually fed into a vertical mini corotating TSE (DSM Micro 15 compounder, DSM, Netherland), having a screw length of 150 mm, a length to diameter (L/D) ratio of 18, and a net capacity of 15 cc. The molten extrudates were shaped into disk and dumbbell specimens by using a mini injection molder (TS/-02 DSM), having maximum injection force of 150 psi. The process conditions were determined and the optimum ratio of starch and glycerol was selected for producing compounding TPCS resins by using a pilot-scale, co-rotating TSE (CENJURY ZSK-30 with a screw diameter of 30 mm and a L/D of 40) and pelletizer. TPCS resins were oven dried at 60 °C for two days before further processing or investigating.

#### 3.2.3 Characterization of TPCS resins

After compounding, the properties of TPCS resins were determined as follows, except for thermal properties and IR spectra, which were measured only for the resins containing the optimum ratio of components.

## Melt flow index (MFI)

A Ray-Ran melt Flow Indexer MK II Digital Model 2 A was used to investigate MFI at  $127 \pm 1 \text{ °C} \cdot 12.16 \text{ kg}^{-1}$  (modified from the American Society for Testing and Materials or ASTM D1238) [11].

## Thermal properties

Thermogravimetric analysis (TGA) was performed, and thermograms of TGA and derivative thermogravimetry (DTG) were recorded using a TGA 2950 (TA instruments, New Castle, DE) to identify the weight change of materials as a function of temperature. The samples in a platinum pan were heated from 23 to 600 °C at a heating rate of 10 °C·min<sup>-1</sup> under nitrogen flow.

The thermal transitions ( $T_g$ ,  $T_m$ , and cold crystallization temperature –  $T_{cc}$ ) and enthalpies of cold crystallization ( $\Delta H_{cc}$ ) and melting ( $\Delta H_m$ ) were determined using a Differential Scanning Calorimetry (DSC) Q100 (TA instruments) equipped with refrigerated cooling system (RCS). Samples were weighed accurately in hermetic aluminum pans. Recommend sample weights and methods were according to ASTM D3418 [12]. The heating rate was 10 °C·min<sup>-1</sup> between the range of -90 and 250 °C or as indicated.

## IR spectra

The IR spectra of cassava starch, glycerol, and TPCS resins were determined from wave number 4000 to 650 cm<sup>-1</sup> by using a Fourier Transform Infrared (FTIR) spectrometer, IR-Prestige 21 (Shimadzu Co., Columbia, MD) with an Attenuated Total Reflectance (ATR) attachment (PIKE Technologies, Madison, WI). The absorbance IR spectra were performed by using 40 scans at 4 cm<sup>-1</sup> resolution.

## 3.2.4 TPCS Sheet fabrication

TPCS sheets were fabricated by using a M CARVER compression molder (Carver Laboratory Press, Menomonee Falls, WI) and pilot-scale, single screw extruders (SSE): KL-100 KILLION blown and a KLB-100 cast film extruders (Killion Extruders, Inc., NJ).

## 3.2.5 Investigation of TPCS sheets

The following properties of sheets were characterized, except color, permeabilities, and water absorption, which were determined only for the sheets containing the optimum ratio of components.

#### Tensile properties

The tensile properties (tensile strength, elongation at break, and modulus of elasticity) of the sheets were investigated using an Instron Tensile Tester 5565 (Instron, Inc., Norwood, MA) following ASTM D882 [13]. Tensile properties of the 70/30 TPCS sheets were measured, using speed of 5.08 cm $\cdot$ min<sup>-1</sup> (2 in $\cdot$ min<sup>-1</sup>) and initial grip separation of 10.16 cm (4 in), while tensile

properties of the 65/35 TPCS sheet were determined at 5.08 cm (2 in, grip) and 50.8 cm  $\cdot$ min<sup>-1</sup> (20 in  $\cdot$ min<sup>-1</sup>, speed).

## Light transmission

A Lambda 25 UV/Vis Spectrophotometer (PerkinElmer, Wellesley, MA) was used to determine light transmission properties. Samples were measured in a range of ultraviolet (UV) and visible light (190 to 800 nm).

Color

The Commission Internationale de l'Eclairage (CIE)  $L^*a^*b$  system was used to measure the color of the sheets using a JY 9800 Integrating Reflectometer (TMI, NY).

## Permeabilities

Sheets were conditioned at 23 °C, 50% RH over 2 days. The oxygen and water vapor permeabilities were assessed at 23 °C, 75% RH using an oxygen permeation analyzer 8001 (Illinois Instruments Inc., IL) and a modified desiccant method (ASTM E96/E96M), respectively [14].

#### Water absorption

Specimens of TCPS sheets, 72.2 mm x 25.4 mm x 0.33 mm. (3 in x 1 in x 0.013 in), were dried in a vacuum oven at  $50 \pm 3$  °C for 24 h before testing for a two-hours immersion at  $23 \pm 1$  °C as indicated in ASTM D570 [15].

#### 3.2.6 Statistical analysis

Statistical Analysis System (SAS) version 9.1 (SAS institute, Cary, NC) was used for running the statistical correlations. Analysis of variance (ANOVA) and Tukey's test were used to determined significant differences.

#### **3.3** Results and discussion

#### **3.3.1** Extrusion conditions and component ratios of TPCS materials

Cassava starch and glycerol were weighed, premixed, and fed into a feeder manually; the extrudates were then introduced to an injection molder to form disc and dumbbell specimens. With the barrel temperature profiles of 100/110/115 °C, the lengths of time of 30 to 60 s, and the injection conditions of 110 to 120 °C at the highest pressure (150 psi), the processability of TPCS depended on the glycerol content. The results are shown in Table 3.1. With the highest glycerol content (50%), TPCS specimens were the clearest, most flexible and processable, but most shrinkable. With low glycerol content ( $\leq 20\%$ ), TPCS extrudates were stiff, which made it difficult to process in an injection molder. The smallest amount of glycerol (10%) was not effective enough to disrupt intermolecular bonds of starch and generate thermoplastic material. Increasing extrusion temperature to around 130-150 °C did not improve the processability of starch but enhanced its thermal degradation.

When cooled down at room temperature, all specimens presented shrinkage, which increased as glycerol content increased. These results correlated with Graaf *et al.*'s that the shrinkage of bar specimens made from various TPSs (wheat, pea, potato, and waxy maize) was dramatic in the injection direction since the orientation of the molecular chains during the injection process relaxed back to a normal configuration (helix) at low energy state [16]. The

higher glycerol content facilitated the faster realignment, relaxation and retrogradation of molecular chains, resulting in increased shrinkage of TPS materials [16]. In addition, the specimens with high starch content ( $\geq$  70%) turned to opaque when they were cooled, which could be attributed to recrystallization of amylose. Teixeira *et al.* reported that the degree of crystallinity ( $X_c$ ) of TPCS after storage decreased with glycerol content [17].

Ratio of starch to glycerol	Specimens	Characteristics
50/50	Complete specimens	Clear, gummy, shrinkable
60/40	Complete specimens	Semi-clear, shrinkable
70/30	Complete specimens	White opaque, shrinkable
80/20	Incomplete dumbbell	Light brown opaque, shrinkable
85/15	Extrudates could not be shaped into specimens	Light brown opaque
90/10	Extrudates could not be produced due to its thermal degradation	Caramel

Table 3.1 Characteristics of TPCS specimens at various ratios of starch and glycerol

Starch and glycerol at ratios between 80/20 and 60/40 were found not only to be processable in this study, but also to produce films or sheets by Pushpadass *et al.* [18]. These results are in accordance with Carvalho *et al.*'s that the optimum ranges of glycerol was 20-40% with starch containing intrinsic moisture content [19]. However, the high fluidity of TPS obtained from using at least 28% glycerol (based on total TPS weight) is crucial for controlling the TPS phase size in the blend [20]. Thus, ratios of starch to glycerol between 70/30 and 60/40 were selected for making compounding TPCS resins.

#### 3.3.2 Extrusion compounding and characteristics of TPCS resins

Cassava starch and glycerol were premixed manually in a plastic bag, kept overnight, and manually fed into a pilot-scale, TSE in which the barrel temperature profiles from feeder to die were 25/100/105/110/115/120/120/120/115/115 °C and motor speed 125 rpm. The 70/30 extrudates were cooled by air blowing, pelletized, and dried at 60 °C for two days before being fabricated into sheets or used to characterize the properties of the resin. The 65/35 extrudates were soft and sticky, and thus extra steps to produce the 65/35 resins were needed. After being cooled down by air blowing, the 65/35 extrudates were cut into long strands, dried at 60 °C for two days, pelletized and dried at 60 °C for one additional day. However, the 65/35 resins (Figure 3.1a) were weak and sticky, leading to clump formation and making them difficult to further process.

The 65/35 TPCS resins showed an MFI of  $15.87 \pm 2.34 \text{ g} \cdot 10 \text{ min}^{-1}$  at  $127.5 \pm 0.5 \text{ }^{\circ}\text{C} \cdot 12.16 \text{ kg}^{-1}$ , which was three times higher than that of the 70/30 TPCS resins (5.04 ± 0.41  $\text{g} \cdot 10 \text{ min}^{-1}$  at  $127 \pm 0.5 \text{ }^{\circ}\text{C} \cdot 12.16 \text{ kg}^{-1}$ .

## **3.3.3** Film formation and characterization

TPCS sheets were not processable by using cast or blown film extrusion. The sheets made of the 70/30 TPCS and processed by cast film extrusion at 132 to 133 °C and screw speed around 70 rpm were brittle and stiff with uneven thickness and surface (Figure 3.1b). Furthermore, the viscosity of the 65/35 TPCS resins was very high, resulting in increased high pressure that was over the pressure limit for the blown film extruder. Thus, TPCS sheets (Figure 3.1c) were made by compression molding in a sequence of preheating at 150 °C for 5 min,

compression at 150 °C and about 9,072 kg (20,000 lb) for 5 min and cooling. Sheets were placed on Teflon<sup>®</sup> plates and conditioned at  $23 \pm 2$  °C and  $50 \pm 5\%$  RH for two days before evaluating their properties. The 65/35 sheets were very sticky due to the leaching of glycerol during conditioning. Therefore, the 65/35 film properties were measured before and after 5-day conditioning when they were taken out from Teflon plates without deformation.



**Figure 3.1** TCPS materials: a) 65/35 TPCS resins; b) 70/30 TPCS sheets made from cast film extrusion at 132 to 133 °C; c) 70/30 TPCS sheets made from compression molding at 150 °C @ 9,027 kg.

The tensile properties of TPCS sheets were measured following ASTM D882 with a grip separation and rate of grip separation of 10.16 cm and 5.08 cm $\cdot$ min<sup>-1</sup> for the 70/30 TPCS sheets and 5.08 cm and 50.8 cm $\cdot$ min<sup>-1</sup> for the 65/35 TPCS sheets, respectively, in order to get initial strain rate of 0.5 and 10.0 mm $\cdot$ mm<sup>-1</sup> $\cdot$ min<sup>-1</sup>, respectively [13]. The results obtained are shown in Figure 3.2. Increased glycerol content decreased stiffness (decreased modulus of elasticity and tensile strength) and improved flexibility (increased elongation at break). It is known that the degree of crystallinity and the mobility of macromolecular chains in the amorphous region

account for the mechanical properties of starch films [5]. Increased glycerol content enhances the hydrogen bond interaction between starch and glycerol, resulting in increasing the free volume and movement of molecular chains, which then in turn increases film flexibility and softening film stiffness. Based on statistical analysis, an increase of glycerol content from 30 to 35 wt% did not significantly improve flexibility of TPCS, but retrogradation and relaxation, which occurred during storage, have strong effects on decreasing flexibility of TPCS ( $P \le 0.05$ ).

Compared with petroleum based polymers, such as PP, TPCS was categorized as a soft and weak material with low tensile strength and Young's modulus and moderate elongation [21]. Sriroth and Sangseethong observed that TPCS sheets (containing 65% cassava starch, 26% glycerol, and 9% water) with 0.5 mm thickness showed tensile strength, elongation, and modulus around 3 MPa, 78%, and 0.5 MPa, respectively [21]. The tensile properties of TPCS sheets in this work were also slightly softer than those of thermoplastic corn starch sheets (containing 30-40% glycerol), which were fabricated by compression molding and kept at  $23 \pm 2$  °C and 40% RH for 24 h. These properties were assessed to have tensile stress at break in the range of around 1.8 to 1.3 MPa, elongation at break of around 46%, and Young's modulus in the range of around 10 to 2 MPa [8].



**Figure 3.2** Tensile properties of TPCS sheets and PP [22] for comparison; 65/35 B and A were 65/35 TPCS before and after conditioning for 5 days @ 50% RH and 23 °C, respectively. Different letters above the bars indicate statistically significant differences at  $P \le 0.05$  (Tukey's test): a) Tensile strength; b) Elongation at break "For interpretation of the references to color in this and all other figures, the reader is referred to the electronic version of this dissertation"

During the 5-day conditioning in controlled environmental conditions, the brittleness of the 65/35 TPCS sheets tested in this work increased rapidly, as shown by highly decreased elongation at break (around 53%) but almost unchanged tensile strength (<1%) ( $P \le 0.05$ ). After 5-day conditioning at 50 ± 5 °C and 37% RH, the highest decrease in elongation at break (around 52%) of thermoplastic corn starch sheets containing 30% glycerol was also reported by Shi *et al.* [23]. The sheets in the Shi *et al*'s study were made of corn starch, which had 12% MC, and glycerol content ranging from 30 to 60 wt% (based on the total weight of the starch-waterglycerol systems), and the sheets were fabricated by compression molding. The brittleness of these sheets increased faster at the beginning of aging (5 days) and decreased with an increase of glycerol content. The authors attributed the TPS brittleness to crystallization of starch molecules during aging [23]. The rapid increasing of strength and stiffness of thermoplastic potato starch sheets within the first week of storage at 20 °C and  $61 \pm 5\%$  RH was also reported by van Soest and Knooren [24]. However, due to a very low degree of crystallinity during the first week of storage and even after long-term aging, the authors attributed the changes in tensile properties of TPS sheets to the formation of crystallinity and helical structures, as well as the relaxation, which was mainly from amylopectin.

Actually, the changes due to the molecular movement of polymers during storage associated with  $T_g$ , which are responsible for increasing the brittleness of TPS, can be divided into two types: the structural relaxation of glassy-state polymers and the retrogradation (recrystallization) of rubbery-state polymers [24-28]. The slow relaxation of the first group happened with the amorphous polymeric regions at temperature below  $T_g$  due to the excess specific volume, entropy, and enthalpy of amorphous material when cooled down below  $T_g$  [28-30]. The excess thermodynamic quantities will relax toward the thermodynamic equilibrium state via the rotation of internal polymeric main chains [27-29]. This relaxation phenomenon, which is enhanced with increasing temperature, is recognized as glassy-state volume and/or enthalpy relaxations, glassy-state structural relaxation, slow densification, or physical aging [27-29, 31].

Above  $T_g$ , the reorganization of macromolecules – retrogradation – is responsible for the aging behavior of the polymers at the rubbery-state, resulting in the development of crystallinity via the formation, aggregation, and crystallization of helical structures of amylose and/or amylopectin [24-26]. These phenomena are accelerated by increasing temperature and environmental humidity, and depend on the mobility of macromolecular chains and the type and

amount of plasticizers [25-26]. As a highly branched macromolecule, the crystallization of amylopectin is slower than that of amylose – a nearly linear macromolecule – which crystallizes within hours during storage [25]. In addition, the higher degree of polymerization of macromolecules (*e.g.* cassava and potato amylose starches) retarded their movement, and thus slowed the rate of crystallization [17].

Compared to water and sorbitol, glycerol reduced the crystallization rate of TPCS due to retarding the movement of amylopectin [24-25]. As reviewed by Ma and Yu, the stronger hydrogen bonds formed between starch and plasticizer reduced the mobility of starch chains, and in turn, slowed the crystallization of TPS [32]. Thus, crystallinity is prohibited in glycerol-rich phase, but with some migration of glycerol the crystallization rate of TPS can occur [25]. However, van Soest and Knooren observed that the crystallization rate of TPS increases with increased glycerol content [24]. They concluded that the higher glycerol content resulted in an increase of water uptake in the materials and the crystallization rate increased due to its higher water content. Further, research is needed to clarify this behavior.

The transmittance of TPCS sheets (Figure 3.3) decreased with starch content, especially the range of UV light, 100-400 nm. These results correlated well with Mali *et al.*'s, explaining that the opacity of starch films was attributed to the amylose content, and an increase of glycerol content improved film transparency [33]. Since a transparent material transmits more than 90% of light from around 330 to 800 nm, the TPCS sheets were seen not to be transparent (Figure 3.3). The light transmission of TPCS sheets in a range of visible light (400-700 nm) is quite close to that of OPP observed in Shiku *et al*, especially at higher wavelengths (> 600 nm) [34]. The lower transmission between 200 and 550 nm may be responsible to the difference opacity of the TPCS sheets. The TPCS sheets exhibited a higher ability to absorb UV light than that of OPP.

This attribute could be used to retard food deterioration, which is mainly affected by the UV-B (315-280 nm) [35]. During conditioning, the transmittance of sheets had a tendency to slightly decrease (<1%) in the range of visible light (400-700 nm).



**Figure 3.3** Percentage of transmission versus wavelength of TPCS sheets and OPP [34] for comparison

Because the 65/35 TPCS resins were difficult to process, and the fabricated sheets were very sticky and deformed easily, the 70/30 TPCS resins, which exhibited superior processability were selected as starch-based material for further studies. Additional characteristics of 70/30 TPCS resins and films were investigated.

## 3.3.4 Investigation of 70/30 TPCS resins and sheets

As hydroxyl-containing hydrocarbons, cassava starch and glycerol had highly similar IR spectra (Figure 3.4a-b). However, there were some peaks – the peaks at 1147 and 1076 cm<sup>-1</sup>, which are ascribed to C-O and C-C stretching – existing only in the cassava starch spectrum,
while the peaks at 1371 and 1211 cm<sup>-1</sup> (C-H and C-OH bending) as well as the peaks (assigned to C-O and C-C stretching) at 1107 (indicating secondary alcohol) and 1031 cm<sup>-1</sup> (indicating primary alcohol) were found only in the glycerol spectrum [36]. After compounding, 70/30 TCPS resins exhibited a wider variety of peak changes than the glycerol and cassava starch spectra, which indicates hydrogen bond interactions between starch and glycerol. The most changes found in the spectrum of 70/30 TPCS resins were a small shift of peaks either to higher or shorter wavenumber (peaks at 1408 cm<sup>-1</sup>), an intensified peak (1336 cm<sup>-1</sup>), and a shift of intensified peak (2924, 1365, 1149, 1103, 1078, 997, 925, and 850 cm<sup>-1</sup>).



**Figure 3.4** IR spectra of cassava starch, glycerol, and TPCS: a) At 3300-2700 cm<sup>-1</sup>; b) at 1800-800 cm<sup>-1</sup>



The intensified peak at 997 cm<sup>-1</sup> (intramolecular hydrogen bonding of the hydroxyl at  $C_6$ of starch) indicated the absorption of more water into starch molecules, which increases with increased glycerol content [18, 23, 37]. The shifted and integrated peak at 3282 cm<sup>-1</sup> indicated the increase of free, intra- and intermolecular-bound hydroxyl groups from water, glycerol, and starch [18, 36, 38-40]. As mentioned by Shi et al., this peak could represent the number of hydrogen bonds between hydroxyl groups that increased with an increase of glycerol content [23].

Besides the loss of glycerol peaks at 2879 and 1031 cm<sup>-1</sup> and the loss of the starch peak at 2889 cm<sup>-1</sup> (Figure 3.4a), the new peaks at 1735, 1238, 1205, and 1016 cm<sup>-1</sup> in this 70/30 TPCS resins emerged (Figure 3.4b). The peak at 1735 cm<sup>-1</sup> ascribed to aliphatic aldehyde 86

carbonyl was related to the yellowish color in TPS materials, which is resulted from the degradation of starch [3]. The double peaks at 1238 and 1205 cm<sup>-1</sup> (C-H and C-OH bending) came from a split of the glycerol peak at 1211 cm<sup>-1</sup>, which could indicate that glycerol forms hydrogen bonds with starch [18, 37, 41]. The existing peak at 1016 cm<sup>-1</sup> was attributed to an amorphous region in the starch matrix [23, 37]. The presence of this peak without the peak at 1047 cm<sup>-1</sup> (indicating a crystalline region in the starch matrix) could indicate that the 70/30 TPCS resins produced in this study were amorphous.

The DSC first-heating curve of 70/30 TPCS resins exhibited a broad endothermic peak above 79 °C (Figure 3.5a). In Mano *et al.*'s study, broad endothermic peaks of corn starch (in the range of room temperature to around 180 °C) and starch/polyester blends were attributed to its gelatinization (a disruption of starch granules and native starch crystallites) in which the enthalpy of gelatinization increased with moisture content [42-43]. As mentioned in Perry and Donald's study, gelatinization at very low water levels under high temperature is a melting process and exhibits a broad endothermic peak in DSC [43]. The addition of sugars and other polyols, such as glycerol, to starch-water systems does not change the gelatinization process (including plasticisation, molecular mobility, swelling, granule disruption, and crystalline melting) but requires higher thermal energy [43-44]. The higher the concentration and/or larger molecular weight of added solute, the more thermal energy input is required, demonstrated as an elevated gelatinization temperature.



Figure 3.5 DSC curves of 70/30 TPCS resins: a) the first heating; b) the second heating

Another assumption about the broad endothermic peak of TPS film found in the first DSC heating was related to melting of recrystallized material [45]. Forssell *et al.* investigated the broad endothermic peaks between 50 and 90 °C in the first DSC heating of thermoplastic barley starch films containing 22-28% water and 20-39% glycerol [45]. The authors ascribed broad peaks to the crystallite melting of recrystallized amylopectins due to the similarity of melting enthalpies found in their study (7-9  $J \cdot g^{-1}$  of dry starch) and amylopectin crystallites in normal starch gels [45]. This assumption is in contrast with theory that recrystallization of amylopectin is a slow process due to its highly branched structure. Recrystallization of amylose and high-amylose starch films can be detected with 1-2 weeks of storage, but it will take more than a month to develop detectable crystallinity in low-amylose starch films [5].

In addition, as mentioned by Mano *et al.*, a broad endothermic peak could be assigned to water absorption above room temperature that occurred during heating, and the enthalpy increased with water content [42]. Mano *et al.* reported a good correlation of this hypothesis to water evaporation above room temperature found in their TGA result, which is also found in this study (mentioned later in the TGA and DTG results).

The DSC second-heating of 70/30 TPCS resins in this study (Figure 3.5b) exhibited only  $T_g$ . The presence of two  $T_g$ s indicated phase separation in the TPCS material [23, 46-47]. Forssell *et al.* reported that the glass transitions of TPS materials are always found at specific temperature ranges, which are in the range of -98 to -38 °C (lower transition) and -14 to 145 °C (upper transition). In this study, the lower  $T_g$  ( $T_{gL}$ ) was around -51 °C – representing the glycerol-rich phase – and the upper  $T_g$  ( $T_{gU}$ ) was 65 °C, characterizing the starch-rich phase. According to the work done by Souza and Andrade, the glass transitions of starch-water-glycerol mixtures could be monophasic or biphasic, depending on the total amount of plasticizers [47]. With a high glycerol content ( $\geq 20\%$ ), TPS exhibited a biphasic  $T_g$ , and increasing glycerol content decreased the  $T_g$  of the glycerol-rich phase [23, 47].

TGA is normally used to characterize the thermal stability of compounds over test conditions [45, 48]. TGA cassava starch in this study was similar to that of other starches, presenting a two-step weight loss (Figure 3.6a). The first-step weight loss occurred from room temperature up to around 144 °C due to evaporation of water from water desorption and water bounded with starch hydroxyls via inter- and intra-molecular condensations [42, 49-51]. The second step of decomposition having onset and end-decomposition temperatures of 315 to 357 °C was attributed to thermal degradation of starch (*e.g.* elimination of polyhydroxyl groups, depolymerization and decomposition), leading to carbonization and ash formation (12.5% at 600 °C) [49, 51-54]. Additional information about compound degradation was obtained by investigating DTG thermograms as shown in Figure 3.6b. The maximum rate of water desorption was at 60 °C; while the maximum thermal degradation rate of starch occurred in two stages. The peak found around 298 °C could be due to the degradation of amylose due to its linear structure, and the maximum degradation rate of starch present at 334 °C was attributed to the decomposition of amylopectin [42, 51].



Figure 3.6 TGA and DTG thermograms of glycerol, cassava starch, and 70/30 TPCS resin: a) TGA thermogram; b) DTG thermogram

The one-step degradation of glycerol presented onset, maximum, and end decompositions around 217, 269, and 283 °C, respectively [Figure 3.6a-b]. The 70/30 TPCS resins exhibited a complex and changes of TGA and DTG curves after the compounding of starch and glycerol – probably indicating new interactions between water and glycerol, water and starch, and glycerol and starch. The first shift of weight change, from room temperature up to 161°C, was mainly due to water desorption and evaporation of water bound with starch and glycerol. The second shift of weight loss between 161 and 296 °C could be attributed to the volatilization of glycerol [42]. However, the maximum decomposition of glycerol in the 70/30 TPCS resins was not observed in this study; whereas Cyras *et al.* reported that DTG curves of glycerol from pure glycerol and cast thermoplastic potato starch films (containing glycerol 32 to 50%) presented as one peak around 200 °C [54]. The onset decomposition of starch (296 °C) in the 70/30 TPCS resins, observed in this study, occurred at lower temperature compared to native cassava starch (315 °C).

This result is well correlated with Cyras *et al's* study [54]. The authors explained that the presence of glycerol and the lower relative crystallinity of TPS films compared to native potato starch make the starch chains easier to disrupt, resulting in lower starch decomposition temperature [54]. However, starch resins in this study also exhibited a little longer thermal stability (presenting end decomposition temperature at 363 °C) compared to native cassava starch (357 °C). TPCS resins yielded 6.7% of residue determined at 600 °C. Compared to native cassava starch, the DTG thermogram of TPCS resin presented at higher temperature with three distinct peaks [Figure 3.6b]. The first peak was the maximum decomposition of bound water and easily volatile compounds (around 152 °C) [49-50]. The peaks at around 308 and 344 °C may be associated with decompositions of amylose and amylopectin, respectively, as defined by Thire *et al.* [51]. Another hypothesis about the overlapping DTG peaks found in starch films was

proposed by García *et al.*[55]. They attributed the DTG peak of cast TPCS film at 241 °C to the maximum decomposition of the glycerol-rich phase and another peak at 291 °C to the maximum decomposition of the starch-rich phase [55].

To characterize the color of 70/30 TPCS sheet perceived by human eyes (in visible light), one of the most commonly used systems – CIE 1976 L\*a\*b (CIELAB) – was applied. The color scales of CIELAB are based on the opponent-color theory, where L\* is the lightness ranging from 0 or black (indicating no reflection of light) to 100 or white (representing perfect reflection), and a\* is the axis extending from negative (green) to positive (red) [56-58]. The last axis, b\*, indicates from blue (negative) to yellow (positive), while the delta values of L\*, a\*, and b\* present the difference between the standard and the sample. According to this concept, the 70/30 TPCS sheet exhibited a high reflection and the combination of a very low redness with a light yellowness (Table 3.2). The delta values of the TPCS sheet compared to the white standard are also shown in the following table.

	L*	a*	b*	$\Delta L^*$	∆a*	$\Delta \mathbf{b}^{*}$
70/30 TPCS sheet	83.21	1.17	9.52	9.25	1.43	7.47

The water and oxygen permeabilities of 70/30 TPCS sheets in this study had to be performed under high RH because the oxygen permeability (OP) values of the TPCS sheets below 75% RH were very low, well below the capacity of the instrument to detect. Under this test condition (23°C, 75% RH), the 70/30 TPCS sheets exhibited OP of 7.3  $\pm$  0.2 x 10<sup>-18</sup> kg·m·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>, which is in the range of medium OP (2.9 x 10<sup>-20</sup> to 9.3 x 10<sup>-18</sup>

kg·m·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>) in Weber's report [59]. Weber also reported that among the polymeric materials having medium OP (TPS, nylon 6, and PLA) under the test condition at 23 °C and 50% RH, TPS showed the lowest OP, while PLA had the highest OP. Compared with TPS in Weber's study, the higher OP of 70/30 TPCS sheets in this study could be attributed to the higher RH of the test condition. As a hydrophilic polymer, the free hydroxyl groups of starch and glycerol promoted water absorption from the environment, especially at high relative humidities (> 70% RH) [60]. This behavior results in a decrease of  $T_g$  of polymers, thus facilitating macromolecular chain movement and increasing the free volume of the amorphous regions in the starch matrix, which makes it easier for non-polar gases, such as oxygen, to permeate through TPS materials.

As reported by Forssell *et al.* and Arvanitoyannis *et al.*, the permeability and/or diffusion of oxygen, nitrogen, and carbon dioxide gases increased as a function of water content in TPS materials [60-61]. Under dry conditions (20 °C and 50% RH), starch films exhibited OP close to that of EVOH films, but the good barrier property of those films is lost in films having high water content (> 20% MC) [60].

As expected the 70/30 TPCS sheets in this study presented high water vapor permeability  $(WVP) - 3.1 \pm 0.2 \times 10^{-13} \text{ kg} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$  – compared to commercial films such as Ingeo<sup>TM</sup> Biopolymer (PLA) 4032D, PET, and PS – 1.1 x 10<sup>-14</sup>, 1.1 ± 0.1 x 10<sup>-15</sup> (at 25 °C in the 40-90% RH), and 6.7 x 10<sup>-15</sup> (at 25 °C) kg·m·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>, respectively) [35, 62]. According to the rule *like dissolves like*, polar vapors, such as water vapor, easily dissolve in and diffuse through TPS materials, which are further enhanced by the increase of hydrophilic plasticizer content and/or environmental humidity [18, 33]. These TPCS sheets had better water barrier than the TPS films

in Pushpadass *et al.* [18]. Those TPS films made from thermoplastic corn starch (comprised of corn starch having 20% MC, 25 wt% glycerol as a main plasticizer, and 0.25-10 wt% urea, stearic acid, or sucrose as a second plasticizer) exhibited WVP in a range of  $3.0-5.5 \times 10^{-12} \text{ kg} \cdot \text{m} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \cdot \text{Pa}^{-1}$  [18].

The 70/30 TPCS sheets also exhibited a very high rate of water absorption. After 10 minutes of immersion, sheets turned to opaque with white color, soft, and disintegrated, leading to failure in measuring the percentage of water absorption. This behavior was attributed to the higher number of available hydroxyl groups in starch and glycerol, which allows them to form hydrogen bonds and absorb more water [17]. The behavior of extruded TPCS strands during water exposure was also reported by Sriroth and Sangseethong [22]. After immersion of TPCS strands (containing 65% cassava starch, 26% glycerol, and 9% water) in water for 10 hours, the strands were swollen with leaching out of some materials into the water.

# 3.4 Conclusions

The processability and properties of thermoplastic cassava starch significantly depended on the amounts of glycerol used; the higher the glycerol content; the softer and stickier were the materials obtained. The optimum ratio of cassava starch and glycerol for polymer blending was selected as 70/30 by weight.

TPCS resin (70/30 w/w) was an amorphous material having phase separation into starch and glycerol rich phases. The thermal stability of TPCS resins decreased with addition of glycerol, but the  $T_{max}$ s of amylose and amylopectin in the TPCS materials increased, indicating chemical interactions between starch and glycerol, which also observed from FTIR spectra. The high viscosity limited sheet fabrication by extrusion. Produced TPCS (70/30 w/w) was a soft and weak material, since TPCS sheets made by compression molding exhibited low tensile strength and modulus with a moderate elongation at break. TPCS sheets showed a high reflection, the combination of a very low redness and a light yellowness, light transmission of 80 to 88% with ability to absorb UV light, a medium level of oxygen permeability, a high level of water vapor permeability, and a high rate of water absorption.

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## 4.1 Introduction

Blending of polymers is an important technique to improve their properties and develop new polymers whenever time and cost-effectiveness are considered. The final properties of polymer blends are related to the compatibility between polymers pair, which is controlled by the interfacial tension of the polymers [1]. Thus, values of interfacial tension are normally used to predict the compatibility, morphology, and final-state physical and mechanical properties of the blends.

Determination of the interfacial tension of polymers and polymer blends can be obtained from estimation from theory-based equations or performed by using direct or indirect measurements [1-2]. A requirement of direct measurement techniques is that molten polymers have to maintain a constant low viscosity during an entire test condition, which makes the techniques inappropriate to assess starch blends because the viscosities of starch blends vary with their moisture/plasticizer contents [1].

The use of lattice theory to derive and estimate interfacial tensions of polymer blends as a function of temperature is also limited due to lack of available data for some parameters (lattice and Flory–Huggins binary interaction parameters) [2]. Thus, the estimation of interfacial tensions of polymer blends is normally derived from indirect measurements performed at ambient temperature [2]. The interfacial tensions at a required temperature are obtained from correcting or extrapolating the estimated interfacial tensions at ambient temperature. Generally,

the estimation of interfacial tensions of polymer blends is based on two properties, solubility parameters or surface energies of polymers, of which the latter is widely used [2].

The surface energies of polymers are calculated from contact angles between solid (polymers) and *liquid* (test solvents) by using equations such as the Antonoff's rule, the geometric mean (GM), the harmonic mean (HM), and/or van Oss, Chaudhury, and Good (VCG) approaches [1-6]. The chemical characteristics of liquids (*i.e.* polar, nonpolar, Lifschitz-van der Waals (LW), and/or acidic and basic components) are important and significant properties of to obtain and validate the surface tension of polymers [5, 7]. To determine the surface energies of polymers and polymer blends via the VCG approach, contact angle measurements for three liquids (two polar and one nonpolar) are needed, while the other approaches require the use of two liquids (one polar and one nonpolar) [1, 3, 5]. Hence, the VCG approach, in which total surface energy is an addition of the Lifshitz-van der Waals surface energy component and the acid/base surface energy component (calculated from the electron acceptor/donor or hydrogenbond donor/acceptor properties), seems to be appropriate to provide adequate information about surface polar components [6, 8]. Currently, there are no other approaches that work better with polar polymers than the VCG approach [6, 8]. However, the lack of data and some criticisms, such as overestimation of the basicity of polymers, mentioned in previous studies somewhat limit the use of the VCG approach compared to the GM or HM [5-6, 8-9].

The most widely used approaches – GM and HM – for estimating the interfacial tension of polymer blends, derive the surface energies of polymers and polymer blends as the sum of dispersive (nonpolar) and non-dispersive (polar) surface energy components, where the polar component includes dipole, induction, and hydrogen bonding energies [1-2, 10]. These approaches are widely applied to polymers having a significant polar surface energy component

even though there are some criticisms, such as the derivation of the polar component, as mentioned in previous studies [1, 4-5, 11]. These semiempirical methods, GM and HM, are practical methods and provide reasonable values of surface energies and interfacial tensions, correlating well with other methods [4].

Overall, the values of the dispersion component obtained from the two methods (HM and GM) are slightly different; while the values of the polar component are lower when obtained with GM than when obtained with HM [4]. Wu has recommended that HM is suitable to predict the surface energy from contact angle measurement and then to predict the interfacial tension between low-energy materials (*e.g.* polymers, organic liquids, and water), while GM works well in estimating the interfacial tension between low-energy materials (*e.g.* polymers, organic liquids, and high-energy materials (*e.g.* mercury, silica, and metal oxides) [10].

In this study, the static contact angle measurements of flat dried polymeric resins were performed by using the two probe-liquid method. One of the best pair of solvents with different polarity – distilled water (polar) and methylene iodide (nonhydrogen bonding) – as mentioned by Wu, was used [3]. A traditional technique – static contact angle measurement – was selected, because it provides both dispersive and nondispersive components of surface energies from the same measurement and from the same polymeric surface; while the advancing and receding contact angles correspond to dispersive and nondispersive components, respectively [6]. Thus, the value obtained from static contact angle measurement is an intermediate between the values obtained from the advancing and receding contact angle measurements, which makes the static contact angle more appropriate to identify the actual characteristic of surface energies [6].

Furthermore, the surface energies of 70/30 TPCS and PLA resins were determined by using the HM method; and values of work adhesion, interfacial tension, and spreading coefficient of

the blends were calculated. The properties of blend resins and sheets such as morphology, thermal properties were investigated to understand the characteristics of physical or non-reactive TPCS/PLA blends.

# 4.2 Experimental

#### 4.2.1 Materials

In-house produced 70/30TPCS (TPCS), previously explained in chapter 3, and PLA 2002D (PLA) (NatureWorks LLC, Blair, NE) were used as a polymer pair. Properties of each polymer are shown in Table 4.1. Methylene iodide (Sigma-aldrich, Milwaukee, WI) was used to determine surface energy. Tetrahydrofuran (THF) (Pharmco-Aaper, Shelbyille, KY) and Polystyrene Shodex STD KIT SM 105 (Showa denko, Japan) were used to determine PLA molecular weight.

	TPCS	PLA	Method
Moisture content*,	$7.15 \pm 0.13$	$0.16\pm0.01$	Vacdried 70 °C (17 h),
%			or AOAC 925.09 [12]
<i>T<sub>g</sub></i> **, °C	$-46.9 \pm 0.3,$ $61.4 \pm 1.4$	$60.1 \pm 0.5$	ASTM D3418 [13]
$T_m^{**, \circ}C$	-	$151.5 \pm 0.4$	ASTM D3418 [13]
Crystallinity**, %	-	$35.10\pm0.02$	ASTM D3418 [13]
<i>T</i> <sub><i>d</i></sub> , °C	296-363	362-412	
(from onset to end) Molecular weight, kDa	-	$163.3 \pm 0.7$	
MFI***, g·10 min <sup>-1</sup>	$5.04 \pm 0.41$	$7.48 \pm 0.41$	ASTM D1238 [14]
Tensile strength, MPa	$0.45\pm0.05$	60****	ASTM D882 [15]
Modulus of	$1.24 \pm 0.58$	3,500****	ASTM D882 [15]
Elongation at break,	83.02 ± 18.55	6.0****	ASTM D882 [15]
OVP,	$7.3 \pm 0.2 \ge 10^{-18}$	-	
kg·m·m <sup>-2</sup> ·s <sup>-1</sup> ·Pa <sup>-1</sup>	@23 °C, 75% RH		
WVP, $-2 -1 -1$	$3.1 \pm 0.2 \times 10^{-13}$	-	ASTM E96/E96M [16]
kg·m·m ·s ·Pa	(a)23 °C, 75% RH	1 10	

Table 4.1 Properties of TPCS and PLA resin and sheet

Note: \*Moisture contents of TPCS and PLA were determined from vacuum dried oven at 70 °C and AOAC 925.09 methods, respectively.

\*\*  $T_g$  was investigated from the second DSC heating, whereas  $T_m$  and crystallinity were investigated from the first DSC heating.

\*\*\*MFI values of TPCS and PLA were determined at  $127 \pm 0.5 \text{ °C} \cdot 12.16 \text{ kg}^{-1}$  and  $210 \pm 0.1 \text{ °C} \cdot 12.16 \text{ kg}^{-1}$ , respectively.

\*\*\*\* Values reported from NatureWorks LLC [17]

#### 4.2.2 Extrusion conditions for a physical blend of TPCS/PLA

TPCS resins were oven dried at 60 °C for 2 days and PLA 2002D resins were vacuum dried at 90 °C for 2 h according to NatureWorks LLC recommendation [17] to reduce hydrolysis of PLA during melt blending. The moisture content of TPCS (%) and PLA resins after drying, which were quantified according to AOAC 925.09, were  $1.57 \pm 0.73$  and  $0.07 \pm 0.01\%$ , respectively [12]. Resins were premixed together at three weight ratios of TPCS and PLA (70/30, 50/50 and 30/70), then melt blended and shaped into dumbbell specimens by using a vertical mini co-rotating TSE (DSM Micro 15 compounder), attached with a mini injection molder (TS/-02 DSM). The optimum ratios of TPCS/PLA blends were selected for upscale production using a pilot-scale, co-rotating TSE (CENJURY ZSK-30) – the details of a DSM Micro 15, a mini injection molder, and a CENJURY ZSK-30 were mentioned in Chapter 3. Different ratios of TPCS/PLA blend resins were produced and their properties were investigated as follows.

# 4.2.3 Characterization of TPCS/PLA resins

#### Surface properties

The TPCS and blend resins were oven dried at 60 °C for 2 days, while PLA resins were vacuum dried at 90 °C for 2 h. After cooling down, resins were prepared to obtain smooth, flat, thin surfaces by using a compression molder under a sequence of heating (65 °C with a pressure of 1-2 tons for 5 min), compressing (65 °C, 9-10 tons for 5 min), and cooling. Samples were wrapped with aluminum foil for further measurement. The sessile drop method, according to ASTM D5946, was used to determine static contact angles between flat, thin resins and solvents – distilled water and methylene iodide – performed by using a NRL C.A. goniometer (Ramè-harl instrument Co., Succasunna, NJ) [18].

## Theoretical background of surface energy

The surface energy of polymers  $(\gamma_i)$  is the addition of non-polar or dispersion  $(\gamma^d)$  and polar  $(\gamma^p)$  components, where the values of these components are calculated from the following two simultaneous equations, derived by Wu [19].

$$(b_1 + c_1 - a_1)\gamma^d \gamma^p + c_1(b_1 - a_1)\gamma^d + b_1(c_1 - a_1)\gamma^p - a_1b_1c_1 = 0$$
(1)

$$(b_2 + c_2 - a_2)\gamma^d \gamma^p + c_2(b_2 - a_2)\gamma^d + b_2(c_2 - a_2)\gamma^p - a_2b_2c_2 = 0$$
(2)

$$a_1 = (1/4)(\gamma_1)(1 + \cos\theta_1) \tag{3}$$

$$b_1 = \gamma_1^d \tag{4}$$

$$c_1 = \gamma_1^p \tag{5}$$

$$a_2 = (1/4)(\gamma_2)(1 + \cos\theta_2) \tag{6}$$

$$b_2 = \gamma_2^d \tag{7}$$

$$c_2 = \gamma_2^p \tag{8}$$

Equations 1 and 2 are applied with values obtained from distilled water and methylene iodide, respectively, where  $\theta_1$ ,  $\theta_2$  are contact angles of distilled water with polymer and methylene iodide with the polymer, respectively. According to the HM equation (determining surface properties between polymers and low-energy materials), distilled water has surface tension ( $\gamma_1$ ),  $\gamma_1^d$ , and  $\gamma_1^p$  of 72.8, 22.1, and 50.7 mN·m<sup>-1</sup>, respectively; methylene iodide has 50.8 ( $\gamma_2$ ),44.1 ( $\gamma_2^d$ ) and 6.7 ( $\gamma_2^p$ ) mN·m<sup>-1</sup> [10, 19].

The work adhesion (the reversible work per unit of interface area required to separate two bulk phases,  $W_{12}$ ) between two polymers is calculated from the surface energy of the polymers, expressed by equation 9

$$W_{12} = \frac{4\gamma_1^d \gamma_2^d}{\gamma_1^d + \gamma_2^d} - \frac{4\gamma_1^p \gamma_2^p}{\gamma_1^p + \gamma_2^p}$$
(9)

where  $\gamma_1^d$  and  $\gamma_1^p$  are the dispersion and polar components of PLA

 $\gamma_2^d$  and  $\gamma_2^p$  are the dispersion and polar components of TPCS

Then the interfacial tension  $(\gamma_{12})$  and spreading coefficient  $(\lambda)$  between PLA and TPCS are obtained from the following equations [19, 20].

$$\gamma_{12} = \gamma_1 + \gamma_2 - W_{12} \tag{10}$$

$$\lambda = \gamma_{12} - \left| \gamma_1 - \gamma_2 \right| \tag{11}$$

### Molecular weight

The PLA fraction in each of the blend resins was extracted by dissolving a blend resin  $(0.11 \pm 0.03 \text{ g})$  in 10 mL of THF for 24 h, and then centrifuged at 1,900 rpm for 20 min. The supernatant was filtered via a 0.45 µm syringe filter, and 100 µL of supernatant was used to determine the PLA molecular weight and molecular weight distribution using a Gel Permeation Chromatograph (GPC) equipped with a Waters 1515 isocratic pump, Waters 717 autosampler, a series of Waters Styragel columns (HR4, HR3, and HR 2), and a Waters 2414 refractive index detector interface with Waters Breeze software (Waters Inc., Milford, MA). THF was used as the mobile phase at a flow rate of 1 mL·min<sup>-1</sup> under a detector temperature of 35 °C. PS standards

kits with molecular weight in the range from  $1.20 \times 10^3$  to  $3.64 \times 10^6$  Da were used as external standards. The calibration curve was calculated by using the third-order polynomial equation. The number average molecular weight  $(M_n)$ , weight average molecular weight  $(M_w)$ , and Polydispersion Index (*PI*) of PLA were determined.

#### Moisture content

The AOAC 925.09 air oven method was used to determine the moisture content of the resins (TPCS, PLA, and TPCS/PLA blends). Resins were dried at 95 to 100 °C for 5 h [12]. Moisture contents of the resins are reported on a wet-basis.

## FTIR and thermal properties

The properties of TPCS/PLA or blend resins were investigated following the methods described in Chapter 3. To investigate the effect of TPCS on the crystallization of PLA in the blends, the first heating DSC scan was used to remove the thermal history of the polymeric resins.  $T_g$ ,  $T_{cc}$ , and  $T_m$  were determined from the second heating, and  $T_c$  was obtained from the cooling step. The percentage of PLA crystallinity ( $X_c$ ) in the blend resins was calculated using the following equation:

$$X_{c} = \left(\frac{\Delta H_{m} - \Delta H_{cc}}{\Delta H_{f}^{*}}\right) / \varphi_{PLA} \times 100$$

where  $\Delta H_m$  and  $\Delta H_{cc}$  are enthalpies of melting and cold crystallization, respectively  $\Delta H_f^*$  is the enthalpy of fusion of a PLA crystal of infinite size, which is 93 J·g<sup>-1</sup> [21].

# $\phi_{PLA}$ is the PLA weight fraction in the blend

#### Morphology (Scanning Electron Microscopy)

To achieve a good phase contrast image of blend morphology, blend resins were immersed in 0.1 N HCl for 3 h to selectively remove the starch phase. Then, the etched resins were air dried in hood overnight, kept with desiccants for 1-2 days to reduce volatiles, and coated with a conductive gold layer to avoid setting charge under the electron beam. A JSM 6400 scanning electron microscope (JOEL, Tokyo, Japan), operating at an accelerating voltage of 7 kV, was used to characterize the morphologies of etched blend resins.

# 4.2.4 Sheet fabrication and characterization of sheet morphology

Blend resins were oven dried at 60 °C for 2 days. Sheet was fabricated by using a castfilm extrusion (Randcastle Extrusion Systems, Inc., Cedar Grove, NJ). The sheet was ultramicrotomed using a diamond knife at room temperature and deposited on Formvar grids. The morphologies of blend films were examined by using a JEOL 100CX transmission electron microscope (TEM) (JOEL USA Inc., Peabody, MA).

### 4.2.5 Statistical analysis

Statistical Analysis System (SAS) version 9.1 (SAS institute) was used for running the statistical correlations. Analysis of variance (ANOVA) and the Tukey's test were used to determine significant differences.

## 4.3 **Results and discussion**

#### 4.3.1 Physical blending of TPCS/PLA resins

The melt blend extrudates of dried TPCS and PLA resins at ratios of 70/30, 50/50, and 30/70 could be produced under the extrusion conditions of 172-175 °C, screw speed of 100 rpm, and length of time 5 min. Hence, this condition was a starting point to determine the optimum extrusion conditions of physical blend resin production at the ratio of TPCS and PLA 50/50 and 30/70. The barrel temperature profile from feeder to die was 25/150/160/165/172/177/177/177/177/177/177/177/172 °C and screw speed of 125 rpm. 7PT extrudate (containing TPCS and PLA at a weight ratio of 30/70) was easily processable, exhibiting a white color.

To produce 5PT resins (comprising of TPCS and PLA at a weight ratio of 50/50), the barrel temperature profile from feeder to die was reduced to 25/150/160/165/170/175/175/175/170/170 °C with screw speed of 125 rpm. The extrudates of 5PT were also easily processable with a light brown color. However, after air cooling and pelletizing, 5PT resins exhibited some non-uniform color (Figure 4.1), indicating non-homogeneous mixing. The golden brown color found in some 5PT resins probably due to the degradation of starch. These effects were clearly seen with 5 PT resins, perhaps due to the high amount of starch.



Figure 4.1 TPCS/PLA resins at ratios of TPCS to PLA: a) At ratio of 50/50 w/w (5PT resins); b) at ratio of 30/70 w/w (7PT resins)

# 4.3.2 Surface properties

The contact angles of flat dried resins are shown in the following table (Table 4.2). The larger the contact angle between water and the resins, the more the polymeric materials are hydrophobic in nature. A smaller contact angle between water and the resins indicates that the polymers have better wetting and adhesiveness and higher surface energy [22]. Methylene iodide represents a high dispersive (nonpolar) character, so it will spread more easily on a nonpolar surface, resulting in a small contact angle [23].

	PLA	TPCS	<b>7PT</b>	5PT
Water				
-θ, °	$65.6 \pm 4.3^{a}$	$32.1 \pm 8.7^{d}$	$57.3 \pm 3.8^{b}$	$47.6 \pm 9.0^{\circ}$
-Cos θ	$0.41 \pm 0.07^{a}$	$0.84 \pm 0.08^{d}$	$0.54 \pm 0.06^{b}$	$0.67 \pm 0.12^{c}$
Methylene iodide				
-θ, °	$29.9 \pm 4.1^{a}$	$32.5 \pm 5.8^{ab}$	$33.2 \pm 3.8^{b}$	$34.4 \pm 3.4^{b}$
-Cos θ	$0.86 \pm 0.04^{a}$	$0.84 \pm 0.06^{ab}$	$0.84 \pm 0.04^{b}$	$0.82 \pm 0.03^{b}$
Surface energy, mJ·m <sup>-2</sup>				
-Polar	$16.4 \pm 1.6^{a}$	$36.2 \pm 4.5^{\circ}$	$21.5 \pm 1.7^{a}$	$27.5 \pm 4.8^{b}$
-Dispersion	$33.3 \pm 0.6^{a}$	$29.9 \pm 1.7^{b}$	$31.1 \pm 0.2^{b}$	$29.9 \pm 1.2^{b}$
-Total	$49.8 \pm 1.5^{a}$	$66.1 \pm 3.7^{c}$	$52.6 \pm 1.5^{a}$	$57.4 \pm 3.8^{b}$
Polarity	$0.33 \pm 0.02^{a}$	$0.55 \pm 0.04^{d}$	$0.41 \pm 0.02^{b}$	$0.48\pm0.05^{c}$

**Table 4.2** Contact angles ( $\theta$ ), Cos  $\theta$ , and surface energies of TPCS, PLA, and TPCS/PLA blend resins

Note: Polarity determined from Polar component divided by total surface energy Numbers followed by the same letter within a row are not statistically significant different at  $P \le 0.05$  (Tukey's test)

According to Bialopiotrowicz, there was a good correlation between starch content and advancing contact angles such that increased starch contents (2 to 12%) resulted in decreased contact angles with water (from 50 to 25 °) due to *like absorbs like* [24]. In contrast with the study by Averous *et al.*, they reported that the contact angles of starch-based materials did not depend on starch content. Reported in the study by Averous *et al.*, the components of four thermoplastic wheat starches are as follows: 74 starch/10 glycerol/16 water; 70 starch/18 glycerol/12 water; 67 starch/24 glycerol/9 water; and 65 starch/35 glycerol. The contact angles between water and the four thermoplastic starches were around 51, 40, 50, and 32 °, respectively [25]. The contact angles of starch-based materials obtained from previous studies vary, resulting in a difference in surface energy of starch-based materials (from 32 to 59 mJ·m<sup>-2</sup>) as shown in Table 4.3.

	Methods	θ, °		Surface energies, mJ·m <sup>-2</sup>			
	-	Water	Methylene iodide	Polar	Dispersion	Total	
Dry potato starch gel film (2-12%) [24]	Advancing	50-25	47-45	-	-	-	
Dry corn starch	Dynamic/						
-High amylose	HM	93.7	52.7	1.6	37.6	39.2	
-Waxy		No angle	49.8	2.9	34.9	37.8	
-Normal		85.9	50.6	-	-	-	
Extruded corn starch ribbons (22% water) [26]	Dynamic/ HM						
- High amylose		98.7 (D), 93 4 (R)	45.6 (D), 45.9 (R)	1.6	37.6	39.2	
-Waxy		96.2 (D), 88.2 (R)	46.3 (D), 51.3 (R)	2.9	34.9	37.8	
-Normal		95.3 (D), 84.9 (R)	42 (D), 35.6 (R)	-	-	-	
Thermoplastic wheat Starch (65 starch/ 35glycerol) [27]	Sessile drop/HM	67	75	12	20	32	
Thermoplastic wheat starch (70 starch/ 18 glycerol/ 12 water) [28]	Sessile drop/HM	45	36	23	36	59	

**Table 4.3** Contact angles  $(\theta)$  and surface energies of starch-based materials from previous studies determined by using two-liquid probe (water and methylene iodide)

Note: D, extruded starch ribbons dried over phosphorus pentoxide ( $P_2O_5$ ) at 21 °C for at least one week

R, extruded starch ribbons stored at 50% RH and 21  $^{\circ}\mathrm{C}$  for at least one week HM, Harmonic method

According to Lawton, there is a limitation of contact angle measurement of water and polar solvents with hydrophilic materials, such as starch [26]. Water and polar solvents interact and rapidly absorb on the surface of starch-based materials, resulting in a decrease of contact angles as a function of time [26]. Determining the contact angles of starches with water at an initial time results in an error because at an initial time water and polar solvents on starch surfaces behave as nonpolar solvents [26]. In his study, Lawton reports the similarity of contact angles of starch with water (85 to 99 °) and starch with methylene iodide (36 to 53 °) in comparison to those of PE, determined in the Wu's study – having contact angle 94 ° (water), 52 ° (methylene iodide), 4.6 mJ·m<sup>-2</sup> (polar component), 29.8 mJ·m<sup>-2</sup> (dispersive component), and 34.4 mJ·m<sup>-2</sup> (surface energy) [10, 26]. As a hydrophilic polymer, the polar component and surface energy of starch must be extremely higher than that of PE, a pure hydrocarbon polymer [26, 29].

Lawton suggests that the use of contact angle measurement to estimate surface energy of starch is possible and useful, but determining contact angle at the equilibrium between polar solvents (liquids) and starch is difficult because of the rapid absorption of polar liquids by starch polymers [26]. Another error is attributed to the roughness of polymeric surfaces: the greater the surface roughness, the lower the contact angle [26]. Lawton observes that starch films had smoother surfaces than extruded ribbons, and normal corn starch-based material had the roughest surface, while high amylose corn starch-based materials exhibited the smoothest surface [26].

Due to a high degree of hydrogen bonding and strong interaction between molecules, TPCS resins in this study exhibited the smallest contact angle with water ( $32.1 \pm 8.7 \circ$ ), the highest nondispersion (polar) component ( $36.2 \pm 4.5 \text{ mJ} \cdot \text{m}^{-2}$ ), and the highest total surface energy ( $66.1 \pm 3.7 \text{ mJ} \cdot \text{m}^{-2}$ ) compared to PLA, 7PT, and 5PT [29]. The surface energy of TPCS in this study is close to that of purified cotton cellulose (hydrophilic material) in the Westerlind's study [30]. Westerlind used the Wilhelmy technique (advancing and receding contact angles) to determine contact angles of purified cotton cellulose, and used HM to calculate the total surface energy (69.5 mJ·m<sup>-2</sup>), the dispersion component (26.5  $\pm$  1.1 mJ·m<sup>-2</sup>), and the polar component (43.0  $\pm$  2.4 mJ·m<sup>-2</sup>) [30].

The highest contact angle with water and the lowest contact angle with methylene iodide contributed to the lowest surface energy of PLA among all polymeric resins (Table 4.2). The value of surface energy can be used to characterize the hydrophobic and hydrophilic natures of polymers, since the surface free energy of polymers containing nonpolar and long-chain molecules is low [31]. Therefore, the lower surface energy of PLA is a substantial support of the more hydrophobic nature of PLA, as compared to TPS. The surface energy of PLA 2002D flat dried resin (49.8  $\pm$  1.5 mJ·m<sup>-2</sup>) in this study was similar to that of the PLA dumbbell specimen investigated in Schwach and Averous (49  $\pm$  2 mJ·m<sup>-2</sup>), as shown in Table 4.4 [27].

**Table 4.4** Contact angles  $(\theta)$  and surface energies of PLA materials compared with previous studies

	PLA Materials				
	Flat dried resin*	Film**[1]	Dumbbell specimen [27]		
Methods	SD/HM	SD/VCG	SD/HM		
θ, °					
-Water	$65.6 \pm 4.3$	$67.7 \pm 4.0$	$67 \pm 2$		
-Methylene iodide	$29.9 \pm 4.1$	$40.1 \pm 3.3$	$36 \pm 1$		
-Dimethyl sulfoxide	-	$30.9\pm4.0$	-		
Surface energies, $mJ \cdot m^{-2}$					
-Polar or AB	$16.4 \pm 1.6$	3.9	$11 \pm 2$		
-Dispersion or LW -Total	$33.3 \pm 0.6$ $49.8 \pm 1.5$	$39.6 \pm 1.7$ 43.5	$\begin{array}{c} 37\pm2\\ 49\pm2 \end{array}$		

Note: \*Values from this work

\*\*Film made from compression molding

SD, VCG, AB, and LW are Sessile drop, van Oss-Chaudhury-Good, Acid/base, and Lifshitz-van der Waals, respectively

The theoretical work of adhesion and interfacial tension between TPCS and PLA in this study and previous studies are shown in Table 4.5. The more affinity or compatibility between a polymer pair can be determined from the greater work adhesion and the lower interfacial tension [20, 27, 32]. According to Wu, besides being calculated from surface energy, the interfacial tension can be estimated from the polarity between a polymer pair, where a greater polarity difference results in a greater interfacial tension [10]. The high interfacial tension (1.5 to 15 mJ·m<sup>-2</sup>) of a polymer pair is attributed to the incompatibility of immiscible polymer blends, leading to a weak interface, inferior properties, and phase instability of the blend polymers (*e.g.* coalescence of the dispersed phase, phase migration, phase separation) [33-35].

Due to the lack of reactive functional groups between PLA (containing hydroxyl and carboxylic acid end groups) and TPS (containing hydroxyl groups), a physical blend of PLA and TPCS in this study exhibited a high interfacial tension  $(7.9 \pm 4.2 \text{ mJ} \cdot \text{m}^{-2})$ , indicating an incompatible polymer blend [33, 36]. Furthermore, the negative value of the spreading coefficient showed that there is no spreading between PLA and TPCS (Table 4.5).

Surface energy of PLA, mJ·m <sup>-2</sup>	Surface energy of TPS, mJ⋅m <sup>-2</sup>	Work adhesion, mJ∙m <sup>-2</sup>	Interfacial tension, mJ·m <sup>-2</sup>	Spreading coefficient, mJ∙m <sup>-2</sup>	Ref.
49.8 ± 1.5	$66.1 \pm 3.7$	$107.9 \pm 3.9$	7.9 ± 4.2	$-8.4 \pm 2.1$	This work
43.5	43.0	85.8	0.61	-	[1]
$49 \pm 2$	$32 \pm 2$	~ 76.5	~ 8	-	[27]

Table 4.5 Surface properties of PLA/TPS blends prepared by physical blending

Therefore, by using physical blending (thermomechanical blending in TSE), the blend resins of TPCS/PLA can be produced, but the blend resins will have weak interfacial adhesion,

resulting in coalescence of the dispersed phase, inferior performance properties and/or phase separation of TPCS/PLA. These results were expected, because blending two or more polymers that have differences in solubility parameters, cohesive energy densities, polarities, molecular structures, and/or large differences in molecular weight normally results in immiscible polymer blends [20, 37]. The results also confirmed that the semiempirical method (static contact angle measurement and HM) used to determine the interfacial tension in this study is a useful technique to predict the compatibility between PLA and TPCS. The difference between the interfacial tensions of this study ( $7.9 \pm 4.2 \text{ mJ} \cdot \text{m}^{-2}$ ) and the Biresaw and Carriere's study (0.61 mJ  $\cdot \text{m}^{-2}$ ) may be the result of the fact that Biresaw and Carriere used the contact angles of normal starch obtained from the Lawton's study to calculate the surface energy of starch [1, 26].

As mentioned above, contact angle values in Lawton's study may exhibit a greater hydrophobic nature than usual, resulting in a greater (hydrophobic) surface energy of normal starch (derived from VCG method), which is very close to the surface energy of PLA in Biresaw and Carriere's work. Thus, the interfacial tension between the extruded normal corn starch ribbon and PLA predicted in the Biresaw and Carriere' study was very low, indicating a compatible, immiscible polymer blend, which possesses a fine dispersion, a large interfacial thickness, a strong interface, and good performance properties obtained from properties of each component [10, 20, 32-34]. However, compatible, immiscible PLA/TPS blends are very hard to obtain by physical blending.

The surface energies of TPCS/PLA blends produced via physical blending as a function of PLA content of this study are shown in Figure 4.2. A substantial decrease in blend surface energies was observed with an increase of PLA content, which is a result of significantly
reducing the polar component and slightly increasing the dispersion component. As a characteristic of polymer blends, all surface properties and polarities of physical TPCS/PLA blends did not follow a linear relation but rather a polynomial regression. Even though the polarities of TPCS/PLA blends were a little greater compared to the polarities that might be obtained from a linear relation, physical blending of TPCS/PLA blends still showed a good trend that the hydrophobicity of the blends will dominate, even though at least 40 wt% of PLA was introduced.



**Figure 4.2** Total surface energies (Total S), surface energy components (Dispersion C and Polar C), and polarities of TPCS, PLA, and TPCS/PLA blends as a function of blend components

Therefore, blending TPCS with PLA will decrease water sensitivity and performance instability properties that are related to water sensitivity. However, phase separation of polymer blends – the main drawback of physical blending – happened when the dried blend resins were compressed with high force (9 to 10 tons) and mild temperature (65 °C). The PLA rich-phase

migrated to the outside, whereas the TPCS-rich phase was inside the flat resin. Similar results were observed in previous studies [38-40]. Phase separation of TPS/biodegradable polyesters (*e.g.* PLA, PCL, and polyesteramide) was found in injection molded specimens due to the migration of low viscous materials (polyesters) during the injection molding process, resulting in specimens that had polyester layers on the outside [38-40]. To avoid phase separation due to the incompatibility of immiscible blends, compatibilization by using a compatibilizer or reactive blending must be conducted [41].

#### 4.3.3 PLA molecular weight of blend resins

Molecular weights of extracted PLA after physical blending are shown in Table 4.6. The reduction of molecular weight ( $M_n$  and  $M_w$ ) and broadening of *PI* indicated chain reduction of PLA after melt blending. Increased starch content slightly retarded chain reductions ( $M_w$ ) of PLA ( $P \le 0.05$ ), The degradation factors of PLA – the ratio between molecular weight and of PLA before and after processing where  $k_n$  and  $k_w$  are ratios between of  $M_n$  and  $M_w$ , respectively – also slightly decreased with increased starch content. Similar results were found by *Jang et al.* with PLA/starch blends at the ratio of 50/50 and 70/30, processed under extruder barrel temperature of 160~190 °C and screw speed of 150 rpm [41]. In Jang *et al* 's study, PLA in the 50/50 blend had extracted  $M_n$  and  $M_w$  (42 and 76 kDa) higher than those of PLA in the 70/30 blend (33 and 66 kDa) with  $k_n$  and  $k_w$  were 2.26 and 2.88 (50/50 blend) and 3.03 to 3.50 (70/30 blend). Jang *et al.* concluded that the reduction of PLA.

Resins	M <sub>n</sub>		M	PI	
	kDa	k <sub>n</sub>	kDa	k <sub>w</sub>	
5PT	$86.9 \pm 2.9^{a}$	$1.21 \pm 0.04^{a}$	$140.0 \pm 3.4^{a}$	$1.17 \pm 0.03^{a}$	$1.61 \pm 0.02^{a}$
7PT	$82.4 \pm 5.5^{a}$	$1.28\pm0.08^{b}$	$134.0 \pm 6.6^{b}$	$1.22 \pm 0.06^{b}$	$1.63 \pm 0.03^{a}$
PLA	$105.2 \pm 1.1^{b}$	-	$163.3 \pm 0.7^{c}$	-	$1.55\pm0.01^b$

**Table 4.6** Molecular weight and molecular weight distribution of PLA extracted from blend

 resins compared to PLA resin before melt blending

Note: Numbers followed by the same letter within a column are not statistically significant different at  $P \le 0.05$  (Tukey's test)

In fact, PLA molecular weight is reduced during extrusion because of the presence of moisture content of resins and extrusion conditions (temperature and resident time) [42]. If the existing moisture content in starch is the main cause PLA chain reduction, addition of higher amount of starch in the blend could increase chain reduction, resulting in a higher degradation factor, which was not found in this study or in Jang *et al*'s study. The main drop of PLA molecular weight found in this study could probably due to thermal degradation of PLA, which normally occurs when PLA is held above its  $T_m$ , especially 10 °C above [43]. In Carlson *et al*'s study, pure PLA after extrusion at 180 °C had  $k_n$  of 1.49 and  $k_w$  of 1.56 [44]. Signori *et al.* reported an increase of pure PLA  $k_n$  as a function of temperature [45]. Under constant speed of 50 rpm and various processing temperatures – 150, 170, 190, and 200 °C, PLA presented  $k_n$  of 1.4, 1.6, 1.7, and 1.7, respectively. Carlson *et al.* and Signori *et al.* attributed the reduction of PLA molecular weight to thermal degradation due to chain scission [44-45].

## 4.3.4 IR spectra

The absorption IR spectra of TPCS and PLA resins investigated in this study are shown in Figure 4.3a-b. The characteristic IR spectrum of TPCS is represented by the peaks at 3282 cm<sup>-1</sup> (indicating free, intra- and intermolecular-bound hydroxyl groups) and 2924 cm<sup>-1</sup> (symmetric and asymmetric C–H stretch of CH<sub>2</sub>) [46-47]. The very strong peak (absorbance value > 1.5) at 1016 cm<sup>-1</sup> corresponds to the amorphous regions, and the very strong peak at 997 cm<sup>-1</sup> attributed to intramolecular hydrogen bonding of the hydroxyl at C<sub>6</sub> of anhydroglucose ring of starch, indicates water sensitivity of starch-based polymers [46-49]. The peaks at 1408, 1365, 1336, 1238, and 1205 cm<sup>-1</sup> are ascribed to C–H and C–OH bends, where the peaks at 1149, 1103, and 1078 cm<sup>-1</sup> correspond to C–O and C–C stretches [27, 40, 46-47, 49]. The C–OH and CH<sub>2</sub> bends of TPCS show a medium peak (absorbance value ~ 0.3-0.7) at 925 cm<sup>-1</sup>[46].



**Figure 4.3** IR spectra of TPCS, PLA, 5PT, and 7PT: a) At 3600-2800 cm<sup>-1</sup>; b) at 1800-650 cm<sup>-1</sup>

The absorption band of the PLA IR spectrum was observed below 3000 cm<sup>-1</sup> without characteristic peaks corresponding to hydroxyl and carboxylic acid end groups, at above 3000 cm<sup>-1</sup> (Figure 4.3a). This is probably due to the high weight average molecular weight of PLA  $(M_w = 163.3 \pm 0.7 \text{ kDa})$  resulting in a very low concentration of PLA terminal groups, which are hard to detect by FTIR-ATR. According to Cam and Marucci, the concentration of the hydroxyl terminal groups becomes insignificant when a viscosity average molecular weight of PLA  $(M_v)$ is greater than 140 kDa (for the same polymer,  $M_v$  is less than  $M_w$ ) [49-50].

The IR peaks of PLA appearing at 2993, 2922, and 2852 cm<sup>-1</sup> are attributed to asymmetric CH<sub>3</sub>, symmetric CH<sub>3</sub>, and CH stretch, respectively [51]. The medium IR peak at 1747 cm<sup>-1</sup> corresponds to C=O carbonyl stretch (Figure 4.3b) [43]. The characteristic asymmetric and symmetric CH<sub>3</sub> bends appeared at 1450 and 1381 cm<sup>-1</sup>, respectively; and the characteristic CH and CH<sub>2</sub> bends appeared at 1359 and 1305 cm<sup>-1</sup>, respectively [51]. According to Kister *et al.*, the splitting characteristic of peaks at 1381, 1359, and 1305 cm<sup>-1</sup> indicates semicrystallinity of PLA, while Ahmed *et al.* assign the two peaks around 1263 and 1180 cm<sup>-1</sup> which are due to C–COO and O–CH stretches, CH<sub>3</sub> rocking, and CH bend, to crystalline bands of PLA [51-52].

The peak at around 752 cm<sup>-1</sup> is also assigned to the crystalline phase, whereas the peak at 866 cm<sup>-1</sup> is attributed to the amorphous phase of PLA [43, 53-54]. This information helps

confirm the semicrystalline state of the PLA 2002D resin used in this study. The medium IR peak around 1041 cm<sup>-1</sup> has been assigned to different characters: C–CH<sub>3</sub> stretch in Kister *et al.*'s study; OH bend in Galotta and Auras *et al.*'s studies; and C–O stretch of–O–C=O group in Wang *et al.*'s study [43, 51, 53, 55]. The C–C backbone stretch and CH<sub>3</sub> rocking appeared at 954 and 920 cm<sup>-1</sup>, and  $\gamma$ C=O were observed around 692 and 673 cm<sup>-1</sup> [51].

The IR spectra of TPCS/PLA blend resins (5PT, 7PT) produced via physical blending in this study are shown in Figure 4.3a-b. The appearances of blend absorption bands are a combination of TPCS and PLA characteristics, where the bands below 2800 cm<sup>-1</sup> are similar to that of PLA, especially with a high PLA content (7PT). An intensity modification and a shift of new peaks, which indicate the interactions between TPCS and PLA, arose in the regions of OH stretch (3600-3000 cm<sup>-1</sup>), CH stretch (< 3000-2800 cm<sup>-1</sup>), C=O stretch (1730-1760 cm<sup>-1</sup>), CO stretch (1010-1030 cm<sup>-1</sup>), and at the low frequency end of the spectrum (750-760 and 650-700 cm<sup>-1</sup>) [56-58], as is summarized on Table 4.7 and shown in Figure 4.3a-b. The IR characteristics of the TPCS and PLA resins are included for comparison.

IR regions	TPCS	PLA	5PT	<b>7PT</b>
-OH stretch	3282 (0.47)	_	↑ 3315 (0.20)	↑ 3313 (0.09)
			† 3300 (0.20)	
			3284 (0.20)	
-CH stretch	2924 (0.30)	2993 (0.07) 2993 (0.08)		2993 (0.06)
		2922 (0.10)	↑ 2941 (0.11)	↑ 2941 (0.08)
		2852 (0.07)	_	2926 (0.08)
			↑ 2883 (0.08)	↑ 2883 (0.05)
-C=O stretch	1735 (0.08)	1747 (0.47)	↑ 1751 (0.64)	1747 (0.45)
-C-O- stretch	1016 (1.38)	_	↑ 1024 (0.91)	-
Low frequency	758 (0.56)	752 (0.21)	\$\)754 (0.35)	\$ 754 (0.21)
	-	692 (0.19)	_	↑ 698 (0.21)
	665 (0.71)	673 (0.19)	↓ 651 (0.38)	↓ 650 (0.21)

**Table 4.7** Spectral shift of the IR absorption bands of TPCS/PLA blend resins and their intensities

Note: The arrows  $\uparrow$ ,  $\downarrow$ , and  $\downarrow$  indicate shift of new peaks to higher, between, and lower wavenumbers, respectively

Values in parentheses indicate intensity of IR absorption peaks.

Overall, the changes of peak intensities depended on TPCS content and the greater the TPCS content (5PT), the higher the peak intensity. An exception was the intensity of the peak at 698 cm<sup>-1</sup> ( $\gamma$ C=O), which increased with high content of PLA (7PT) [51]. According to the harmonic oscillator model described in Ma *et al.*'s study, the spectral shift of IR bands depends on the intensity of chemical interaction (weak or strong), governed by the force constant of the functional groups [59]. The force constant between atoms of each group, such as carbon and oxygen atoms in the C–O group, is reduced when the C–O group chemically interacts with another group, such as hydrogen (*i.e.* C–O····H–), resulting in a shift of the oscillating frequency of the C–O group to a lower wavenumber (*red shift*) [59]. The stronger the new chemical bonds,

the greater are the shift to a lower wavenumber, corresponding to the characteristic peak [59]. Based on the harmonic oscillator model, TPCS and PLA had interactions exhibited in the low frequency end of the spectrum (Table 4.7). Unfortunately, the interactions between PLA and TPCS in blend resins could not be determined by using only the absorption bands, appearing in this region, because the characteristic bands in this region are not specific enough. They represent the characteristic bands of O–H deformation, C–O–C bend, and ring vibrations of starch and  $\gamma$ C=O of PLA [51-60].

Due to the ester carbonyl groups along a PLA molecular chains and to the functional groups of PLA (hydroxyl and carboxylic acid end groups) and hydroxyl groups of TPCS, the characteristic peaks at the functional group region (4000-1300 cm<sup>-1</sup>) and finger print region (1300-910 cm<sup>-1</sup>) are very useful for interpreting the interactions between this polymer pair [36, 61]. However, the shift in the IR absorption bands of blend resins to a higher wavenumber does not correlate with the harmonic oscillator model as mentioned above.

A shift-up in IR absorption bands corresponding to characteristic peaks is attributed to a weaker interaction of molecules assigned to characteristic peaks by many authors [62-65]. For example, Meaurio *et al.* investigated the shift in the IR band assigned to hydrogen-bonded hydroxyl strength (3380 cm<sup>-1</sup>) to a higher frequency, when poly(vinylphenol) (PVPh) was blended with PLLA [66]. The weak interaction, resulting in a shift to a higher wavenumber, was due to the replacement of hydroxyl-hydroxyl hydrogen-bonded multimers of PVPh by the weaker hydrogen-bonded hydroxyl between hydroxyl groups of PVPh and carbonyl groups of PLLA [66]. According to their study, the formation of hydrogen bonding between PVPh and PLLA is confirmed by a shift of the C=O strength band to a lower wavenumber [66].

A shift in IR bands to a higher wavenumber could contribute to the formation of an *improper, blue-shifting hydrogen bond*. The mechanism of *improper, blue-shifting hydrogen bonding* via an indirect process and examples, such as  $C-H\cdots\pi$ ,  $C-H\cdots0$ , are mentioned elsewhere [67-68]. The formation of hydrogen bonds via an indirect process –"the electron-density transfer to a non-participating part of proton donor (X-H)" – strengthens the X–H covalent bond (*e.g.* C–H), leading to the bond's contraction and a shift of X–H stretch frequency to a higher wavenumber [67].

Contrary to a *red shift* (a shift to a lower wavenumber or frequency), there is no correlation between the strength of the blue shift hydrogen bond and the shift of X-H stretch frequency [67]. According to the red shift/blue shift concept, the intermolecular interaction between TPCS and PLA in this study could occur from the *blue-shifting hydrogen bonding* between C-H···O- (in 5PT and 7PT) and C=O···H-(5PT), as evidence by a shift-up of peaks corresponding to hydrogen-bonded hydroxyl stretch (3300-3315 cm<sup>-1</sup>), ester carbonyl stretch (1751 cm<sup>-1</sup>), and C-O stretch (1024 cm<sup>-1</sup>). However, due to weaker hydrogen bonding, the miscibility between TPCS/PLA should not be feasible.

Furthermore, a shift in the IR band to a higher wavenumber (*blue shift*) is very useful to determine a phase separation of polymer blends since it indicates a decrease of the intermolecular interaction between polymer pairs [64]. Based on this concept, TPCS/PLA resins in this study exhibit phase separation at both compositions: 5PT and 7PT. This is because of the greater difference in surface energies due to a lack of reactive functional groups between TPS and PLA. Interestingly, a number of blue-shift peaks and their intensities increased with increased TPCS (Table 4.7). At this point the results investigated by FTIR-ATR and contact

angle measurement/HM correlate very well and confirm that TPCS/PLA resins obtained via physical blending are incompatible, immiscible blends.

Another characteristic of polymers that shows up in the IR spectra is crystalline/ amorphous phases. The IR spectra of TPCS/PLA showed all of the IR peaks corresponding to crystalline (1381/1359/1305, 1263/1180, 752 cm<sup>-1</sup>) and amorphous (866 cm<sup>-1</sup>) phases of PLA (Figure 4.3b). Therefore, PLA in the blend resins is semicrystalline. It is noteworthy that the intensity of the crystalline/amorphous peaks increases with an increase of the TPCS content. Therefore, TPCS could have a nucleation effect, enhancing the crystallinity of PLA [53, 69-70]. In contrast to PLA, the IR peaks corresponding to crystalline (1047 cm<sup>-1</sup>) and amorphous (1016 cm<sup>-1</sup>) phases of TPCS did not appear in the blend spectra (Figure 4.3b), except for the amorphous band of 5PT (C–O stretch), which arose at the higher wavenumber (1024 cm<sup>-1</sup>) with a reduction of the band intensity. This could indicate that TPCS in 5PT is amorphous.

## 4.3.5 Thermal properties of TPCS/PLA resins

The characteristic DSC curves of TPCS and PLA resins are shown in Figure 4.4a-b. A broad endothermic peak of TPCS (indicating gelatinization or water absorption of material) and a melting peak of PLA ( $T_m = 151.5 \pm 0.2$  °C,  $\Delta H_m = 33.42 \pm 0.20$  J·g<sup>-1</sup> and  $X_c = 35.9 \pm 0.2\%$ ) were found only in the first heating [71]. The lack of recrystallization in the cooling stage and the second heating could indicate a slow crystallization rate of both polymers [69]. PLA had  $T_g$  around 60 °C, where TPCS exhibited two  $T_g$ s: -47 and 61 °C due to phase separation between a glycerol-rich phase and a starch-rich phase [46, 72-73].



Figure 4.4 DSC curves of polymeric resins: a) TPCS; b) PLA; c) physical blends

#### Figure 4.4 (cont'd)



As obtained from physical blending, the blend resins (5PT and 7PT) exhibited a combination of TPCS and PLA DSC curves (Figure 4.4c). A broad endothermic peak at around 55-125 °C belonged to TPCS, whereas  $T_g$ , cold crystallization and melting peaks were characteristic of PLA. To investigate effects of TPCS on crystallization of PLA in polymer blends, the DSC thermal properties of the polymer pair and polymer blends obtained from the second heating were used (Table 4.8).

	PLA	<b>7</b> PT	5PT	TPCS
<i>T<sub>g</sub></i> , °C	$60.1 \pm 0.5$	$58.2 \pm 0.1$	$58.7 \pm 0.5$	$-46.9 \pm 0.3, 61.4 \pm 1.4$
<i>T<sub>m</sub></i> , °C	-	$147.5\pm0.3$	$146.6\pm0.9$	_
Crystallinity, %	_	$4.1 \pm 1.4$	$11.1 \pm 1.94$	-
$\Delta H_{broad \ peak}, \mathrm{J} \cdot \mathrm{g}^{-1}$	_	$1.7 \pm 0.7$	$2.1\pm0.2$	_

Table 4.8 DSC thermal properties of PLA, 7PT, 5PT, TPCS

Note: The values were obtained from the DSC second heating

 $T_m$ s and  $T_g$ s of the blend resins were lower than  $T_m$  (obtained from the first heating) and

 $T_g$  of PLA. The existence of a single  $T_g$  at a lower temperature (from around 61 to 58 °C) in TPCS/PLA blends in this study does not present a characteristic of miscible blends, as evidenced by the high interfacial tension of TPCS/PLA. According to Schwach *et al.*, the changes in heat capacity at  $T_g$  of TPCS are very small, which makes them not easily detectable [74].

Furthermore, decreases of  $T_g$  of PLA in the blends may be due to an increase of hydrolysed PLAs, such as oligomeric lactic acids, which occurred during physical blending. Hydrolysed PLAs function as plasticizers for PLA to enhance the molecular mobility of PLA chains [74]. The assumption that a decrease of blends'  $T_g$  resulting from hydrolysed PLAs is consistent with values of  $M_w$  and PI of PLA in the blends. 5PT, which had  $M_w$  of 140.0 ± 3.4 kDa and PI of 1.61 ± 0.02, exhibited  $T_g$  around 58.7 ± 0.5 °C, where 7PT, which had  $M_w$  of 134.0 ± 6.6 kDa and PI of 1.63 ± 0.03, exhibited  $T_g$  around 58.2 ± 0.1 °C.

There is no evidence of recrystallization of TPCS and PLA in the blends during the cooling step. Again, this behavior is due to slow crystallization rate for both polymers [69]. The

enthalpy of the broad endothermic peak of TPCS, enthalpies of crystallization and melting of PLA, and thus the percent crystallinity increased with an increase of TPCS content. Similar results are reported in Jang *et al.* study, where percent crystallinity of PLA in PLA/starch blends increased from 0 to 2-9% with 30-50% starch [41]. An increase of percent crystallinity from 23 to 29-35 with 25-60% plasticized wheat starch is mentioned in the Schwach *et al.* study [74]. An increase of crystallinity of PLA in starch (TPS)/PLA blends is related to the hydrolysed products of PLA, which occurred during processing, where the lower molecular weights possess high crystallinity and high crystallization rate [41]. Furthermore, as mentioned, the hydrolysed products serve as a plasticizer, increasing the chain mobility and hence the final crystallinity of PLA [74].

Another assumption is that starch (TPS) functions as a nucleating agent, leading to the crystallization of PLA [41, 74]. According to Ke and Sun, the destructurized starches occurred during the thermomechanical process of polymer blending and the migration of some glycerol at the PLA and starch interface induced the crystallization of PLA, resulting in the production of many crystal nuclei and then formation of a large amount of starch and PLA crystals [75]. In this study, it is noteworthy that  $T_{cc}$  of 5PT (120 °C) appeared at a lower temperature than that of 7PT (128 °C). Thus, an increase in the crystallinity of PLA in this study is mainly due to the destructurized starches, because 5PT had greater concentrations of starch and glycerol, a higher molecular weight of PLA, and a narrower molecular weight distribution (*PI*) compared to 7PT.

Applying starch, which may function as a nucleation agent, decreased  $T_m$  of PLA in polymer blends. In this study,  $T_m$  of PLA in the blend resins decreased with an increase of TPCS content, as shown in Table 4.8. The PLA crystals obtained from starch-induced crystallization

have thinner lamellae than pure PLA crystals [71]. The higher the starch content, the smaller and more irregularly shaped the crystals are (*e.g.* spherulite) [53]. Hence, a lower energy (heating) is needed to disrupt the crystals of PLA in polymer blends.

TGA curves of the TPCS/PLA resins are shown in Figure 4.5a. Whereas 5PT (50% PLA) exhibits its TGA curve as a combination of TGA curves that belong to TPCS and PLA, the TGA curve of 7PT (70% of PLA) is similar to that of PLA. Overall, thermal stabilities of the blend resins increase with an increase of PLA content due to the higher thermal stability of PLA [76]. Interestingly, blending PLA into TPCS not only improves thermal stability of blends compared to TPCS at temperature below ca. 393 °C, but at temperatures above 393 °C the blends also have higher thermal stabilities than TPCS and PLA. The onset and end temperatures of TPCS, PLA, 5PT, and 7PT were 293-363, 362-412, 323-425, and 355-429 °C, respectively. More information regarding compound degradation of the polymer pairs and polymer blends is clearly seen from the DTG curves, compared to the TGA curves, as shown in Figure 4.5b.



Figure 4.5 Thermal stabilities of TPCS, PLA, 5PT, and 7PT resins:a) TGA thermograms;b) DTG thermograms137

Pyrolysis of PLA found the decomposition temperature or  $T_{max}$  (the temperature at the maximum rate of weight loss) at around 398 °C (31.8% remaining weight), where TPCS exhibited a complex degradation process (Figure 4.5b) [71, 77-78]. Below 250 °C, TPCS exhibited  $T_{max}$  around 152 °C (89.3% remaining weight), which could be ascribed to decomposition of bound water and volatile materials. Above 250 °C, the bimodal peak of TPCS exhibited  $T_{max}$  at 308 (64.3% remaining weight) and 344 °C (30.1% remaining weight), which could be ascribed to decompositions of amylose and amylopectin, respectively.

The characteristics of the DTG curves of 5PT and 7PT resins are related to the ratio of TPCS and PLA components, as shown in Figure 4.5b. The DTG curve of the 5PT resin exhibited an overlap peak ( $T_{max} = 241$  °C and 90.3% remaining weight) below 300 °C, which could be assigned to volatilization of free and bound glycerol. A split peak of 5PT above 300 °C presented  $T_{max}$  at 341 (70.8% remaining weight) and 410 °C (26.6% remaining weight), corresponding to decomposition of starch – (the TPCS component) and the PLA component, respectively. Contrary to 5PT, the 7PT resins exhibited an overlapped peak, which mainly belongs to decomposition of PLA. Whereas decompositions of glycerol and starch in the TPCS component of 7PT are not easily determined, the PLA component of 7PT exhibited two decomposition temperatures: 393 (45.4% remaining weight) and 404 °C (31.5% remaining weight).

A decrease of decomposition temperatures of the TPCS component (from 344 to 341 °C) in 5PT and of the PLA component (from 398 to 393 °C) in 7PT is due to thermal degradation of TPCS and PLA processed under high temperature and shear rate [45, 78-79]. The thermal degradation of PLA in blend resins in this study is not facilitated by the degradation products of

DTPS (thermoplastic dry starch) as mentioned in Wang *et al.*'s study [76]. In this study, greater TPCS content in the blend resins (5PT) did not enhance thermal degradation of PLA during the extrusion blending process, as evidenced by the  $T_{max}$  (from DTG) and  $M_w$  and *PI* (from GPC).

The value of  $T_{max/PLA}$ ,  $M_w$ , and PI of 5PT were as follow: 410 °C; 140.0 ± 3.4 kDa; and 1.61 ± 0.02, where 7PT had values around 393 and 404 °C, 134.0 ± 6.6 kDa, and 1.63 ± 0.03, respectively. In general, thermal degradation of PLA is significant when PLA is exposed to high temperatures (above its  $T_m$ ) for an interval residence time either under air or nitrogen [80]. This degradation process is enhanced by temperature, time, residual catalysts, and impurities, such as trace amounts of water, hydrolyzed monomer/oligomers of PLA [49, 80]. Based on this concept, a reduction of the thermal stability – ( $T_{max}$ ) of the PLA component in 7PT could due to a higher processing temperature (around 2 °C) which resulted in a greater hydrolysed PLA compared to 5PT.

The blend resins obtained in this study exhibited an increase of  $T_{max}$ s of the PLA component around 12 °C (5PT) and 5 °C (7PT). Improvement in the thermal stability of PLA components in TPCS/PLA blends is probably due to an increase of interaction between TPCS and PLA, as evidenced by FTIR-ATR, and mentioned by previous study [71, 76, 79, 81].

#### 4.3.6 Morphology

The morphologies of etched 5PT and 7PT resins after melt-blending (physical blending) were characterized by SEM (Figure 4.6a-b). The blend resins presented two immiscible phases, where the TPCS phase that was removed from the resins by etching with hydrochloric acid (0.1 N) appears as separated black areas, and PLA appears as a continuous grey area. These

morphologies are characteristic of a dispersed particle-matrix structure where the dispersed phase belongs to the polymer with high viscosity or a small amount, and the polymer having a low viscosity or a large amount is the a continuous phase [20, 37].



**Figure 4.6** SEM micrographs of morphology of TPCS/PLA blend and collapsed droplets (under white circles): a) 5PT; b) 7PT

In this study, either for 5PT or 7PT, TPCS appeared as a dispersed phase in PLA. A nonuniform size and non-homogeneous distribution of the TPCS droplets in the PLA matrix suggest a type of incompatible, immiscible blend, which was predicted by the higher interfacial tension between TPCS and PLA ( $7.9 \pm 4.2 \text{ mJ} \cdot \text{m}^{-2}$ ). A bigger and a broader size and a poorer distribution of TPCS droplets in PLA matrix sharply increase with high amounts of TPCS (Figure 4.6a-b). Weak adhesion between the interface of TPCS and PLA results in coalescence of TPCS droplets, found in both blends (shown by the white circles). According to Everaert *et al.*, the probability of collision increases with an increase of the dispersed phase concentration due to a nearness of droplets [82]. In this study, the 5PT resins exhibited two types of morphology. The main one is the dispersed particle-matrix structure mentioned above; another one is the co-continuous structure (a dispersed phase become continuous phase) shown in Figure 4.7a. Where the first morphology improved the impact properties of the blends, the latter one provides a combination of the characteristics of the polymer pairs [83].



**Figure 4.7** Morphologies of the TPCS/PLA materials: a) SEM micrograph exhibited the co-continuous structure of 5PT resins; b) TEM micrograph of 7PT sheet

In general, these morphologies depend on the intrinsic properties of the polymer pair (*i.e.* interfacial tension, viscosities and the ratio of their viscosities), the volume fractions, and the processing conditions (*e.g.* temperature and residence time) [84]. Co-continuous polymer blends are observed when the concentrations of the polymer pairs are close to the phase inversion regions, at shorter or a longer mixing times, or at various compositions above the percolation threshold (the onset of the continuity regions) [27, 33, 85]. Unfortunately, the factors governed the co-continuous structure of 5PT are not well understood. But, it was clearly seen that the weak adhesion of the incompatible, immiscible TPCS/PLA blends obtained from physical blending was incapable of preventing the coalescence of the TPCS droplets in 7PT when this resin was

fabricated into sheet by cast extrusion, as evidenced by TEM micrographs (shown in Figure 4.7b). According to Huneault and Li, a larger size of the dispered phase could initiate cracks in the polymeric materials, leading to premature failure [86]. Thus, to prevent this problem, the compatibility of TPCS/PLA need to be improved.

### 4.4 Conclusions

A high value of interfacial tension indicated that TPCS/PLA blend is incompatible and immiscible. The phase separation and weak interactions of TPCS and PLA were evident in FTIR spectra. Thermal degradation of PLA increased after blending with TPCS, but an increase of TPCS content did not increase the degradation factors and reduction of  $M_w$  of PLA. An addition of TPCS increased degree of crystallinity and  $T_{max}$  of PLA; meanwhile the drawbacks of TPCS due to low processability and high water sensitivity were decreased with an increase of PLA. However, the distribution of TPCS domains in the PLA continuous phase observed from the SEM morphology of blended resins was non-homogeneous. Coalescence of the TPCS domains in the PLA continuous phase occurred in the blend film, which was fabricated via cast-film extrusion. BIBLIOGRAPHY

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## 5.1 Introduction

The research, development, and commercial use of poly(lactic acid) PLA is exponentially increasing due to its being produced from biobased resources, biodegradable and recyclable [1]. Although PLA has many advantages such as transparency and good mechanical properties, some of its drawbacks such as low heat deflection temperature and fragility has concentrated efforts from many researchers in improving PLA's limitations by blending with nonbiodegradable and biodegradable polymers, elastomers, and rubbers as well as annually renewable biodegradable materials including starch, reinforcement with fiber, and blending with micro and nano-composites [2-5]. The main key to improve the desirable PLA properties and enhance its functional properties is to increase the compatibility or surface adhesion of PLA and those materials.

Thus, the attempts to produce biobased, biodegradable compatibilizers from PLA has been investigated and extensively studied using free-radical melt grafting of maleic anhydride (MA), the most successive monomer used for commercial maleated polyolefins and PS, by reactive extrusion or melt-solution [6-7]. MA is food grade approved. Improvement of compatibility, surface adhesion, and mechanical properties by using maleated PLA is mentioned elsewhere; meanwhile research continues for comprehensively understanding the process and improving the properties of maleated PLA [8-10].

Among the grafting techniques, free-radical melt grafting performed during extrusion has been considered as one of the most practical and cost-effective methods [11-12] since it offers a better degree of mixing, it is solvent-free, and it has shorter-time production as well as the feasibility of mass production. However, by itself free-radical grafting is very complicated and has concurrent side reactions that limit the degree and quality of grafting [13]. There are many factors involved in improving the degree of grafting, minimizing side reactions, and organizing the microstructure of grafts formed, *e.g.* MA concentration, type and amount of peroxide initiator, processing conditions (temperature, residence time, pressure), and screw/extrusion design including venting and mixing efficiency [13-14]. Interactions between those factors can also be important. Information indicative of the effects of maleation variables and especially the effects of variable interactions on maleation of PLA and its side reactions is scarce.

Thus, response surface methodology (RSM) was applied in this work to obtain a statistical and mathematical design of experiments (DOE) in order to identify the significant parameters affecting grafting of MA onto PLA and provide a predicted model to optimize grafting of MA [15]. RSM is an effective and widely used tool for determining the conditions that optimize a process, selecting of operating conditions to fulfill specifications, or mapping a response surface over a specific region of interest [15].

In the present work, RSM was used to investigate the influences of three main factors (MA concentration, peroxide initiator concentration, and screw speed of the twin screw extruder – TSE) and their interactions on percentage of grafted MA (PLA-g-MA), molecular weight of PLA-g-MA (an indicator of main side reaction), and molecular weight stability during storage, in order to set up the boundary conditions for optimizing maleation of PLA.

## 5.2 **Experimental**

#### 5.2.1 Materials

Ingeo<sup>™</sup> Biopolymer 2003D (PLA) was provided by NatureWorks LLC (Minnetonka, MN). Maleic anhydride (MA, 95%) and 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (Luperox 101 or L101, 90%) were obtained from Sigma-Aldrich Chemical Company, Inc. (Milwaukee, WI). All materials and/or chemical agents were used as received or as mentioned.

## 5.2.2 Response surface experimental design

A uniform precision central composite design (CCD) of response surface methodology (RSM) was performed in this study using JMP<sup>®</sup> 8.0 software program SAS Institute Inc., (Cary, NC). Three factors (input variables),  $X_1 = MA$  content (wt% on PLA basis),  $X_2 = L101$  content (wt% on PLA basis), and  $X_3 =$  screw speed of TSE (rpm) were investigated and an  $\alpha$  for rotatability of 1.682 was used. Factors and levels of each factor were acquired from preliminary work conducted by the author. The experimental design was composed of twenty experimental trials which were six center-full factorial points, eight full factorial points, and six axial factorial points. The coded and actual levels of variables are listed in Table 5.1. The levels of the coded variables ( $X_i$ ) were defined as follows:

$$X_{j} = \frac{Actual \, level - \frac{High \, level + Low \, level}{2}}{\frac{High \, level - Low \, level}{2}} \tag{1}$$

Run	Pattern	Туре	Coded levels		Actual levels			
			MA	L101	TSE screw speed	MA (wt%)	L101 (wt%)	Screw speed* (rpm)
1		F	-1	-1	-1	2	0.2	10
2	_++	F	-1	1	1	2	0.65	25
3	+_+	F	1	-1	1	7	0.2	25
4	++-	F	1	1	-1	7	0.65	10
5	000	С	0	0	0	4.5	0.425	18
6	000	С	0	0	0	4.5	0.425	18
7	+	F	-1	-1	1	2	0.2	25
8	-+-	F	-1	1	-1	2	0.65	10
9	+	F	1	-1	-1	7	0.2	10
10	+++	F	1	1	1	7	0.65	25
11	000	С	0	0	0	4.5	0.425	18
12	000	С	0	0	0	4.5	0.425	18
13	a00	А	-1.682	0	0	0.296	0.425	18
14	00a	А	0	0	-1.682	4.5	0.425	5
15	0a0	А	0	-1.682	0	4.5	0.047	18
16	0A0	А	0	1.682	0	4.5	0.803	18
17	A00	А	1.682	0	0	8.704	0.425	18
18	00A	А	0	0	1.682	4.5	0.425	30
19	000	С	0	0	0	4.5	0.425	18
20	000	С	0	0	0	4.5	0.425	18

Table 5.1 Coded and actual levels of the uniform precision rotatable CCD with three factors

Note: F, C, and A types = full factorial, center-full factorial, and axial factorial points, respectively.

\*The calculated actual screw speed levels of 17.5, 4.9, and 30.1 rpm were adjusted to 18, 5, and 30 rpm, respectively, to fit the actual capacity of the TSE.

#### 5.2.3 Reactive functionalization of PLA-g-MA

PLA resins were vacuum dried at 90 °C for 6 h, premixed with mixtures of ground MA and L101, and fed into the feed throat of a 32-mm counter-rotating conical TSE having a L/D ratio of 13:1 (C.W. Brabender<sup>®</sup> Instuments, Inc, South Hackensack, NJ). The barrel temperatures from the feed throat to the die were set at 165/185/185/165 °C. The two zones of the extruder were set at 185 °C to compromise between extensive thermal degradation of PLA and half-life time ( $t_{1/2}$ ) of L101 ( $t_{1/2} = 69$  s @ 180 °C) [16]. The formulations and TSE screw speed used were mentioned in Table 5. 1. The screw speeds (10, 18, and 25 rpm) correspond to approximate residence times at 185 °C of 6.5 ± 0.1, 4.5 ± 0.2, and 3.5 ± 0.2 min, respectively, which were measured by a simplified carbon black residence times methodology modified from Agur [17], to get complete decomposition of organic peroxide with no residuals [18].

The extrudates were cooled by air blowing, pelletized, and kept in an aluminum container at  $23 \pm 2$  °C and  $50 \pm 10\%$  RH until further testing. The controls (extruded PLA – ePLA) were prepared from PLA resins that were processed at the similar conditions without MA and L101. ePLA 10R is indicative of neat PLA which was extruded at a screw speed of 10 rpm, *etc.* PLA-*g*-MA and ePLA resins were vacuum dried at 130 °C for 24 h to evaporate unreacted MA and also complete cyclization (transform any diacid into the cyclic anhydride form) before characterization of grafted MA and film fabrication for FTIR measurements [19].

### 5.2.4 Film fabrication and FTIR spectroscopy

Approximately five gram of resins were vacuum dried at 130 °C for 24 h as mentioned and were fabricated into thin films using a M CARVER compression molder (Carver Laboratory Press, Menomonee Falls, Wisconsin). Dried resins were placed between poly(tetrafluoroethylene) (PTFE) sheets and preheated at 160 °C for 20 min, then pressed at 680 kg for 5 min, removed from the compression molder, placed between PTFE sheets with new metal plates, double wrapped with aluminum foil, and cooled down in a freezer ( $\sim$  -20 °C) for 15 min. Films were kept with desiccants in a desiccator for a few days before measuring the ATR-FTIR spectrum using an IR-Prestige 21 (Shimadzu, Columbia, MD) over the wavenumber range 4000-650 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> with 40 consecutive scans.

### 5.2.5 Amount of MA grafting

A titration method modified from Fowlks and Narayan and from Lee and Ohkita was used to determine the percentage of MA grafted on PLA [20-21]. Dried PLA-*g*-MA or ePLA  $(1.51 \pm 0.01 \text{ g})$  was dissolved in 150 mL of chloroform. Hydrochloric acid (1 M) 1.5 mL was added into the supernatant, which then was vigorously shaken for 45 min. Finally, the supernatant was precipitated with 700 mL of methanol, filtered, and vacuum dried at 80 °C for 15 h. The dried precipitant  $(1.20 \pm 0.05 \text{ mg})$  was dissolved in a mixed solution of chloroform and methanol (3/2 v/v). Phenolphthalein (8 to 10 drops) in ethanol (1% w/v) was added, and then the solution was titrated with 0.03 N standardized potassium hydroxide (KOH) in methanol. The end point was determined by using both color and pH. The ePLAs were used as controls. The acid number and grafted MA (%) were calculated as follows [22-23]:

Acid number (mg KOH/g) = 
$$V_{KOH} \times N_{KOH} \times 56.1 \div M_{sample}$$
 (2)

$$Grafted MH(\%) = Acid number \times 98 \div 2 \div 561$$
(3)

where  $V_{KOH}$  and  $N_{KOH}$ , were volume (mL) and normality of the standardize KOH, respectively

M<sub>sample</sub> was the weight of the sample in g.
#### 5.2.6 Molecular weight

PLA, ePLA, or PLA-*g*-MA resins ( $20 \pm 5 \text{ mg}$ ) were dissolved in 10 mL of HPLC grade THF (Pharmco-Aaper) at ambient temperature for three days. In case of incomplete dissolution, the solution was heated at 40 °C for several minutes, cooled, and then filtered through a 0.45 µm PTFE filter. The filtrate (100 µL) was injected into a Waters<sup>®</sup> gel permeation chromatography (GPC).The detail of GPC analysis was mentioned in Chapter 4. The number average molecular weight ( $M_n$ ), weight average molecular weight ( $M_w$ ), polydispersion Index (*PI*), and intrinsic viscosity (*IV*) of PLA resins, ePLA, and PLA-*g*-MA were determined using the Waters breeze GPC software. *K* (0.0174 mL·g<sup>-1</sup>) and  $\alpha$  (0.736) values of dilute PLA solution in THF at 30 °C were used in order to convert relative to absolute PLA molecular weight [24].

#### 5.2.7 Data analysis

The response variables of PLA-g-MA, which were grafted MA (wt%), molecular weight properties ( $M_n$ ,  $M_w$ , PI, and IV), and molecular weight stability of PLA-g-MA during storage ( $M_n$  reduction (%), PI increasing (%)), were fitted to a second order response surface model (equation 4) to estimate the response function and obtain a regression fit.

$$E\{Y\} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3$$

$$(4)$$

where  $E{Y}$  = Estimate response of interest

- $X_1$  = MA content (wt% on PLA basis)
- $X_2 =$  L101 content (wt% on PLA basis)

<i>X</i> <sub>3</sub> =	Screw speed of TSE (rpm)
$\beta_0 =$	Intercept
$\beta_1, \beta_2, \beta_3 =$	Linear main effects
$\beta_{11}, \beta_{22}, \beta_{33} =$	Quadratic main effects
$\beta_{12}, \beta_{13}, \beta_{23} =$	Interaction effects

JMP 8.0 and SAS<sup> $\mathbb{R}$ </sup> 9.2 ADX software programs (SAS Institute Inc., Raleigh, NC) were used to analyze and visualize the fitted models.

# 5.3 Results and discussion

## 5.3.1 Functionalized PLA resins (PLA-g-MA) and FTIR spectrum

The PLA-g-MA extrudates produced from different amounts of MA and L101, and differing TSE screw speeds had various colors from pale yellow to orange as shown in Figure 5.1. Unfortunately, 4 treatments: #14(00a, the lowest screw speed), #16 (0A0, the highest amount of L101), #17 (A00, the highest amount of MA), and #20 (000, the center point) could not be made due to unforeseen technical problem of TSE during production. However, this did not hinder the analysis of the information, which was evaluated as an incomplete CCD response surface methodology.

Figure 5.1 shows that the PLA extrudates changed from clear to yellow-orange colors after reactive grating; noticeably related to amounts of MA and L101 but not to the screw speeds (or residence times). The extrudates functionalized from the lowest amount of L101 (0.047 wt%, #15: 0a0) had a pale yellow color (Figure 5.1a); an increasing of L101 to 0.2 and 0.425 wt%

enhanced the yellowness (Figure 5.1b and 5.1c). PLA-*g*-MA extrudates produced using a high level of L101 (0.65 wt%) had a stronger yellow color than those produced using a low level of L101 (0.2 wt%) (Figure 5.1b and 5.1d). The use of the lowest MA amount (0.296 wt%, #13: a00) resulted in PLA-*g*-MA extrudates having a light yellow color (Figure 5.1e). Increasing MA content to 2, 4.5, and 7 wt% offered yellow extrudates without noticeable difference in colors (Figure 5.1f to 5.1h). It should be noted that extrudates produced using 2 wt% of MA and 0.65 wt% of L101 at either low or high screw speeds had the strongest color (orange, Figure 5.1d).



**Figure 5.1** PLA-*g*-MA resin produced from various MA/L101/screw speed: a) 0a0 b) --+ c) 000 d) -++ e) a00 f) --- g) 00A h) +--

The coloration of grafted polymers is an undesirable side reaction of free-radical melt grafting [14, 25]. Maliger *et al.* reported that colors of  $\text{Enpol}^{\mathbb{R}}$  functionalized with MA and dicumyl peroxide (DCP) varied from white to light-pink, dark-pink, brown, brownish-black, and black with an increasing of MA content from 0.5, to 1, 1.5, 2, 3, and 5 wt%, respectively [26].

The information of coloration is limited and less well understood [13]. Gaylord *et al.* mentioned that colored complexes resulting from an interaction of electron donor compounds with MA (a strong electron acceptor) could be reduced by using tri(nonylphenyl) phosphite (TNPP) [25]. However, TNPP also reduced the percentage grafting of MA with linear low-density polyethylene (LLDPE) from about 0.58-1.64 to 0.07-0.54 wt% [25]. The use of styrene as a comonomer improved MA grafting of HDPE from about 2.1-2.2 to 2.2-2.8 wt%, decreased gel content (crosslinking side reaction), and reduced its coloration [14].

The presence of MA grafted on PLA was identified by using FTIR measurements compared to neat PLA extruded at the same condition without MA and L101 (ePLA) (Figure 5.2). The new peak of PLA-g-MA films observed at 1849 cm<sup>-1</sup> was ascribed to the asymmetric C=O stretching of the succinic anhydride ring (or saturated cyclic anhydride ring) [27]. The peaks at 1794 and 1788 cm<sup>-1</sup> were indicative of symmetric C=O stretching of succinic anhydride end-groups and saturated cyclic anhydride symmetric C=O stretching of oligomeric end-grafting [27-28]. The absorbance peak at 1728 cm<sup>-1</sup> was also assigned to the symmetric C=O stretching of saturated cyclic anhydride rings, whereas the weak bands at around 1860 and 1716 cm<sup>-1</sup> could represent the asymmetric C=O stretching of saturated cyclic anhydride rings and carboxylic acid C=O stretching, respectively [29-31]. These peaks indicated that MA monomers were grafted onto the PLA backbone, during which MA was transformed to a saturated anhydride (succinic anhydride) [27].



Figure 5.2 FTIR spectra of PLA-g-MA and ePLA

Peaks at 1788 and 1849 cm<sup>-1</sup> belong to oligomeric end-grafting (Figure 5.3a); and peaks at 1794 and 1860 cm<sup>-1</sup> represent succinic anhydride end-grafting (Figure 5.3b), a desirable structure of grafted polymers [31-32]. Those chemical structures are the effective anhydride forms, which will interact with functional groups such as amine and hydroxyl of other polymers to improve their compatibility, adhesion, and/or paintability [11]. Whereas grafted maleic acids (Figure 5.3c) are acid forms obtained by hydrolysis of anhydride groups to carboxylic acids, these two forms are interchangeable by an addition or removal of water [33-34].



**Figure 5.3** Possible chemical structures of PLA-g-MA: a) oligomeric end-grafting; b) succinic anhydride end-grafting; c) carboxylic acid or maleic acid end-grafting, modified form Zhang *et al.* [35].

The presence of oligomeric end-grafting indicated that homopolymerization of MA occurred during maleation. Polymaleic anhydride (PMA) absorbs at 1784 cm<sup>-1</sup>; the shift of the peak to a higher wavenumber (*e.g.* 1788 cm<sup>-1</sup>) implies a shorter average length of grafted oligomer moieties [27-28]. PMA, which is a brittle, colored solid, and also is found in, *e.g.* commercial polypropylene grafted MA (PLA-*g*-MA), is an undesirable form of polymer grafted MA due to the resulting reduction in the number of chains available for adhesion or compatibilization [25, 31]. The use of bromomaleic anhydride (NBS) was suggested to change the grafting schemes and types of grafted PP from succinic and oligomeric end-grafting to inchain grafting of single succinic anhydride moieties (bridging type), which improves the degree of grafting, and reduces chain degradation [32].

# 5.3.2 Grafted MA and molecular weight properties of PLA-g-MA

The properties of PLA-*g*-MA, grafted MA content (wt%) and molecular weight, including *IV*, are presented in Table 5.2. In overview, there was an inverse linear correlation between grafted MA and molecular weights: PLA-*g*-MA with higher grafted MA possessed a lower  $M_n$ ,  $M_w$ , and *IV* and a broader molecular weight distribution (Figure 5.4a-b) (P < 0.05). The processing times and temperature did not have any significant impact on the molecular weight properties of ePLA resins ( $M_n$  of about 77.5 to 81.8 kDa, *PI* of 1.478 to 1.536, and *IV* of 0.918 to 0.932) compared to those of neat PLA resins ( $M_n$  of 81.0 kDa, *PI* of 1.512, and *IV* of 0.936) (P < 0.05). These results are in agreement with some previous research indicating that the dominant side reaction of PLA maleation prepared by free-radical melt grafting is degradation [10, 36-37]. The good correlation between an increase of grafted MA with reduction in  $M_n$  of PLA-g-MA indicated that the grafting sites might occur at the ends of molecular chains [38].

Run	Pattern	Grafted MA, wt%	<i>M<sub>n</sub></i> , kDa	<i>M<sub>w</sub></i> , kDa	PI	IV
1		$0.256 \pm 0.022$	$67.3 \pm 3.7$	$104.7\pm1.2$	$1.559\pm0.070$	$0.834 \pm 0.009$
2	<b>_</b> ++	$0.517\pm0.021$	$44.0\pm8.7$	$83.2\pm4.3$	$1.937\pm0.301$	$0.694\pm0.032$
3	+_+	$0.255\pm0.008$	$64.4\pm4.1$	$106.3 \pm 1.5$	$1.654\pm0.080$	$0.843\pm0.010$
4	++-	$0.499\pm0.016$	$47.8\pm6.9$	$86.7\pm6.9$	$1.828\pm0.149$	$0.718\pm0.045$
5	000	$0.397\pm0.004$	$54.1\pm4.5$	$93.2\pm2.4$	$1.729\pm0.099$	$0.760\pm0.017$
6	000	$0.356\pm0.013$	$53.9\pm3.9$	$93.2\pm2.3$	$1.733\pm0.088$	$0.760\pm0.016$
7	+	$0.222\pm0.016$	$69.1\pm7.3$	$109.1\pm6.5$	$1.583\pm0.067$	$0.860\pm0.040$
8	-+-	$0.466\pm0.015$	$40.0\pm5.2$	$83.5\pm12.7$	$2.091\pm0.176$	$0.694\pm0.081$
9	+	$0.190\pm0.011$	$54.3 \pm 15.7$	$97.5\pm13.8$	$1.868\pm0.384$	$0.786\pm0.089$
10	+++	$0.458\pm0.028$	$47.3\pm1.9$	$88.8\pm2.4$	$1.877\pm0.033$	$0.730\pm0.016$
11	000	$0.384\pm0.062$	$53.5\pm7.9$	$95.1\pm6.4$	$1.795\pm0.165$	$0.771\pm0.041$
12	000	$0.397\pm0.028$	$51.5\pm2.9$	$92.2\pm1.2$	$1.795\pm0.081$	$0.753\pm0.009$
13	a00	$0.148\pm0.003$	$61.0\pm5.9$	$101.9\pm2.7$	$1.679\pm0.116$	$0.815\pm0.018$
15	0a0	$0.054\pm0.015$	$73.8\pm8.5$	$114.9\pm2.6$	$1.571\pm0.157$	$0.896\pm0.018$
18	00A	$0.371\pm0.019$	$46.5\pm4.7$	$90.7\pm1.5$	$1.966\pm0.181$	$0.741\pm0.011$
19	000	$0.386\pm0.026$	$48.0\pm1.8$	$90.6\pm0.8$	$1.888\pm0.055$	$0.741\pm0.006$

Table 5.2 Grafted MA, molecular weight properties including IV of PLA-g-MA



**Figure 5.4** Molecular weight properties as a function of grafted MA compared with PLA and ePLA 10R, 18R, 25R, and 30R, the diagonal, two curved dotted lines, and two linear straight lines indicate the line of fit, 95% confident intervals, and prediction intervals: a) Grafted MA vs.  $M_n$ ; b) Grafted MA vs. *PI* 

Carlson *et al.* proposed that the chemical reactions occurring during free radical branching (PLA with L101) and maleation (PLA with L101 and MA) in extrusion were radical-induced branching, radical-induced crosslinking, grafting, radical-induced chain scission, backbiting, and thermohydrolysis [6, 39]. In addition a thermo-oxidative reaction could be involved in the reactive extrusion in this work since the reactive extrusion was performed without oxygen removal. Oxygen could also generate maleation (grafting of MA) and crosslinking, and enhance reactions initiated during reactive extrusion [40].

The maleation of PLA is performed when peroxides (in this work L101, a member of difunctional di-tertiary alkyl peroxide group) are thermolyticly decomposed into tertiary alkoxy radicals (RO•, primary radicals) (Scheme 5.1a) [41-42]. The decomposition of L101 is more complex as reviewed by Moad [13]. Furthermore, at high temperatures under conditions of poor radical scavenging ability, the tertiary alkoxy radicals undergo  $\beta$ -scission resulting in alkyl radicals (R•, secondary radicals) (Scheme 5.1b) [41]. When there is a high amount of peroxide in the environment, the tertiary alkoxy radicals also react, un-decomposing peroxides to form tertiary alkoxys (Scheme 5.1c). Both types of radicals have a potential for hydrogen abstraction, but the alkyl radicals have a propensity for addition to double bonds. Thus, the use of peroxide initiated alkoxy radicals is expected to reduce a side reaction, homopolymerization [13].



$$R-O' + H_3C \xrightarrow{CH_3} O \xrightarrow{CH_3} O \xrightarrow{CH_3} CH_3 \xrightarrow{CH_3} R-OH + H_3C \cdot HC \xrightarrow{CH_3} CH_2 + H_3C \xrightarrow{CH_3} O \xrightarrow{CH_3} CH_3$$



**Scheme 5.1** Possible reaction mechanisms for free-radical melt-grafting of MA onto PLA using L101 as peroxide initiator, modified from de Roover *et al.*, Avella *et al.*, Carlson *et al.*, Arkema Inc., and Yuan *et al.* [27, 36, 39, 41-42]

Next, the alkoxy radicals abstract hydrogen at the secondary carbon atoms from the PLA backbone; and MA reacts to trap those radicals formed on the PLA backbone and/or its chain ends (scheme 5.1d), which then may homopolymerize with other MAs, chain transfer (*i.e.* abstraction of hydrogen atoms from PLA or ROH) and undergo  $\beta$ -scission (scheme 5.1e or 5.1f and 5.1g), or combine with macroradicals [27, 39, 43]. The PLA radical backbone can also undergo  $\beta$ -scission (scheme 5.1h) or combine with other PLA radicals [39, 42]. The byproducts of those reactions (*e.g.* hydroxyl and carboxylic end groups and oligomers) including residual monomers enhance PLA thermal degradation, resulting in reduction of molecular weight and weight loss [6, 39, 44]. The parameters used to graft MA into PLA such as concentrations of MA and peroxides including residence times play an important role in the degree of grafting and molecular weight change of PLA-g-MA, as were identified via the RSM analysis and discussed below.

## 5.3.3 RSM model of grafted MA of PLA-g-MA

Table 5.3 shows the results of the regression coefficients after fitting the RSM equation 4 (second-order polynomial equation). The response, grafted MA, had R<sup>2</sup> value of 0.91, indicating a good response between the predicted model and experimental data in which 91% of the grafted MA variation was explained by the fitted model (Figure 5.5a). The significant lack-of-fit may result from high variability. However, this predicted model can be further used due to a good fit of R<sup>2</sup>, the proper residual, normal, and leverage plots without any violations (Figure 5.5b). The ANOVA indicated a highly significant effect of L101 (P < 0.01) and probable significance of MA (0.05 < P < 0.10). A linear increase of L101 improved the grafted amount of MA onto the PLA backbone as evidenced by the positive estimated parameter as well as the contour and

surface profiles (Figure 5.6a). Contrarily, an increase of MA from 0.296 to 4.5 wt% (PLA basis) improved the percentage of grafted MA, but after 4.5 wt% it declined (Figure 5.6a). There were no statistically significant effects of TSE and cross-products (interaction between main factors) on grafting of MA onto the PLA backbone (P > 0.10). An unaffected screw speed of TSE could imply that the minimum residence time used in this work (3.5 min at 185 °C) were sufficient to completely decompose L101 at any concentration. Thus, increase of the residence time (4.5 and 6.5 min at 185 °C) did not enhance degree of grafting.

**Table 5.3** Parameter estimates and significant regression models for molecular weight properties and viscosity of PLA-g-MA

Term	Grafted MA	M <sub>n</sub>	$M_w$	PI	IV
Intercept	0.3820***	52074.7***	92759.6***	1.791***	0.756***
MA	0.0054	-711.3	-266.2	0.002	-0.002
L101	0.1399***	-9414.5***	-9565.4***	0.128***	-0.062***
TSE screw speed	-0.0086	1833.5	2019.8***	-0.031	0.013**
MA x L101	0.0009	3607.6**	2343.8***	-0.088**	0.016***
MA x TSE	0.0017	479.9	837	-0.004	0.005
L101 x TSE	-0.0018	-1045.9	-1434.3**	0.010	-0.009**
MA x MA	-0.0578*	2868.8**	2841.7***	-0.046	0.018***
L101 x L101	-0.0112	2141.2	1793.4**	-0.009	0.011**
TSE x TSE	0.0234	-2960.8**	-2193.2***	0.073	-0.014***
R <sup>2</sup>	0.91	0.97	0.99	0.87	0.99
ANOVA, Prob>F	0.0166**	0.0009***	<0.0001***	0.0384**	<0.0001***
Lack of fit, Prob>F	0.0021***	0.3028	0.6382	0.1415	0.6584

Note: \*\*\*, \*\*, and \* indicate statistical significance at type I error ( $\alpha$ ) of 0.01, 0.05, and 0.10, respectively



**Figure 5.5** Regression analysis plots of grafted MA: a) experimental vs. predicted values, the diagonal and two curved dotted lines indicate a line of fit and 95% confident intervals;

b) residual by predicted plot



**Figure 5.6** Contour (left graph) and surface (right graph) profilers illustrated effects of variables on grafted MA: a) L101 vs. MA; b) MA vs. TSE screw speed; c) L101 vs. TSE screw speed

Figure 5.6 (cont'd)



An increase in L101 content was expected to improve the percentage of grafted MA since the primary radicals of L101, generated by thermal decomposition during extrusion, initiated the available grafting sites on the PLA backbone. As a consequence, MA monomers readily react and trap those radical sites resulting in an increase of grafted MA onto the PLA backbone. Hence, the more peroxide initiator content is used, the more radical sites are available to interact, and the higher grafted MA is obtained. However, the results indicated that the amount of MA had an optimum limit, 4.5 wt%. It is known that the efficiency of MA on trapping the radical sites of macroradicals (polymer backbone) relies on viscosity, polarity, and solubility between monomer and polymer [13, 45-46]. The decrease of grafted MA beyond the critical (optimum) concentration of MA content is accounted for by an induced phase separation of MA and

polymer. As a consequence, side reactions (*e.g.* chain degradation, homopolymerization of MA, discoloration, and crosslinking) or terminal reactions take place [13, 45, 47].

Similar results that peroxide initiators had more significant effect on grafted MA than MA content was observed from the melt-maleation of ethylene-propylene-diene terpolymer using 2,5-dimethyl-2,5-di-(*t*-butylperoxy)hexane as a peroxide initiator [45], maleation of PBAT using L101 as a peroxide initiator [30], and maleation of PP using 2,5-dimethyl-2,5-di(*t*-butylperoxy) hexane [48]. At this point, the use of MA of  $\leq$  4.5 wt% and L101 of 0.65 wt% is preferable for functionalization of MA onto PLA at any screw speed (10 to 30 rpm) or residence time (3.5 to 6.5 min). However, the effect of MA, L101, and screw speed on side reactions as a function of molecular weight will be considered and discuss in the following section.

# 5.3.4 RSM models of molecular weight properties of PLA-g-MA

Table 5.3 shows that the RSM regression analyses provide a good fit of the experimental data and the predicted models for  $M_n$ ,  $M_w$ , PI, and IV of 0.97, 0.99, 0.87, and 0.99, respectively. Additionally, the non-significant lack-of-fit suggested that the fitted RSM models were adequate. Since the PI, IV, and  $M_w$  are correlated to  $M_n$ , only the  $M_n$  and PI will be discussed further in detail (Figure 5.7).



**Figure 5.7**. Actual and predicted value plots of  $M_n$  and PI, the diagonal and two curved dotted lines indicate a line of fit and 95% confident intervals: a) experimental values of  $M_n$  vs. predicted values; b) experimental values of PI vs. predicted values

L101 had a highly significant effect on  $M_n$  of PLA-g-MA (P < 0.01); increasing L101 content decreased  $M_n$  of PLA-g-MA (Table 5. 3). Quadratic main effect of MA and interaction of MA with L101 depict positive significant on  $M_n$  of PLA-g-MA, whereas quadratic main effect of TSE provides adversely significant impact (P < 0.05). The contour and surface profiles of MA vs. L101 on  $M_n$  clearly illustrate that at a low concentration of MA, the reduction of  $M_n$  was almost linear with increasing L101 (Figure 5.8a). At a high concentration of MA, the reduction of  $M_n$  occurred gradually. Interestingly, at a high concentration of L101, increasing MA retarded and protected against the degradation of the PLA backbone, *i.e.* PLA-g-MA produced using 2 wt% MA and 0.65 wt% L101 had  $M_n$  of about 40 to 44 kDa, whereas PLA-g-MA maleated using 7 wt% MA and 0.65 wt% L101 had  $M_n$  of about 48 kDa (Table 5.2). The TSE screw speed of around 20 rpm provided the minimum reduction of  $M_n$ .



**Figure 5.8** Contour and surface profilers illustrated effects of variables on  $M_n$  of PLA-g-MA: a) MA vs. L101; b) TSE screw speed vs. L101; c) TSE screw speed vs. MA;

Figure 5.8 (cont'd)



The reduction of PLA-g-MA's  $M_n$  at a low concentration of MA (especially with increasing the amount of L101) could be attributed to an increase of primary radicals from the presence of L101. Under the condition of limited MA, the primary radicals had insufficient MA to react with, so the main reaction was driven to  $\beta$ -scission of the PLA backbone (scheme 5.1h). This reaction is fast and preferable at high temperature especially with high peroxide initiators; therefore, the more peroxide initiators were used the faster the reactions, and the higher the PLA degradations [27]. An increase in MA enhanced the competitions between radicals trapped by MA (maleation) and the  $\beta$ -scission reaction of PLA backbone. However, the chain transter reactions of grafted succinic acid radicals after maleation resulted in alkoxy radicals or macroradicals (scheme 5.1f), which can go through  $\beta$ -scission [31].

At a high concentration of MA with a low level of L101, the degradation of PLA chains was slower than the degradation at low concentration of MA. This can be attributed to the limited amount of primary radicals, thus limiting the available grafting sites. Again, grafted succinic acid radicals obtained after maleation abstract secondary hydrogen atoms from the PLA backbone, leading to  $\beta$ -scission of the backbone. Increasing the L101 concentration generated more available grafting sites on the PLA backbone, more maleation reactions, more chain transfer and  $\beta$ -scission reactions, and in addition more probability of recombination [43]. The competition between those reactions resulted in a gradual decrease in  $M_n$  of PLA-g-MA and finally slightly increased of  $M_n$ .

As mentioned, the high concentration of MA could induce phase separation between MA and PLA. Thus, in the MA phase, a high concentration of MA and the presence of peroxide initiator at high concentration, the homopolymerization of MA (scheme 5.1e) and discoloration could take place [14, 45]. In the polymer phase with a high concentration of L101, the competition between  $\beta$ -scission, chain transfer, and combination reactions could happen. To minimize the degradation of PLA backbone during maleation, the reactive extrusion should be adjusted to about 20 rpm. Either a higher or a lower screw speed under high concentration of MA and L101 could enhance the chain degradation of PLA-g-MA.

Interestingly, there is no significant effect of TSE screw speed on the distribution of PLA-g-MA molecular weight (*PI*) (Table 5.3). But the increase of the PLA-g-MA's *PI* values was highly significant with an increased L101 content (P < 0.01) (Figure 5.9a). An interaction of MA with L101 accounted for a lower *PI* values (P < 0.05) which was more pronounced at a high concentration of MA (Figure 5.9a). This result showed that chain degradation of PLA backbone is a dominant reaction of PLA maleation obtained by using L101. The addition of MA may help

narrow the molecular weight distribution via grafting, chain transfer, and combination as mentioned.



**Figure 5.9** Contour and surface profilers illustrated effects of variables on *PI* of PLA-*g*-MA: a) L101 vs. MA; b) TSE screw speed vs. MA; c) TSE screw speed vs. L101

Figure 5.9 (cont'd)



Hence, functionalization of PLA with high amounts of MA and L101 should not be a feasible choice since the product, PLA-*g*-MA, will contain high impurities (*e.g.* unreacted MA, homopolymer of MA, undesirable color) and low grafting efficiency (*e.g.* PLA-*g*-MA functionalized from 2 wt% of MA and 0.65 wt% of L101 having 0.47 to 0.52 wt% of grafted MA, whereas PLA-*g*-MA functionalized from 7 wt% of MA and 0.65 wt% of L101 having 0.46 to 0.50 wt% of grafted MA). Those lower grafted amount of MA onto PLA cannot compromise with an increase of  $M_n$  of PLA-*g*-MA from around 42 kDa (2 wt% MA and 0.65 wt% of L101) to 48 kDa (7 wt% MA and 0.65 wt% of L101). The use of MA content not higher than 4.5 wt%, L101 content less than 0.65 wt%, and screw speed of 20 rpm appear to produce the optimum PLA-*g*-MA.

## 5.3.5 PLA-g-MA's molecular weight during storage

The molecular weight properties of PLA-*g*-MA resins and extrudates – kept in aluminum containers or wrapped with aluminum foil, under controlled atmosphere (23 ± 2 °C and 50 ± 10% RH) — were unstable. PLA-*g*-MA after 10-month storage had lower  $M_n$  and higher *PI* than those of PLA-*g*-MA after production, whereas  $M_n$  and *PI* of ePLA did not change after 10-month storage. The reduction of PLA-*g*-MA's  $M_n$  can be related to the initial amounts of MA and L101 (*i.e.* the higher MA content the higher the  $M_n$  degradation, which could be divided into three groups from high to low levels – PLA-*g*-MA produced from 7 wt% MA, PLA-*g*-MA produced from 4.5 wt% MA including 0a0 and 00A, and PLA-*g*-MA produced from 2 wt% MA including a00 (see Figure 5.10a). The degree of  $M_n$  reduction within each group was related to the amount

of L101 used: the lower the L101 amount the higher the  $M_n$  reduction. The increased PI can be correlated with the lower content of L101 used, and the higher PI obtained (Figure 5.10b).

Run	Pattern	<i>M<sub>n</sub></i> reduction, %	PI increasing, %
1		32.2	15.9
2	_++	-2.1	-7.3
3	+_+	84.3	51.1
4	++-	68.6	7.5
5	0	59.4	20.0
6	0	50.0	10.5
7	+	15.5	0.9
8	-+-	-7.9	-14.8
9	+	76.2	21.7
10	+++	65.7	-2.4
11	0	53.2	4.8
12	0	44.1	2.7
13	a00	10.4	8.9
15	0a0	68.9	71.2
18	00A	57.1	4.1
19	0	54.3	12.8
	ePLA10R	-0.2	0.1

**Table 5.4**.  $M_n$  and PI values of PLA-g-MA after 10-month storage



Figure 5.10 Changes of PLA-g-MA molecular weight properties based on initial amounts of MAand L101 used:a)  $M_n$  reduction;b) PI increasing

The molecular weight instability of PLA-g-MA (lower  $M_n$  and higher PI) is dramatically changed when low to mid levels of L101 were used ( $\leq 0.425$  wt%). Furthermore, the instability of molecular weight is more pronounced when medium to high levels of MA were used ( $\geq 4.5$ wt%). The excess radicals or active species generated during free-radical melt grafting by extrusion account for auto-degradation of the polymeric backbone during storage. To the best of the author's knowledge, information about the stability of maleated polymers after extrusion and production is limited.

Continho and Ferreira investigated effects of antioxidants and peroxide initiators on grafting efficiency and initiator oxidative index of rubbers containing diene and propylene modified with MA [49]. They reported that under a high concentration of MA (5 phr) antioxidants reduced grafting efficiency, whereas the use of peroxide initiators influenced oxidative index but not grafting efficiency, and the use of a suitable initiator to control oxidative index was more appropriate than addition of antioxidant. It was also reported that PP-g-MA is photo-oxidized and the use of stabilizer is more effective to inhibit thermal- and photo-oxidations of PP but not effective enough for protection of PP-g-MA [50]. More investigation and information is essential to produce PLA-g-MA with optimum and stable properties.

This work demonstrated the use of an RSM design to investigate the effects of MA and L101 content, and TSE screw speed (in turn, residence time) on maleation of PLA. It also helped to indicate the optimum boundaries for PLA maleation via three main categories, which are:

1. Degree of grafted MA on PLA increased with an increase of L101 content and reached a maximum amount with MA content  $\leq$  4.5 wt%.

2. The dominant side reaction, chain degradation, was with an increase L101 and slightly slowed with addition of MA at the expense of MA homopolymerization and discoloration. Thus,

the amounts of MA, L101, and screw speed were framed at  $\leq$  4.5 wt%, < 0.65 wt%, and 20 rpm, respectively.

3. The molecular weight of PLA-g-MA was not stable during storage. The reduction of  $M_n$  and increase of *PI* were sensitive to the initial MA content higher than 4.5 wt% and L101 content higher than 0.425 wt%.

A final question remain unanswered, which is the minimum degree of grafted MA content and the minimum  $M_n$  of PLA-g-MA that effectively facilitates compatibilization of PLA and improves the mechanical property of the final polymer blends. The effects of  $M_n$  and grafted MA content of PLA-g-MA on reactive compatibilization of binary and ternary blends are reported in Chapter 6

#### 5.4 Conclusions

PLA-g-MA— functionalized from MA content of 0.296 to 7 wt%, L101 content of 0.047 to 0.65 wt%, and TSE screw speed of 10 to 30 rpm obtained by RSM design — had percentage of grafted MA of 0.054 to 0.517 wt% and  $M_n$  of 40 to 73.8 kDa. FTIR peaks at 1860, 1849, 1794, 1788, 1728, and 1716 cm<sup>-1</sup> were indicative of grafted succinic anhydride, oligomeric end-grafting, and maleic acid end-grafting. Yellow and orange colors were enhanced with an increase of L101 and MA content. L101 exhibited highly significant effects on every property: increasing L101 content improved the degree of grafted MA, increased *PI*, and enhanced chain degradation. The optimum concentrations of MA for improving maleation were limited to below or equal to 4.5 wt%, but high MA content decreased *PI* and retarded chain degradation. TSE screw speed had impact only on  $M_n$  with the optimum value predicted at 20 rpm. The boundary

concentrations of MA, L101, and TSE screw speed, which were established considering the grafted MA content, molecular weight, and stability during storage are MA content of  $\leq 4.5$  wt%, L101 content between 0.425 and 0.65 wt%, and TSE screw speed of 20 rpm. The PLA-*g*-MA produced could be used for reactive compatibilization or adhesion of PLA blends and/or (nano)composites.

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# CHAPTER 6: INVESTIGATION OF THE EFFECTS OF MOLECULAR WEIGHT AND GRAFTED MA OF PLA-g-MA ON THE REACTIVE COMPATIBILIZATION OF TPCS/PLA BLENDS

## 6.1 Introduction

PLA, a biobased, recyclable and biodegradable polymer, is mostly used to replace commercial petroleum-based polyesters whenever ecosystem and environmental issues are a concern. PLA, a stiff and brittle material having mechanical properties comparable to PS, is widely used in many applications such as packaging, textile, medical, automobile, and environmental [1]. However, some properties such as low elongation at break, poor flexibility and toughness, low HDT, and slow nucleation, crystallization, and biodegradation rates limit some of its uses [2]. Blending of PLA with other polymers is one of the most cost-effective methodologies to tailor-make the desired properties of the blend in a commercial production. The blends of PLA with nonbiodegradable polymers (*e.g.* polyolefins, vinyl and vinyldene, elastomers and rubbers), biodegradable polymers (*e.g.* polyanhydrides, aliphatic polyesters, aliphatic-aromatic copolyesters, lipids, proteins, carbohydrates), and plasticizers are reviewed elsewhere [3-4].

Starch is one of the best candidate polymer pairs whenever cost, renewable resources, and biodegradability are involved. Starch acts as a nucleating agent enhancing the crystallization rate of PLA [4]. Furthermore, the use of thermoplastic starch (TPS) imparts flexibility and ductility to PLA. However, PLA, a hydrophobic material, and starch, a hydrophilic material, have different chemical structures, resulting in different surface energies and in compatibility. It was previously shown in Chapter 4 that the surface energies of PLA and TPCS having 30 wt%

glycerol are about 50 and 66 mJ·m<sup>-2</sup>, respectively. As a consequence, the physical blends of TPCS/PLA made by extrusion melting exhibited work adhesion and interfacial tension of around 108 and 8 mJ·m<sup>-2</sup>, respectively, indicating the physical blends of TPCS/PLA are incompatible producing immiscible blends. TEM micrographs of the physical blend films of TPCS/PLA fabricated by cast extrusion showed coalescence of TPCS domains in the PLA matrix.

Reactive compatiblization is an effective tool to improve compatibility of polymer pairs [5]. The first step, functionalization, is generating reactive polymers by mixing of functional groups (*e.g.* anhydride, isocyanate, and epoxide), suitable initiators (*e.g.* peroxide), and non-reactive polymers. The last step, reactive blending, occurs when the reactive polymer forms a graft copolymer with the polymer pair directly at their interfaces. As a consequence, interfacial tension of the two immiscible phases is decreased, and interfacial adhesion improves, resulting in a finer and more uniform/stable morphology as well as facilitating stress (energy) transfer between the two phases, improving their mechanical properties [6]. Among the functional groups, MA, a polar monomer, is preferably used due to its low toxicity, high reactivity, low potential to polymerize itself under free radical grafting conditions, and ease of handling [7-8].

The use of grafted MA for reactive compatibilization of TPS or starch and biodegradable polymers is mentioned elsewhere; some works showed the effects of grafted MA levels (amounts) on properties of starch or TPS and other polymers (*e.g.* PLA, PBAT, PCL, Enpol<sup>®</sup>, PP, PE), in which the grafted MA levels usually referred as initial content or amount of MA and peroxides than as grafted MA content [7-16]. Furthermore, the effects of molecular weights of functionalized polymers on properties of starch or TPS and other polymers have rarely been investigated. Although, improvement in properties due to use of functionalized polymers having

higher molecular weight have been reported to involve, *i.e.*, finer and more stable morphology of polystyrene (PS)/PS grafted MA/polyamide 6, and an increase of storage moduli of maleinized soybean oil triglycerides/epoxidized soybean oil triglycerides/PP grafted MA blends [17-18].

Therefore, in this work, PLA-g-MA having differences in grafted MA levels and/or molecular weight were generated using a TSE. PLA-g-MA properties were examined, and their effects in terms of grafted MA levels and/or molecular weight on properties and morphology of the reactive binary and ternary blends of TPCS and PLA were investigated compared to those of PLA and the physical blend.

## 6.2 Experimental

#### 6.2.1 Materials

Ingeo<sup>TM</sup> Biopolymer 2003D (PLA) was provided by NatureWorks LLC (Minnetonka, MN). Tapioca starch (cassava starch) was kindly donated by Erawan Marketing LTD (Bangkok, Thailand). Food grade glycerol (> 99%), maleic anhydride (MA, 95%), and 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (Luperox 101 or L101, 90%) were obtained from Sigma-Aldrich Chemical Company, Inc. (Milwaukee, WI). Chemically modified polypropylene, PP-*g*-MA, containing 0.5 wt % of MA (Polybond<sup>®</sup> 3150) was donated by Chemtura Inc. (Middlebury,

CT). All materials and/or chemical agents were used as received or as mentioned.

## 6.2.2 Compounding of TPCS

70/30 TPCS material was compounded in a co-rotating TSE (CENJURY ZSK-30) as mentioned in Chapter 3. The extruded strands were kept in an aluminum container at  $23 \pm 2$  °C and  $50 \pm 10\%$  RH.

#### 6.2.3 Reactive functionalization of PLA and determination of grafted MA on PLA

PLA resins, dried in a vacuum oven at 90 °C for 6 h, were premixed with ground MA and L101. The reactive functionalization of PLA was performed in a 32-mm counter-rotating conical TSE (C.W. Brabender Instruments). The processing temperatures and screw speeds of TSE were set to get complete decomposition of L101 ( $t_{1/2} = 69$  s @ 180 °C) with no residual and minimize thermal degradation of PLA [19-20]. [The detail of TSE and processing temperature are found in Chapter 5, whereas the compositions and screw speeds used are listed in Table 6.1. The weight percentages of MA and L101 used were based on PLA weight. After reactive functionalization, the extruded strands were cooled by blown air, pelletized, and kept in an aluminum container at 23 ± 2 °C and 50 ± 10% RH.

Sample	MA, wt%	L101, wt%	TSE screw speed, rpm
PLA-g-MA A	4.5	0.047	18
PLA-g-MA B	2	0.2	10
PLA-g-MA C	4.5	0.425	18
PLA-g-MA D	2	0.65	10
PLA-g-MA E	2	0.65	25
PLA-g-MA F	7	0.65	10

 Table 6.1 Sample composition and screw rotary speed of functionalized PLA

To determine the percentage grafting of the functionalized PLA (PLA-g-MA), the PLAg-MA resins were vacuum dried at 130 °C for 24 h to remove unreacted MA, purified and hydrolyzed to convert the anhydride groups into carboxylic acid groups, and then titrated. Details of this methodology are described in Chapter 5.

### 6.2.4 Reactive blending of binary and ternary polymers

For binary polymer blending, PLA or PLA-*g*-MA resins were blended with TPCS resins at the ratio of 70/30 by weight. Before blending, PLA, PLA-*g*-MA, and TPCS resins were dried under vacuum conditions at 90 °C for 6 h, 130 °C for 24 h, and air dried at 60 °C for two days, respectively. The dried resins were premixed and then fed in a vertical mini, co-rotating TSE (DSM Micro 15 compounder). The molten extrudates were shaped into disk, bar, and dumbbell specimens using a mini injection molder TS/-02 DSM. The extrusion and injection conditions are listed in Table 6.2, with the conditions for PLA resins provided for comparison. Sample 7PT, a non-reactive or physical blend, was a blend of PLA and TPCS, while samples 7rPT A, B, C, and D identified the reactive blends, the blends of TPCS with PLA-*g*-MA A, B, C, and D, respectively.

Sample	Extrusion condition: temperature profile, screw speed, and residence time	Injection molding condition: temperatures of transfer tube/mold, mold residence time, injection pressure)
PLA	190/190/190 °C, 100 rpm, 5 min	190 °C/38 °C, 10 s, 145 psi
7PT	172/172/172 °C, 100 rpm, 5 min	173 °C/38 °C, 10 s, 150 psi
7rPT A	167/167/167 °C, 100 rpm, 5 min	168 °C/38 °C, 10 s, 140 psi
7rPT B	167/167/167 °C, 100 rpm, 5 min	168 °C/38 °C, 10 s, 120 psi
7rPT C	160/160/160 °C, 100 rpm, 5 min	162 °C/38 °C, 10 s, 140 psi
7rPT D	160/160/160 °C, 100 rpm, 5 min	162 °C/38 °C, 10 s, 100 psi

**Table 6.2** Extrusion and injection molding conditions of PLA, physical blend (7PT), and reactive binary blends (7rPT A, B, C, and D)

Ternary polymer blending was also performed in the DSM Micro 15 compounder. Dried PLA, PLA-*g*-MA or PP-*g*-MA, and TPCS resins were weighed and mixed at various ratios (Table 6.3). The extrusion and injection conditions are showed in Table 6.3. The MA content in the reactive blends is weight of MA based on PLA and PLA-*g*-MA.

PLA/PLA-g-MA or PP-g-MA/TPCS by weight	Extrusion condition	Injection molding condition
63/7/30	172/172/172 °C, 100 rpm, 5 min	172 °C/38 °C, 10 s, 145 psi
56/14/30	172/172/172 °C, 100 rpm, 5 min	172 °C/38 °C, 10 s, 130 psi
35/35/30	168/168/168 °C, 100 rpm, 5 min	169 °C/38 °C, 10 s, 110 psi
14/56/30	162/162/162 °C, 100 rpm, 5 min	162 °C/38 °C, 10 s, 95 psi

**Table 6.3** Extrusion and injection molding conditions of reactive ternary blends

## 6.2.5 Molecular weight

PLA or PLA-*g*-MA resins (20 ± 5 mg) were dissolved in 10 mL of HPLC grade THF at ambient temperature for three days. In case of incomplete dissolution, the solution was heated at 40 °C for several minutes, cooled, and then filtered through a 0.45 µm PTFE filter. 100 µL of filtrate was injected into Waters<sup>®</sup> (Waters Inc.). The detail of this methodology is explained in Chapter 4, and *K* (0.0174 mL  $\cdot$  g<sup>-1</sup>) and  $\alpha$  (0.736) values of dilute PLA solution in THF at 30°C were used in order to obtain accurate molecular weights [21].

## 6.2.6 ATR-FTIR spectroscopy

ATR-FTIR spectra of PLA and all blends in the form of disk specimens were acquired using an IR-Prestige 21 (Shimadzu) equipped with an ATR attachment from PIKE Technologies. The disk specimens were kept with desiccant for over a week, then the absorbance spectra were measured over the wavenumber range 4000-650 cm<sup>-1</sup> at a resolution of 4 cm<sup>-1</sup> with 40 consecutive scans. Three specimens were evaluated for each sample.

## 6.2.7 Thermal properties

TGA and DTG thermograms were obtained using a TGA 2950 (TA Instruments). The disk specimens were cut, weighed ~13-18 mg, and tested using a temperature range of 30-600 °C at a heating rate of 10 °C ·min<sup>-1</sup> under a nitrogen atmosphere. Three replicates were tested for each sample. Thermal degradation temperatures at five percent weight loss ( $T_{d5}$ ) from TGA curves and onset ( $T_o$ ), maximum ( $T_{max}$ ), and end decomposition ( $T_e$ ) were observed from the DTG curves.

DSC (TA instruments) equipped with a refrigerated cooling system was used to determine the  $T_g$ ,  $T_{cc}$ , and  $T_m$  from the second heating scan, and  $T_c$  from the cooling step. Disk specimens of 8-10 mg were cut and weighed accurately. The blend samples were heated from 25 to 175 °C for the first heating scan, held at 175 °C for 3 min, cooled to -50 °C, and reheated to 180 °C for the second heating scan. The analyses were conducted with a ramp rate of 10 °C ·min<sup>-1</sup> under nitrogen atmosphere. Three replicates were evaluated for each sample. PLA and PLA-g-MA were tested under the same conditions except those samples were cooled to 0 °C. The degree of crystallinity ( $X_c$ ) of PLA-g-MA or PLA in the blends was calculated according to the following equation:

$$X_{c} = \left(\frac{\Delta H_{m} - \Delta H_{cc}}{\Delta H_{f}^{*}}\right) / \varphi \times 100$$

where  $\Delta H_m$  and  $\Delta H_{cc}$  are enthalpies of melting and cold crystallization, respectively  $\Delta H_f^*$  is the enthalpy of fusion of a PLA crystal of infinite size, which is 93 J·g<sup>-1</sup> [22]  $\phi$  is the weight fraction of PLA-g-MA or PLA in the blends, or weight fraction of MA in PLA-g-MA

## 6.2.8 Dynamic mechanical analysis (DMA)

The measurement of the storage or elastic modulus (E') and loss or viscous modulus (E'') and tan delta  $(tan \ \delta)$  as a function of time was conducted in a single cantilever mode using a DMA Q800 (TA Instruments, New Castle, DE). Bar specimens with dimensions of about 30 mm × 12.7 mm × 3 mm were conditioned at 23 ± 2 °C and 50 ± 5% RH for not less than 60 h. Specimens were cooled from room temperature to -100 °C at a ramp rate of 10 °C·min<sup>-1</sup>, held for 2 min, and heated to 120 °C at the rate of 3 °C·min<sup>-1</sup>. The frequency and oscillation amplitude were 1 Hz and 30 µm, respectively. Three specimens were evaluated for each sample.

#### 6.2.9 Electron microscopy

A variable pressure scanning electron microscope (VP-SEM) EVO<sup>®</sup> LS25 (Carl Zeiss NTS, LLC, Peabody, MA) was used to evaluate fractured surfaces of PLA and the blend specimens. The bar specimens were immersed in liquid nitrogen and then fractured. The fractured samples were mounted on aluminum stubs using adhesive tape. The micrographs were imaged under extended pressure at various magnifications.

SEM was also used to investigate the morphology of etched samples which were prepared as following. The bar specimens were notched using a notching cutter (Testing Machines Inc., Islandia, NY) and impact fractured with a 2.268-kg pendulum at ambient temperature. The impact fractured samples were etched using hydrochloric acid (HCl, 6 N) for 3 h to remove the TPCS phase, generating surface contrast [23]. The etched samples were air dried

in a hood, kept with desiccant for at least one day, mounted on aluminum stubs with carbon adhesive tape, and then gold-coated using an Emscope SC500 sputter coater (Emscope Laboratories Ltd., Ashford, UK). SEM images were obtained with a SEM JSM 6400 (JOEL) at magnifications x3000 and accelerating voltage of 10 kV.

## 6.2.10 Tensile properties

Tensile properties of dumbbell specimens with gage dimensions of 30 mm x 12.7 mm x 3 mm and initial grip distance of 25.4 mm were evaluated using a Universal Testing Machines (United Calibration Corp. and United Testing Systems Inc., Huntington Beach, CA). Specimens were conditioned at  $23 \pm 2$  °C and  $50 \pm 10\%$  RH for not less than 48 h. The measurement was carried out with a load cell of 4.45 kN, a crosshead speed of 2.54 mm·min<sup>-1</sup>, and at least five specimens were evaluated for each sample.

#### 6.2.11 Statistical analysis

ANOVA and statistical mean comparisons using Tukey's HSD (Honestly Significant Difference) were analyzed by using  $JMP^{\mathbb{R}}$  8 software program from SAS Institute Inc.

## 6.3 Results and discussion

#### 6.3.1 Properties of PLA-g-MA used in binary blends

PLA-g-MAs with different  $M_n$  (*i.e.* about 70, 50, and 30 kDa) were used to blend with TPCS at the ratio of 70/30 (w/w). The molecular weight, grafting (%), and thermal properties of the PLA-g-MAs are listed in Table 6.4. PLA-g-MA C that had  $M_n$  similar to PLA-g-MA B (about 50 kDa), was specially used to investigate the effects of MA content (functionality levels) on the properties of the reactive binary blends (*i.e.* PLA and TPCS) at a particular  $M_n$ . Since the dominant side reaction during melt free radical grafting is a degradation of the polymer backbone or chain scission [24-25], PLA-g-MA with a higher degree of grafting had lower molecular weights and higher *PI* value (Table 6.4). The *IV* values of PLA-g-MAs are better correlated to the  $M_w$  than to the  $M_n$  and *PI* values; the higher  $M_w$  raised the *IV*. A detailed discussion of the effects of MA, L101, and screw speed (residence time) on the molecular weight properties and stability of the functionalized PLA including the optimum processing variable values for producing maleated PLA can be found in Chapter 5.

	PLA	PLA-g-MA A	PLA-g-MA B	PLA-g-MA C	PLA-g-MA D
<i>M<sub>n</sub></i> , kDa	$81.0 \pm 8.8^{a}$	$70.1 \pm 1.2^{a}$	$51.1 \pm 2.9^{b}$	$51.4 \pm 3.3^{b}$	$31.9 \pm 2.0^{\circ}$
$M_{W}$ , kDa	$121.5 \pm 2.6^{a}$	$110.5 \pm 1.4^{b}$	$87.7 \pm 4.3^{c}$	$90.7 \pm 1.4^{c}$	$61.6 \pm 0.6^{d}$
PI	$1.51 \pm 0.14^{a}$	$1.58\pm0.01^{ab}$	$1.71 \pm 0.02^{abc}$	$1.77 \pm 0.09^{bc}$	$1.94 \pm 0.10^{\circ}$
IV	$0.94 \pm 0.02^{a}$	$0.87\pm0.01^{b}$	$0.73 \pm 0.03^{c}$	$0.74 \pm 0.01^{c}$	$0.55\pm0.00^d$
Grafting, %	$0^{a}$	$0.05\pm0.01^b$	$0.26 \pm 0.02^{c}$	$0.40\pm0.00^d$	$0.47 \pm 0.02^{e}$
<i>Tg</i> , °C	$62.3 \pm 0.3^{a}$	$62.5 \pm 0.7^{a}$	$62.1 \pm 0.5^{a}$	$61.5\pm0.3^{ab}$	$60.9 \pm 0.3^{b}$
$T_{cc}$ , °C	$118.7 \pm 0.6^{a}$	$127.2 \pm 1.0^{b}$	$130.5 \pm 0.4^{c}$	$134.6 \pm 1.1^{d}$	$133.6 \pm 1.2^{d}$
$T_m$ , °C	$152.7 \pm 0.8^{a}$	$154.5 \pm 1.1^{ab}$	$154.6\pm0.8^{ab}$	$155.2 \pm 0.1^{b}$	$154.1 \pm 0.4^{ab}$
Crystallinity, %	$2.0\pm0.9^{ab}$	$3.0 \pm 0.6^{a}$	$0.5 \pm 0.2^{b}$	$0.7 \pm 0.1^{b}$	$1.3 \pm 0.5^{b}$
<i>Td5</i> , °C	$364.6 \pm 0.7^{a}$	$365.0 \pm 2.6^{a}$	$364.7 \pm 1.5^{a}$	$356.6 \pm 4.5^{b}$	$355.9 \pm 0.3^{b}$
<i>T₀</i> , °C	$363.9 \pm 1.5^{a}$	$365.2 \pm 4.4^{a}$	$365.4 \pm 3.1^{a}$	$362.6 \pm 4.4^{a}$	$361.2 \pm 3.4^{a}$
$T_{max}$ , °C	$407.4 \pm 3.0^{a}$	$408.9 \pm 2.1^{a}$	$410.2 \pm 1.4^{a}$	$409.8 \pm 3.4^{a}$	$409.3 \pm 1.5^{a}$
<i>T</i> <sub>e</sub> , °C	$417.3 \pm 3.4^{a}$	$420.9 \pm 3.8^{a}$	$421.5 \pm 2.1^{a}$	$419.0 \pm 4.2^{a}$	$421.6 \pm 2.7^{a}$

Table 6.4 Properties of PLA-g-MA\* for reactive binary blends, PLA was used for comparison

Note: \*PLA-g-MA A, B, C, and D were the resins after about five-month production

Numbers followed by the same letter within a row are not statistical significant different at  $P \le 0.05$ 

PLA and PLA-g-MAs did not show crystallization peaks during cooling at 10 °C·min<sup>-1</sup>, indicating slow crystallization of both samples. The  $T_{cc}$  values of PLA-g-MAs significantly increased with an increase of grafted MA and then gradually leveled off (Table 6.4). The  $T_g$ values of PLA-g-MAs slightly decreased from 62.5 to 60.9 °C with high MA content and all PLA-g-MAs had  $T_m$  values a little higher (about 1.4 to 2.5 °C) than that of PLA. Although there were no statistically significant differences between the crystallinities of PLA and PLA-g-MAs, crystallization peaks of PLA-g-MAs having high amounts of grafted MA ( $\geq 0.4$  wt%) were not seen (Figure 6.1). Change in the transition temperatures and enthalpy of fusion are influenced by competing factors, decreasing molecular weight of the polymer backbone improves its segmental mobility resulting in a reduction of  $T_g$  but also increasing the degree of order which facilitates crystallization [26-27]. However, a crystallization decrease was observed with a higher degree of  $M_w$  reduction since a smaller  $M_w$  decreases order [27]. Addition of the bulky MA group into the polymer backbone retards the chain folding resulting in an increase of the  $T_g$  and  $T_c$  values [28-29]. Simultaneously, the polarity of MA also increased the percentage of crystallinity [27]. Similar results (*i.e.* dramatic increase of  $T_c$  and slight raise of  $T_m$ ) were observed from MAgrafted PBAT (MA-g-PBAT) made by reactive extrusion [30].



Figure 6.1 DSC second heating scan of PLA and PLA-g-MAs

The TGA curves of PLA and PLA-g-MAs exhibited a single-stage decomposition reaction. There were no significant differences between  $T_o$ ,  $T_{max}$ , and  $T_e$  values of PLA and PLA-g-MAs; however, all PLA-g-MAs had a little improvement of  $T_{max}$  and  $T_e$  values (about 1.5 to 2.8 °C, and 1.7 to 4.3 °C, respectively), but  $T_o$  values of PLA-g-MAs having high grafted MA ( $\geq 0.4$  wt%) were little lower (about 1.3 to 2.7 °C) than that of PLA (Table 6.4). PLA-g-MAs having  $\geq 0.4$  wt% grafted MA also had  $T_{d5}$  values considerably lower than the others (about 8 to 8.7 °C). The significant difference of  $T_{d5}$  values between PLA-g-MA B and C could imply that high grafted MA had somewhat of an adverse impact on thermal stability.

It is noteworthy that the thermal stability of polymer-g-MAs diverges, depending on grafting methods, conditions, and formulations. For example, a significant improvement of  $T_o$  for PLA-g-MA by about 94 °C was reported when PLA/MA/benzoyl peroxide (25/15/1 by weight) were solution grafted for 4 h without noticeable differences between molecular weights of their PLA ( $M_n = 23.2$  kDa,  $M_w = 28$  kDa) and PLA-g-MA ( $M_n = 23.3$  kDa,  $M_w = 28.6$  kDa) [31]. Chiang and Ku reported that a longer solution grafting reaction ( $\geq 60$  min) improved the initial decomposition temperature of MA-grafted plasma-treated LDPE [32]. Carlson *et al.* showed also lower thermal stabilities of PLA-g-MAs than that of PLA by 2 to 7° C when working with PLA-g-MAs having  $M_n$  of 83.2 to 101 kDa prepared by reactive extrusion grafting using 2 wt% MA/0.1-0.5 wt% L101 @ 180 or 200 °C [33]. The pristine PLA had  $M_n$  of 121 kDa.

## 6.3.2. IR spectra of reactive binary blends

The IR spectrum of the physical PLA/TPCS blend (7PT) at the ratio of 70/30 by wt (Figure 6.2a-b) presented the combination of PLA peaks below 3000 cm<sup>-1</sup>, and the broad TPCS peaks at above 3000 cm<sup>-1</sup> which were ascribed to the O-H stretching of inter- and intramolecular bounding of the hydroxyl groups of the starch. The peak at 2920 cm<sup>-1</sup> was attributed to the C-H stretching of CH<sub>2</sub> of starch [34-35]. Some PLA peaks in 7PT slightly shifted to a lower wavenumber, *a red shifting*, attributed to the amorphous phase of PLA (shifted from 868 to 864 cm<sup>-1</sup>) and C-H stretching of CH<sub>3</sub>(sym) (shifted from 2943 to 2941 cm<sup>-1</sup>) [36]. *A blue shifting*, a shift to higher wavenumber due to a replacement of weaker interactions, was observed from the peaks that contributed to the helical backbone vibrations with CH<sub>3</sub> rocking (shifted from 955 to 957 cm<sup>-1</sup>), C-O in -CH-O stretching (shifted from 1180 to 1182 cm<sup>-1</sup>), and C=O stretching (shifted from 1748 to 1751 cm<sup>-1</sup>) [36-38]



Figure 6.2 IR spectra of PLA, physical (7PT) and reactive blends (7rPT A, B, C, and D): a) At 3750-2800 cm<sup>-1</sup>; b) at 1900-1300 cm<sup>-1</sup>

Figure 6.2 (cont'd)



The IR spectrum of 7rPT A was similar to the blend without reactive compatibilizer (7PT) except some new peak signals appeared at above 3500 cm<sup>-1</sup> (Figure 6.2a). Furthermore, the number of new peaks emerging above 3500 cm<sup>-1</sup> increased with increasing grafted MA. The *blue shifting* of some peaks was observed in the reactive blends having  $\geq 0.26$  wt% grafted MA *i.e.* -CH- deformation bending (shifted from 1360 to 1362 cm<sup>-1</sup>), and with the reactive blends having  $\geq 0.4$  wt% MA *i.e.* -CH<sub>3</sub> bending (shifted from 1452 to 1454 cm<sup>-1</sup>) (Figure 6.2b) [39]. Unexpectedly, when the reactive blends had more than 0.26 wt% grafted MA, the C=O stretching peak appeared at 1749 cm<sup>-1</sup> which was close to that of PLA (1748 cm<sup>-1</sup>) (Figure 6.2b).

A similar trend was also observed when the reactive blends had  $\ge 0.4$  wt% grafted MA, the amorphous peak emerged at 866 cm<sup>-1</sup> where the amorphous peak of PLA is located at 868 cm<sup>-1</sup>. Several small intensity peaks appeared around 1300 to 1717 cm<sup>-1</sup> in the reactive blends having  $\ge 0.4$  wt% grafted MA (Figure 6.2b). Among these peaks, the one at 1717 cm<sup>-1</sup> could be attributed to the carboxyl groups of hydrolyzed anhydride on PLA-g-MAs which occurred when the anhydride groups of PLA-g-MAs interacted with the hydroxyl groups of starch (and/or glycerol) from TPCS polymer to form ester linkages as shown in scheme 6.1 [7, 10]. These carboxyl groups of the hydrolyzed anhydrides could also form hydrogen bonds with the hydroxyl groups of the starch and/or glycerol.



Scheme 6.1 Esterification of anhydride group from PLA-g-MA and hydroxyl group from starch

Interaction between hydroxyl groups and anhydride groups in the other reactive blends were readily observed with FTIR technique. For examples, new absorption peaks due to ester carbonyl stretching from ester linkages were investigated at 1728, 1739, and 1752 cm<sup>-1</sup> in the reactive blends of LDPE/starch/PE-grafted MA (PE-g-MA), PCL-grafted MA/starch, and polyethylene-octene elastomer (POE)/POE-MA/starch, respectively [9, 40-41]. The small peak observed at 1709 cm<sup>-1</sup> in the LDPE/starch/PE-g-MA blends was due to carboxyl groups of hydrolyzed anhydrides obtained from esterification [9].

In contrast, the absorption peaks of ester and carboxyl groups obtained from esterification between anhydride and hydroxyl groups were rarely found in the reactive binary or ternary blends of PLA-g-MA with starch or TPS. This may because the new absorption peak that was normally observed around 1760 to 1710 cm<sup>-1</sup> could somewhat overlap with the C=O stretching peak of PLA. Although in this work, the new absorption peak of ester groups due to esterification of anhydride and hydroxyl groups was also not observed in the reactive blends. However, the appearance of a small peak at 1717 cm<sup>-1</sup>, which was attributed to carboxyl groups of hydrolyzed anhydrides found in the reactive blends having  $\geq 0.4$  wt% grafted MA (7rPT C and D), could imply that the chemical interactions between the anhydride groups of PLA-g-MA and TPCS were established. But, it was hardly detectable; this may because of the small interactions or overlapping of new peaks with the C=O stretching peak of PLA.

## 6.3.3 Thermal and dynamic mechanical properties of reactive binary blends

7PT showed multi-stage decomposition (Figure 6.3a-b). The degradations around 100 °C, broad peak around 150 to 260 °C, and peaks at 338 and 403 °C were related to water evaporation, volatilization of free and bound glycerol, and decomposition of starch and PLA,

respectively. Reactive blending of TPCS with PLA-*g*-MAs resulted in increased thermal stability at about 100 to 320 °C, and thermal degradation at around 350 to 410 °C, compared to 7PT (Figure 6.3a). Significant differences in thermal stability properties between PLA and PLA-*g*-MAs were observed with an increase of grafted content (Table 6.5).

Overall, the narrowing of glycerol peaks with the shift to lower temperatures, the broadening of starch peaks to 250-300 °C, the overlap of starch and PLA peaks, and the shift of PLA peaks to lower temperatures were enhanced with an increase of grafted MA and a lower molecular weight of PLA-g-MAs (Figure 6.3b). Complete overlapping between starch and PLA peaks was observed with PLA-g-MAs having high grafted MA ( $\geq 0.4$  wt%) (Figure 6.3b and Table 6.5). Interestingly, the considerable changes in  $T_{max}$  values of the starch and PLA peaks between PLA-g-MA B and MA C which had the same  $M_n$  may indicate that the increase in grafted MA is the major cause of the degradation of PLA and an overlap of PLA and starch peaks.



Figure 6.3 Thermal stabilities of physical blend, reactive blends, and PLA: a) TGA thermogram; b) DTG thermogram

	T <sub>max</sub> , °C					
-	Water peak	Glycerol peak	Starch peak	PLA peak		
7PT	$103.0 \pm 3.0^{a}$	$213.3 \pm 3.3^{a}$	$338.2 \pm 3.1^{a}$	$402.9 \pm 1.7^{a}$		
7rPT A	$101.7 \pm 1.9^{a}$	$197.0 \pm 24.4^{ab}$	$341.5 \pm 2.1^{a}$	$400.2 \pm 3.4^{a}$		
7rPT B	$102.9 \pm 2.5^{a}$	$171.5 \pm 3.8^{bc}$	$343.6 \pm 4.6^{a}$	$400.1 \pm 2.1^{a}$		
7rPT C	$105.0 \pm 2.9^{a}$	$166.1 \pm 1.2^{c}$	-	$392.7 \pm 2.5^{b}$		
7rPT D	$105.3 \pm 3.7^{a}$	$164.2 \pm 1.5^{c}$	-	$373.8 \pm 0.7^{c}$		

**Table 6.5**  $T_{max}$  of physical and reactive blends

Note: Numbers followed by the same letter within a column are not statistical significant different at  $P \le 0.05$ 

The improvement of thermal stability between at about 100 to 320 °C and then high degradation at about 350 to 410 °C found in the binary reactive blends that was enhanced with an increase of grafted MA could possibly be attributed to the compensation effect of grafted MA. The higher grafted MA could enhance the interfacial adhesion between the polymer pair resulting in better thermal stability; meanwhile the higher grafted MA could increase the thermal degradation of PLA-*g*-MA under high temperature/pressure/shear during reactive extrusion. Similar results (*i.e.* improvement of  $T_{d5}$  and the inward shifting of TPS and PLA peaks after reactive blending) was observed from a one-step reactive extrusion blend of TPS/PLA/MA/DCP (dicumyl peroxide) at a ratio of 50/50/0.5/0.05 by weight and reported by Wang *et al.* [42]. They ascribed the closeness of  $T_{max}$  values of DTPS and PLA to an increase of compatibility of the polymer pair.

The enhanced partial miscibility of the polymer blends is readily indicated by the inward shifting of the polymer pair's  $T_{g}$ s [6]. Unfortunately, the low content of TPCS (30 wt%) resulted

in a very low change in heat capacity ( $\Delta C_p$ ), so the  $T_g$ s of glycerol and starch in the blends could not be detected by DSC. Previous work by the authors showed that TPCS polymer containing 30 wt% of glycerol content had  $T_g$ s of glycerol and starch at around -47 and 60 °C, respectively. The inward shifting of PLA's  $T_g$  in the physical blend (7PT) to a lower temperature by about 2 °C (Table 6.6) may be due to some degree of miscibility or the plasticization effect of glycerol [43-44]. All the reactive blends had PLA  $T_g$  values significantly lower than PLA and 7PT, especially the 7rPT D having the highest grafted MA and the lower  $M_n$ . Lower molecular weight chains could also improve the segmental mobility of PLA, and MA also worked as a plasticizer reducing the  $T_g$  of PLA in the reactive blends as previously demonstrated [13].

					Tm, °C		
	<i>Tg</i> , ℃	<i>Т<sub>сс</sub></i> , °С	$H_{cc}$ , J·g <sup>-1</sup>	first	second	$H_m, \mathbf{J} \cdot \mathbf{g}^{-1}$	<i>X<sub>c</sub></i> , %
PLA	62.3±0.3 <sup>a</sup>	118.7±0.6 <sup>a</sup>	23.2±0.5 <sup>a</sup>	-	152.7±0.8 <sup>bc</sup>	25.0±0.3 <sup>abc</sup>	2.0±0.9 <sup>ab</sup>
7PT	60.1±0.2 <sup>b</sup>	123.1±0.8 <sup>b</sup>	15.6±0.3 <sup>b</sup>	-	151.0±0.1 <sup>d</sup>	18.4±1.2 <sup>d</sup>	4.2±1.3 <sup>bc</sup>
7rPT A	59.4±0.3 <sup>c</sup>	117.3±0.4 <sup>a</sup>	23.4±0.4 <sup>a</sup>	147.5±0.3 <sup>a</sup>	154.4±0.3 <sup>a</sup>	23.6±0.6 <sup>c</sup>	0.3±0.3 <sup>a</sup>
7rPT B	58.9±0.1 <sup>c</sup>	114.4±0.5 <sup>c</sup>	22.4±0.5 <sup>a</sup>	146.2±0.4 <sup>b</sup>	153.8±0.2 <sup>ab</sup>	24.4±0.5 <sup>bc</sup>	3.0±1.4 <sup>b</sup>
7rPT C	59.0±0.1 <sup>c</sup>	111.3±0.3 <sup>d</sup>	21.9±0.4 <sup>a</sup>	145.0±0.4 <sup>c</sup>	153.5±0.3 <sup>ab</sup>	25.8±0.1 <sup>ab</sup>	6.0±0.5 <sup>c</sup>
7rPT D	57.9±0.2 <sup>d</sup>	111.2±0.6 <sup>d</sup>	22.9±0.8 <sup>a</sup>	143.5±0.0 <sup>d</sup>	152.3±0.2 <sup>cd</sup>	26.7±0.8 <sup>a</sup>	5.8±0.3 <sup>c</sup>

**Table 6.6** Transition properties of physical and reactive blends

Note: Numbers followed by the same letter within a column are not statistical significant different at  $P \le 0.05$ 

Either physical or reactive blending of PLA with TPCS did not result in a crystallization peak for PLA during cooling at 10 °C·min<sup>-1</sup>. A dramatic increase of PLA's  $T_{cc}$  and decrease of PLA's  $\Delta H_{cc}$  was observed in the physical blend, whereas the  $T_{cc}$  values of the reactive blends decreased with an increase of grafted MA and then leveled off (Table 6.6). However, the  $\Delta H_{cc}$ values of the reactive blends were not affected by grafting of MA and low  $M_n$ . The presence of low molecular weight agents such as plasticizers, coupling agents, and low molecular weight polymers facilitates segmental movement of high molecular weight polymers, resulting in a decrease of transition temperatures, whereas chemical interactions with grafted MA reduce the segmental mobility of the polymer [13, 45-46]. This could explain why an improvement of segmental mobility resulted in a decrease of  $T_{cc}$  values, which were very strong with an increase of grafted MA and lower  $M_n$ . At the highest grafted MA (0.5 wt%) the chemical interactions of grafted MA with starch and/or glycerol seemed to be dominant and counteracted the segmental mobility, resulting in a leveled-off  $T_{cc}$  value.

It is noteworthy that all the reactive blends, even the reactive blend having low grafted MA (0.05 wt%), exhibited double melting peaks, whereas the physical blend and PLA had a single melting peak (Figure 6.4). The second  $T_m$  value of PLA in the 7PT sample was lower than that of PLA ( $P \le 0.05$ ), implying that the crystalline structure of PLA had some defects [45]. Only 7rPT A had a second  $T_m$  value slightly higher than PLA, indicative of high-regularity crystals. Those  $T_m$  values decreased around 0.8 to 2.1°C with a reduction of PLA-g-MAs'  $M_n$ , whereas the first  $T_m$  values of PLA in the reactive blends significantly decreased with an

increase of grafted MA, indicating that grafted MA and their  $M_n$  could be responsible for the crystal defects ( $P \le 0.05$ ) (Table 6.6). The double melting peak behavior was also observed in an additive free, fibrous PLLA resin, PLA/thermoplastic acetylated starch blends, compatibilized blends of PLA/starch, PLA composites, and other structures [13, 43, 47-50]. According to Radjabian *et al.*, there are three main mechanisms that can be responsible for the double-melting behavior of PLLA: melt-recrystallization, dual (or multiple) lamellae populations, and dual (or multiple) crystal structures [51].

Among those mechanisms, melt-recrystallization (the original crystals melt during the first heating scan, then recrystallize; the small and imperfect crystals melt at a lower melting temperature and reorganize to stable/highly regular crystals at a few degree above, and finally remelt at the higher melting temperature) is mostly accepted as explaining the double-melting behavior of compatibilized PLA/starch blends [13, 49-50, 52-53].



Figure 6.4 Crystallization and melting peaks of physical and reactive blends

The 7PT sample also showed the lowest  $\Delta H_m$  values ( $P \leq 0.05$ ) (Table 6.6). The reactive blends showed  $\Delta H_m$  values close to PLA and those  $\Delta H_m$  values had a tendency to increase with an increase of grafted MA. The same trend was ascribed to the  $X_c$  values of reactive blends but the crystallinity was stable with high grafted MA ( $\geq 0.4$  wt%). As mentioned, the crystallization behavior was influenced by a competition of plasticizing/lubricating effect and chemical interactions. It also should be noted that the transition temperature properties of PLA-g-MAs used as a polymer pair (Table 6.4) did not match the  $T_g$ ,  $T_m$ , and  $T_c$  of their reactive blends (Table 6.6).

The slightly increase of crystallinity in the range of 7rPT C, 7rPT D > 7PT > PLA could imply that TPCS acts as a nucleating agent to improve the crystallinity of PLA and this effect is enhanced when the blends were compatibilized with high grafted MA. This may be because the crystallization rate of PLA was improved by the addition of the TPS phase and enhanced when the blend was compatibilized with PLA-*g*-MA as also investigated by Li and Huneault [46]. The effect of grafted MA on transition temperature properties of the reactive blends is clearly seen with a comparison between 7rPT B and 7rPT C having the same  $M_n$  (Table 6.6). The higher grafted MA significantly decreased  $T_{cc}$  and the first  $T_m$  values, enhanced the  $X_c$  value and slightly increased  $\Delta H_m$ , indicating that compatibilization with grafted MA at up to levels of 0.4 wt% facilitated the crystallization of PLA.

### 6.3.4 Mechanical properties and morphology of reactive binary blends

The physical and reactive blends exhibited higher stiffness (*i.e.* larger E') than PLA at below -10 °C, then the stiffness gradually decreased with increasing temperature (Figure 6.5a), indicating that addition of TPCS improved the flexibility of the blends at -10 to 55°C. The storage modulus of the blend decreased abruptly at about 55 °C. The effect of functionalized PLA was clearly seen in the rubbery region of the blends (*i.e.* below 60 °C). At above 70 °C, the reactive blends, especially the 7rPT D (the reactive blend with highest grafted MA and lowest  $M_n$ ), had lower stiffness compared to the physical blend (7PT), indicating that the chain mobility was increased, which could be attributed to the lower  $M_n$  of PLA-g-MA compared to that of PLA. The abrupt increase of E' due to the crystallization of PLA can be seen at around 84 °C. The crystallization peaks of the reactive blends occurred at lower temperature than those of PLA and 7PT, indicated that PLA crystallization was improved after functionalization and blending with TPCS.



Figure 6.5 Storage and loss Moduli of physical and reactive blends: a) Storage modulus; b) Loss modulus

The loss modulus of the physical blend (7PT), measured at the temperature range of -100 to 80 °C, exhibited three transitions. The peak at about -52 °C represented the  $T_{\beta}$  of the glycerolrich domain ( $\beta$  relaxation); and the peak at around 4°C represented the  $T_{\alpha}$  of the starch-rich domain ( $\alpha$  relaxation), indicating the phase separation of TPCS which is normally found in typical TPS [42]. The peak at about 61 °C was ascribed to the  $T_g$  of PLA. The reactive blends also exhibited the three transitions, but with more inward shifting of the glycerol peaks (shifting to higher temperature) and changes of peaks as follows. The peaks of the starch-rich domain of the reactive blends were broadened and overlapped more with the peaks of the glycerol-rich domain (Figure 6.5b). The change in peak intensity was pronounced with the glycerol-rich domain, in which the peak modulus decreased with high grafted MA ( $\geq 0.4$  wt%) (Table 6.7), but the effects of  $M_n$  and functionality of PLA-g-MA on the modulus of the starch-rich domain were unclear due to the overlapping of the starch-rich domain.

Albeit there is no significant change of PLA-g-MA loss modulus (Table 6.7), it should be noted that only the reactive blend having the highest grafted MA or lowest  $M_n$  (7rPT D) had a loss modulus (E'') value lower than the physical blend. A similar result was observed with PE/TPS blends compatibilized with PE-g-MA [54]. The addition of PE-g-MA, having a  $M_n$  of about 31 kDa and MA concentration of 3.9%, decreased the amplitude of  $T_\beta$  peaks, but the amplitude of the  $T_\alpha$  peaks did not vary significantly with an increasing of PE-g-MA content.

	Loss Modulus, MPa		<i>T<sub>g</sub></i> s from <i>Tan δ</i> (°C)		
	Glycerol-rich domain	PLA	Glycerol- rich domain	Starch-rich domain	PLA
PLA			-	-	$68.2 \pm 0.5^{a}$
7PT	$709.4 \pm 6.1^{a}$	$897.9 \pm 54.6^{a}$	$-47.2 \pm 0.8^{a}$	$11.7 \pm 1.4^{a}$	$66.4 \pm 0.4^{b}$
7rPT A	$703.6 \pm 28.3^{a}$	$945.7 \pm 49.1^{a}$	$-46.3 \pm 0.3^{a}$	$1.8 \pm 2.2^{b}$	$66.3 \pm 0.1^{b}$
7rPT B	$615.2 \pm 19.7^{ab}$	$908.7 \pm 35.3^{a}$	$-43.1 \pm 0.5^{b}$	$12.8 \pm 0.6^{a}$	$66.8 \pm 0.3^{b}$
7rPT C	$595.2 \pm 81.0^{b}$	$918.5\pm58.0^a$	$-41.7 \pm 0.6^{bc}$	$16.6 \pm 6.8^{a}$	$66.5 \pm 0.1^{b}$
7rPT D	$559.0 \pm 17.6^{b}$	$876.6 \pm 36.3^{a}$	$-41.2 \pm 0.4^{c}$	$17.7 \pm 1.6^{a}$	$66.4 \pm 0.2^{b}$

Table 6.7 Loss Modulus and tan  $\delta$  values of PLA, physical and reactive blends

Note: Numbers followed by the same letter within a column are not statistical significant different at  $P \le 0.05$ 

The effects of PLA-g-MA on shifting of  $T_g$ s were more clearly identified from the  $Tan \delta$  determinations compared to the loss modulus due to less overlapping of the starch-rich domain with the glycerol-rich domain (data not shown). Addition of 30 wt% TPCS in PLA resulted in a decrease of PLA's  $T_g$  value by about 2 °C ( $P \le 0.05$ ), whereas the  $T_g$ s of the glycerol-rich and starch-rich domains appeared at around -47 and 12 °C, respectively (Table 6.7). Although there was no difference between the  $T_g$  values of PLA observed from the physical and reactive blends, there was a trend that the  $T_g$  shifts of the glycerol-rich and starch-rich domains increased with an increase of grafted MA and then leveled off at  $\ge 0.4$  wt% grafted MA.

Compared among the reactive blends having different  $M_n$  and grafted MA values of PLA-g-MA (7rPT A, B, and D), the inward shifts of the TPCS components toward PLA's  $T_g$  strengthened with an increase of grafted MA and a decrease of  $M_n$  of PLA-g-MA. Furthermore,

comparison between the reactive blends having similar  $M_n$  values of PLA-g-MA (7rPT C and D) showed that an increase of grafted MA increased the inward shifting of the starch-rich domain's  $T_g$  value by about 4 °C. The increase of inward shifting of TPCS'  $T_g$  values of the reactive blends with an increase of grafted MA could be attributed to an increase of the ester formation between the anhydride groups of PLA-g-MA and the hydroxyl groups of glycerol and starch. Therefore, the inward shifting of TPCS'  $T_g$  values could be used as evidence that the reactive comptibilization of PLA and TPCS via grafted MA was established.

It also should be noted that a noticeable inward shift of the glycerol-rich domains exhibited in the reactive blends having the lower grafted MA (0.26 wt% with  $M_n$  of 50 kDa), whereas the noticeable inward shift of the starch-rich domains found in the reactive blends having  $\geq 0.4$  wt% grafted MA with  $M_n$  of  $\leq 50$  kDa. This result is related to the finding of Tanquet *et al.* that MA will first interact at the interfacial glycerol-rich layer, especially with high glycerol content [54]. This may be because glycerol has lower viscosity than starch [10]. Once the glycerol layer thickness decreases or the grafted MA is high enough, PE-g-MA will interact with the starch-rich phase [54]. Hence, it may be assumed that 0.4 wt% grafted MA of PLA-g-MA having  $M_n$  of 50 kDa is effective enough for reactive compatibilization of PLA and TPCS at a ratio of 70/30 by wt. Further SEM and tensile measurements were carried out to prove this result.

The VP-SEM micrograph of the fracture surface of the physical blend (7PT) showed good interfacial adhesion between the TPS domains and the PLA continuous phase because there were no voids between the two phases. The TPCS domains had globular and irregular shapes (Figure 6.6a). The blend surface was rough, indicating somewhat ductile behavior. Thus, the flexibility of the physical blend may be improved with the addition of TPCS. In this case, glycerol should facilitate good miscibility between the two phases. It reduced the TPS viscosity, resulting in an increase of TPS flowability, a reduction in size of TPS domains, and increase in starch chain mobility which facilitates hydrogen bonding between the starch and PLA [54-56]. Taguet *et al.* investigated the effect of glycerol content on the reduction of TPS domain size in TPS/HDPE blends and revealed that the glycerol threshold is close to 28 wt% [54]. Good interfacial adhesion of the physical blend was also observed from the cryogenic fracture surface of a 40/60 PCL(1)/TPS blend, in which the glycerol content in a starch-water-glycerol suspension was 28 wt% [55].



**Figure 6.6** VP-SEM fracture surface micrographs of physical and reactive blends: a) 7PT; b) 7rPT B; c) 7rPT C; d) 7rPT D

Markedly changes in fracture surfaces of the reactive blends compared with 7PT were observed with blends having grafted MA  $\geq$  0.26 wt% and  $M_n \leq$  50 kDa (7rPT B, C, and D – Figure 6.6b-d). The fracture surfaces of those reactive blends seem to be smoother; the number of small domains of TPCS increased and better dispersion was observed with an increase of grafted MA and/or decreased  $M_n$  of PLA-g-MA. Comparing the reactive blends having the same  $M_n$  of PLA-g-MA (7rPT B and C), the reactive blend having a higher grafted MA (7rPT C) exhibited a larger amount of a small TPCS domains (Figure 6b-c). Additional information about the effects of grafted MA and  $M_n$  of PLA-g-MA on TPCS domain size, shape, and dispersion was observed by removing the TPCS phase with acid etching. The dispersion of the TPCS domains in the PLA phase for the physical blend was not uniform (Figure 6.7a). The TPCS domains were somewhat spherical with some domains presenting irregular shapes with a high variation of domain sizes.



**Figure 6.7** SEM micrographs after removing TPCS domains by acid etching of physical and reactive blends: a) 7PT; b) 7rPT A; c) 7rPT B; d) 7rPT C; e) 7rPT D

## Figure 6.7 (cont'd)



Interestingly, the dispersion and uniformity of TPCS domains in the PLA-g-MA continuous phase of 7rPT A was dramatically improved even when PLA-g-MA having a small amount of grafted MA (0.05 wt%) was used (Figure 6.7b). TPCS domains of the reactive blends were nearly spherical, and TPCS domain sizes decreased noticeably with an increase of grafted MA. This can be attributed to the interaction of anhydrides of PLA-g-MA with hydroxyl groups of starch and glycerol during the extrusion melt-blending. This covalent bonding reduced the interfacial tension between the TPCS domains and the PLA-g-MA continuous phase, resulting in

smaller particle sizes, better domain dispersion, and a finer and more uniform morphology, as also shown elsewhere [8, 42, 56]. These results emphasized that reactive compatibilization in the TPCS blends existed when the functionalized PLA was used as a polymer pair even having a very low content of grafted MA (0.05%); hence, the mechanical properties of these reactive blends were expected to improve, as shown later on.

Surprisingly, the most uniform domain size was observed with the reactive blend containing a low amount of grafted MA and a high  $M_n$  with a low *PI* value (7rPT A). Unexpectedly, reactive blending of TPCS with PLA-*g*-MA containing a high amount of grafted MA content ( $\geq 0.4$  wt%) generated a huge TPCS domain phase (Figure 6.7d-e). The numbers of huge domains increased with an increase of grafted MA and decreased  $M_n$ . Similar results to ours were found in reactive two-step 27% TPS/PLA blends where 20% of the pure PLA was substituted by PLA grafted using nominal 2 wt% MA and 0.5 wt% L101 [8] and in the reactive poly(butylenes terephthalate)/styrene-acrylonitrile copolymer blend where 5 wt% low molecular weight methyl methacrylate-*co*-glycidyl terpolymer, having 11.0 wt% glycidyl methacrylate and  $M_n$  of 19 kDa, was used as a compatibilizer [57].

Reactive compatibilization not only lowered the interfacial tension between the two polymer phases but also suppressed the coalescence of droplets via introducing steric stabilization, resulting in a finer and more stable morphology [57-58]. However, shear- or flowinduced coalescence (dynamic coalescence) was found in compatibilized systems at sufficiently high shear rate and/or prolonged mixing due to a decrease of the polymer matrix viscosity and/ or the removal of graft copolymers from the interfaces [59-60]. The phase coalescence is enhanced with decrease in molecular weight and thus in matrix viscosity, since those factors reduced the dispersive forces at the origin of the particle break-up and the interface generation [61].

In this work, the presence of a high quantity of finer domains in the sub-micron levels with a small quantity of large domains ( $\geq 4 \ \mu m$ ) of TPCS in the PLA-g-MA matrix having high grafted MA ( $\geq 0.4 \ wt\%$ ) and lower  $M_n$  ( $\leq 50 \ kDa$ ) could be related to effects of grafted MA and its  $M_n$ . An increase of grafted MA reduced the interfacial tension, resulting in finer domains, but a decrease in matrix viscosity due to the lower  $M_n$  of the PLA-g-MA enhanced dynamic coalescence, resulting in large domains.

Furthermore, a reduction of the PLA-*g*-MA viscosities could be enhanced by an increase of chain scission produced by the high shear, high temperature, and especially high MA content during the reactive extrusion. This could be the main reason for the dynamic coalescence observed in this work, since the reactive blends (7rPT B) having similar  $M_n$  (about 50 kDa) but lower grafted MA (0.26 wt%) did not present large domains of PLA as 7rPT C did (Figure 6.7cd). The large domains may act as stress concentrators, which may finally deteriorate the sample mechanical properties. To prove this assumption, the tensile properties of 7rPT B and 7rPT C were investigated and compared to those of PLA and the physical blend. The 7rPT B and 7rPT C were selected because these two reactive blends presented noticeable inward shifts of TPCS  $T_gs$ , significant reduction of domain size, and a differed in the presence/absence of large domains.

Ductility improvement of the physical blend (7PT) due to an introduction of a ductile polymer, TPCS, into the PLA matrix was emphasized by its tensile properties. PLA, a brittle polymer, had Young's modulus, tensile strength at break, and elongation at break of  $2.8 \pm 0.7$  GPa,  $65.9 \pm 1.4$  MPa, and  $2.8 \pm 0.4\%$ , respectively. Compared to PLA, the Young's modulus and

tensile strength at break of 7PT decreased by about 43 and 28%, respectively whereas elongation at break increased by about 1390% with an addition of 30 wt% TPCS. Blending of 30 wt% TPCS with PLA-g-MA having similar  $M_n$  but difference in functionality levels (grafted MA) provided the reactive blends with different tensile behaviors as shown later in Figure 6.8. 7rPT B exhibited the tensile properties similar to 7PT with a slight enhancement of stiffness resulting from an improvement of interfacial chemical interactions, mainly ester linkages, between the TPCS domains and PLA-g-MA matrix. Compared to PLA, the tensile strength of 7rPT B decreased by about 39%, while the elongation at break increased by about 1100%.

As expected, an increase of grafted MA (0.4%) tremendously deteriorated the ductile properties of 7rPT C, its Young's modulus, tensile strength at break, and elongation at break compared to PLA decreased by about 14%, 53%, and 57%, respectively. Decreased tensile properties of the reactive blends due to an increase of grafted MA were also mentioned elsewhere [7, 11]. In this work, the large domain size shown in Figure 6.7d may act as a stress concentrator resulting in inferior tensile properties, since it induced cracks and then produced premature failure during the tensile testing. So, better tensile properties may be achieved from the blends containing less than 0.4 wt% grafted MA. Therefore, the optimum grafted MA providing the better tensile properties was further investigated by substitution of PLA content with different amounts of PLA-g-MA and blending with 30 wt% TPCS. The approach of creating a ternary blend was used to concentrate on the effect of grafted MA.
#### 6.3.5 Tensile properties and morphology of reactive ternary blends

For the ternary blends, PLA-g-MA E, having grafted MA of  $0.52 \pm 0.02$  wt% and  $M_n$  of

44.9  $\pm$  1.0 kDa, was used as a PLA substitute since its  $M_n$  was comparable to PLA-g-MA B and C but with higher grafted MA. The  $M_n$  of PLA-g-MA around 45-50 kDa was selected for the ternary blend study since it showed evidence of better interfacial adhesion where the morphologies of the reactive blends depended on the amount of grafted MA on PLA-g-MA (Figure 6.7c-d). Furthermore, with the higher grafted MA, the ternary reactive blends could be tailor made to provide reactive blends having different levels of grafted MA, which would be comparable with the previous reactive binary blends. The ternary blends having PLA-g-MA E of 7, 35, and 56 wt% had grafted MA comparable to 7rPT A, 7rPT B, and 7r PT C, respectively. Finally, the ternary blend having PLA-g-MA E of 14 wt% had grafted MA based on PLA-g-MA and PLA weights around 0.1 wt%. The tensile properties of dumbbell specimens of the reactive PLA/PLA-g-MA E/TPCS blends compared to PLA and 7PT are shown in Figure 6.8.



Figure 6.8 Tensile properties of PLA/PLA-g-MA E/TPCS blends, PLA, and 7PT

PLA exhibited necking without drawing. Addition of 30 wt% TPCS, a ductile component, resulted in an increase in the plastic region after the yield point with a reduction of stiffness. 7PT had tensile properties of  $38.9 \pm 0.4$  MPa, Young's Modulus of  $2.2 \pm 0.2$  GPa, and elongation at break of  $81.2 \pm 18.2$ %. Compared to 7PT, increasing of the substituted PLA-*g*-MA E content up to 35 wt% slightly improved the Young's modulus but had almost no effect on the tensile strength. However, an increase in elongation at break of the ternary blends was observed when a low amount of the PLA-*g*-MA E (up to 14wt%) was substituted; beyond this value the ternary blends completely lost the cold drawing characteristic (plastic region). The highest value

of elongation at break,  $145.1 \pm 45.6$  %, was obtained from the blends at a ratio of 56/14/30 (PLA/PLA-g-MA E/TPCS); this reactive ternary blend also had tensile strength of  $38.9 \pm 0.4$  MPa and Young's modulus of  $2.4 \pm 0.3$  GPa.

The highest amount of PLA-*g*-MA E used (56 wt%) deteriorated both strength and ductile properties of the reactive blend; this ternary reactive blend had tensile strength ( $32.5 \pm 2.2$  MPa) reduced by half compared to PLA, Young's modulus of  $2.1 \pm 0.2$  GPa, and elongation at break ( $2.3 \pm 0.7$  %) less than PLA. According to Zhang and Sun, the mechanical properties of the composites were not further improved if the concentrations of grafted copolymer (compatibilizer) at the interface increased beyond a critical level [7]. Another reason why increasing reactive compatibilizer content did not improve mechanical properties of the reactive blends could be attributed to the deteriorative intrinsic mechanical properties of PLA-*g*-MA E due to chain scission reducing its molecular weight during reactive functionalization. Similar results (*i.e.* blends of TPS with PLA functionalized by MA dramatically improved elongation at break but almost do not affect the tensile modulus and strength) were reported by Huneault and Li [8].

In their work, the maximum increase of elongation at break of reactive TPS/PLA blends (about 205 to 185%) was obtained when PLA was completely replaced by PLA-*g*-MA made from 2 wt% MA and 0.25 wt% L101 (the grafting level was 0.8 wt%), regardless of TPS content (27, 43, and 60 wt%). However, in this work the highest elongation at break of the 70 wt% PLA and 30 wt% TPCS was observed when 20 wt% PLA was replaced by PLA-*g*-MA having 0.52 wt% grafted MA. This clearly shows the effectiveness of PLA-*g*-MA as a reactive compatibilizer for PLA and TPCS blends. Only the low grafted MA was essential and sufficient to produce a finer and more stable morphology, resulting in an improvement of tensile properties of the

blends. The etched SEM micrographs of the reactive ternary blends (Figure 6.9) revealed that the best tensile properties (56/14/30) resulted not only from the better dispersion of TPCS domains, the smaller domain sizes, and the stable morphology, but also from the narrow distribution of domain sizes (Figure 6.9c).



**Figure 6.9** Etched SEM micrographs of binary and ternary blends: a) 7PT; b) 63/7/30 of PLA/PLA-g-MA E/TPCS; c) 56/14/30 of PLA/PLA-g-MA E/TPCS; d) 35/35/30 of PLA/PLA-g-MA E/TPCS; e) 56/14/30 of PLA/PLA-g-MA F/TPCS; f) 56/14/30 of PLA/PP-g-MA/TPCS

#### Figure 6.9 (cont'd)



Furthermore, it was evident that the reactive blends having 0.4 wt% grafted MA either used in the form of a functional polymer pair (binary blend: 7rPT C) or used in the form of reactive compatibilizer (ternary blend: 14/56/30) exhibited poor tensile properties compared to PLA and the physical blend. Interestingly, the reactive blend having about 0.26 wt% grafted MA in the form of a binary blend (7rPT B) had better tensile properties, closer to those of the physical blend than the ternary blend (35/35/30), which exhibited tensile strength of  $32.5 \pm 2.2$  MPa, Young's modulus of  $2.1 \pm 0.2$  GPa, and elongation at break of 4.6%. This may be because the reactive binary blend (Figure 6.7c) had narrower distribution of TPCS domain sizes than the reactive ternary blend (Figure 6.8d). In comparing the reactive blends having 0.05 wt% MA content, the reactive binary blend, 7rPT A, showed better dispersion and a finer morphology than the reactive ternary blend, 63/7/30 (Figure 6.7b and 6.9b). It is noteworthy that functionalized PLA used in the 7rPT A blends, PLA-*g*-MA A, had higher  $M_n$  (about 70 kDa) than the one used in the 63/7/30, PLA-*g*-MA E having  $M_n$  of about 45 kDa.

The tensile properties and blend morphologies indicated that the functionality level (grafted MA level on PLA) of PLA-*g*-MA played an important role in improving the dispersion of TPCS domains, controlling TPCS particle sizes and distribution of domain sizes, and finally stabilizing the domains. As a consequence, the compatibility between the polymers in the blend, and hence, the tensile properties were improved. However, due to the finding that the 7rPT A had a finer morphology than the 63/7/30; those reactive blends had similar MA content but differed in  $M_n$  of PLA-*g*-MA. Therefore, the molecular weight of PLA-*g*-MA may be another parameter that has a significant effect on controlling the morphology and mechanical properties of the final reactive blends.

To prove this assumption, PLA-g-MA having a similar functionality level as PLA-g-MA E (0.52 ± 0.02 wt% grafted MA) but differing in  $M_n$  was investigated. Unfortunately, PLA-g-MA having 0.5 wt% grafted MA and higher  $M_n$  ( $\geq$  60 kDa) could not be produced by simple reactive functionalization of PLA/MA/L101 since an increase of MA resulted in a higher amount of grafted MA with a reduction of grafted PLA molecular weight (Chapter 5). Hence, only PLA-g-MA F having grafted MA of 0.50 ± 0.02 wt% and  $M_n$  of 15.0 ± 1.9 kDa was further used to prepare the ternary blends at the ratios of 63/7/30 and 56/14/30 since these ratios provided the better tensile properties of the ternary blends compared to the physical blend.

The 63/7/30 PLA/PLA-g-MA F/TPCS blend had a tensile strength of 40.8  $\pm$  0.5 MPa, Young's modulus of 2.6  $\pm$  0.4 GPa, and elongation at break of 16.2  $\pm$  14.7%. Increasing PLA-g-MA F to 14 wt% tremendously diminished the ductility of the final blend. The 56/14/30 blend exhibited a tensile strength of 38.6  $\pm$  0.7 MPa, Young's modulus of 2.2  $\pm$  0.4 GPa, and elongation at break of 3.1  $\pm$  0.7%. Compared with the ratio that provided the best mechanical properties (14 wt% of PLA-g-MA E) and the physical blend (Figure 6.9c and 6.9a, respectively), the etched morphology of the reactive ternary blend containing 14 wt% PLA-g-MA F (Figure 6.9e) presented the poorer distribution of TPCS domain with slightly bigger TPCS domain sizes than those of the reactive blend containing 14 wt% of PLA-g-MA E. Thus, it can be stated that the  $M_n$  of PLA-g-MA had a significant effect on controlling the morphology and tensile properties of the reactive PLA/TPCS blends. The distribution of the TPCS domains, the decrease of domain sizes, the finer morphology, and then the tensile properties were enhanced with the higher  $M_n$  of PLA-g-MA when the same amounts at a low concentration of PLA-g-MA were used.

Similar results were found by Park *et al.* that 5 wt% high molecular weights of functionalized PS with MA ( $M_n$  of 100 to 125 kDa) were more effective in decreasing and stabilizing the dispersed domain size of PA6 and PS blends than the low molecular weight ones ( $M_n$  of 15 to 68 kDa) [62]. They also observed that increasing the adhesion strength improved with the addition of high  $M_w$  functionalized PS [62]. Lastly, a reactive blend compatibilized with PP-g-MA was produced to investigate whether the commercial reactive compatibilizer having a different chemical composition and architecture would have a better effect on the morphology and mechanical properties of the ternary reactive blends. Unfortunately, the authors could not find grafted MA on biodegradable polymers commercially available. Hence, PP-g-MA with a similar graft level was used for comparison. At a ratio of 56/14/30, the reactive blend, compatibilized with PP-g-MA, exhibited a slight increase in elongation at break (5.0 ± 0.7 %) with its modulus and strength (tensile strength of 39.7 ± 0.7 MPa, Young's modulus of 2.1 ± 0.4

GPa) close to the blends which were reactively compatibilized with PLA-g-MA F at a similar ratio.

Interestingly, the etched surface of the blend compatibilized with PP-g-MA (Figure 6.9f) seemed to be rougher than the blend compatibilized with PLA-g-MA (Figure 6.9a-e). Compared among the blends having 14 wt% reactive compatibilizer, the dispersion of TPCS domains in the blend containing PP-g-MA was better than in the blends containing the lowest  $M_n$  PLA-g-MA (PLA-g-MA F) but had a broader distribution of domain sizes. However, the concentration used may not be the optimum amount of PP-g-MA to create a finer and stable morphology. The use of PP-g-MA proofs that the *in situ* reactive compatibilizer, PLA-g-MAs, was effective as a reactive compatibilizer or reactive (functionalized) polymer of biodegradable blends, PLA/TPCS.

#### 6.4 Conclusions

PLA-g-MA having grafted MA of 0.05 to 0.47 wt% and  $M_n$  of about 70 to 30 kDa exhibited transition temperatures close to PLA, but  $T_{cc}$  values of PLA-g-MA increased with an increase of grafted MA and then leveled off. The  $T_{d5}$  values of PLA-g-MA decreased with high grafted MA.

A new IR peak at 1717 cm<sup>-1</sup>, inward shifting of PLA's  $T_g$  values observed from DSC, and inward shifting of  $T_g$  values of the glycerol and starch-rich domains observed from DMA were found especially from the reactive binary blends of 30 wt% TPCS and 70 wt% PLA-g-MA having high grafted MA. These indicate that chemical interactions between anhydride groups of PLA-g-MA and hydroxyl groups of starch and glycerol was present. The formation of these ester linkages resulted in a decrease of interfacial adhesion between PLA-g-MA and TPCS phases, subsequently by a reduction of TPCS domain sizes and an improvement of domain dispersion and uniform morphology, which were observed even for blends having a low grafted MA content (0.05 wt% on PLA basis).

Compared to the physical blends, the reactive binary blends exhibited higher thermal stabilities at around 100 to 320 °C, but also higher thermal degradation at around 350 to 410 °C. The  $T_{cc}$  values of the reactive binary blends decreased, and the crystallinity slightly increased with the reactive blends having high grafted MA. Furthermore, double-melting peaks were observed only in reactive blends – the  $T_m$  values of a new peak (first  $T_m$ ) in the double-melting peaks appeared at a lower temperature and decreased with an increase of grafted MA. But, the second  $T_m$  values in the double-melting peaks appeared near the  $T_m$  of PLA and their  $T_m$  value slightly decreased with a decrease of PLA-g-MA's  $M_n$ . The morphology of the reactive binary blends improved with an increase of grafted MA, but the reactive blends having  $\geq 0.4$  wt% grafted MA had a small number of large TPCS domain sizes, which deteriorated their tensile strength and elongation at break.

The reactive ternary blends exhibited the same trend as the reactive binary blends (*i.e.* increasing grafted MA improved TPCS dispersion and lowered TPCS domain sizes). Broader TPCS domain size and poor tensile properties were observed in reactive blends having  $\geq 0.26$  wt% grafted MA (35/35/30 by wt of PLA/PLA-g-MA E/TPCS). Reactive compatibilizer had a strong impact on flexibility, but did not affect modulus and tensile strength. The highest (optimum) elongation at break was observed in the reactive blend having 0.1 wt% grafted MA (PLA basis); the reactive compatibilizer (PLA-g-MA) used in this blend had  $M_n$  of 45 kDa.

Compared to PLA-g-MA having the same  $M_n$ , increasing grafted MA had significant impacts on PLA properties of reactive blends (*i.e.* an increase of thermal degradation, decrease of  $T_{cc}$  and the first  $T_m$  values in the double-melting peaks, and an increase of crystallinity). TPCS domain sizes were decreased in this case, but there were small numbers of big TPCS domains, which could act as stress concentrators and reduce tensile strength and flexibility of the reactive blend. On the other side, PLA-g-MA having similar grafted MA but higher  $M_n$  offered noticeably better TPCS dispersion, a finer and more uniform morphology, and also a larger elongation at break. The reactive binary blends having the same grafted MA and  $M_n$  of functionalized PLA showed better morphology and elongation at break than the reactive ternary blends.

Thus, PLA-*g*-MA is very effective as a reactive polymer pair or reactive compatibilizer with TPCS when PLA is used as a main component. The low amount of grafted MA (0.1 wt%) and its  $M_n$  of 45 kDa is suitable and also offers the highest elongation at break for the reactive blend having 30 wt% TPCS. The use of PLA-*g*-MA having 0.1 wt% grafted MA and  $M_n$  not less than 45 kDa as a reactive polymer could benefit and improve the morphology and mechanical properties of TPCS blends.

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## CHAPTER 7: SUMMARY, OVERALL CONCLUSIONS, AND RECOMMENDATIONS FOR FUTURE WORK

### 7.1 Summary

This research has been performed aiming to develop biobased biodegradable polymers from thermoplastic cassava starch-based material to meet the requirements of short-life, singleuse disposable packaging applications and offer compostability, since some properties of TPCSbased material such as high viscosity, relaxation and retrogradation behaviors, and water sensitivity limit its use in packaging application. Thus, to achieve our original aim, TPCS-based material was blended with modified hydrophobic biobased biodegradable polymer, poly(lactic acid) to improve compatibility and enhance mechanical properties. The research was organized in four phases as follows.

# 7.1.1 Phase I: Production and characterization of physicochemical properties of TPCS materials

Cassava starch was blended with glycerol at various ratios by using a co-rotating TSE. TPCS-based material having starch and glycerol at a ratio of 70/30 by weight was selected for further processing during the second to fourth phases since the viscosity and melt flow of TPCS at this ratio facilitates flowability when TPCS is blended with other polymers like PLA, resulting in a finer morphology of the produced blends. The FTIR spectrum of TPCS resins indicated hydrogen bond interactions between the starch and the glycerol in the amorphous material confirmed, by DSC. TGA and DSC data provided evidence of phase separation between the starch and the glycerol. Unfortunately, the high viscosity of TPCS limited the film production by extrusions; hence, TPCS sheets were prepared by compression molding.

TPCS sheets were glossy with high reflection and a combination of very low redness with light yellowness. TPCS sheets were less than 90% transparent, but they have better ability to absorb UV light compared to OPP. Produced TPCS sheets were weak and soft due to low tensile strength and Young's modulus as well as moderate elongation at break. TPCS sheets exhibited the lowest OP among the polymers that have a medium level of OP (*e.g.* PLA, nylon 6) and of course high water permeability with a very high rate of water absorption.

# 7.1.2 Phase II: Extrusion of melt-compounded TPCS/PLA and investigation of the properties of the physical blends

TPCS resins having 30 wt% of glycerol were physically blended with PLA resins using a co-rotating TSE at ratios of 50/50 and 30/70 by weight. The surface energy of the neat polymers (TPCS and PLA resins) and the blend resins was investigated to estimate the miscibility of the blends. TPCS had higher surface energy and polarity than PLA, indicating a more hydrophilic nature, whereas the surface energy of the blend decreased with increasing PLA content. The high value of interfacial tension calculated from the surface energy indicated that the blends of TPCS/PLA are incompatible and immiscible as expected. The decrease of polarity after blending with PLA implied a reduction of water sensitivity of the starch blend, which was an initial objective of this research. The PLA's  $M_w$  decreased with addition of TPCS content in the blend, but the blends having high content of TPCS had a noticeable higher Mw and lower (thermal) degradation factors

*A blue shifting hydrogen bonding* in the FTIR spectrum of the blend was suggestive of a weak interaction and a phase-separation between starch and PLA. An increase of TPCS content enhanced crystallinity of PLA since TPCS acts as a nucleating agent. Thermal stability of PLA in

the blend also improved with a higher content of TPCS as evidenced by the higher  $T_{max}$  values from DTG. The increase of PLA thermal stability may be attributed to interactions between starch and PLA. However, SEM micrographs presented a non-homogeneous distribution of TPCS droplets in a PLA continuous phase. Furthermore, TEM micrographs of the blend films fabricated by cast-film extrusion showed coalescence of the TPCS droplets in the blend. The coalescence of TPCS domains emphasized that the compatibility between the polymer pair needs to be improved.

# 7.1.3 Phase III: Functionalization of PLA and evaluation of the effects of processing variables on PLA-g-MA

The initial intention of this project was to use a compatibilizer that was biobased and biodegradable; however, such a material is not commercially available yet. Therefore, PLA was modified by grafting maleic anhydride (MA) onto PLA using a reactive extrusion technique, which is the preferable industrial technique/method for modifying polyolefins and PS. Due to incomplete information on the effects of the processing conditions and their interactions on maleation of PLA, design of experiments, specifically a RSM, was used to analyze the effect of MA and 2,5-bis(*tert*-butylperoxy)-2,5-dimethylhexane (L101) contents, and TSE screw speed on the degree of grafting of MA onto PLA, and the molecular weight properties of functionalized PLA (PLA-*g*-MA). PLA-*g*-MA produced from free-radical melt grafting using a counter-rotating TSE had colors from pale yellow to yellow and orange depending on the contents of L101 and MA used. The new peaks observed on the FTIR spectrum suggested that MA was attached to the PLA backbone and oligomeric MA may occur. The possible microstructures of grafts formed including possible mechanisms during free-radical melt grafting of PLA are described in Chapter 5. The dominant side reaction of free-radical melt grafting of MA on PLA is chain degradation.

L101 content had a significant effect (P < 0.01) on PLA-g-MA; increasing L101 increased the degree of grafting and decreased  $M_n$ , but the  $M_n$  and PI of PLA-g-MA during storage were stable with PLA-g-MA performed using a high content of L101. MA showed an optimum concentration for the maximum degree of grafted MA at about 4.5 wt%, but increasing MA content especially under a high concentration of L101 retarded the reduction of  $M_n$ . The PLA-g-MA's  $M_n$  and PI stabilities during storage deteriorated with high MA content. TSE screw speed affected only the molecular weight properties of PLA-g-MA during maleation. The predicted optimum value of TSE screw speed was 20 rpm.

Finally, the boundary conditions of MA, L101 and TSE screw speed were framed under the three criteria of percentage of grafted MA, molecular weight, and molecular weight stability during storage, to obtain the optimum PLA maleated samples, which were: MA content of  $\leq 4.5$ wt%, L101 content in between 0.425 and 0.65 wt%, and TSE screw speed of 20 rpm. The outcome of this phase generated two other main questions: what are the effects of grafted MA content and  $M_n$  of PLA-g-MA on compatilization of the PLA/TPCS blends? and what is the stability of PLA-g-MA during storage?

# 7.1.4 Phase IV: Investigation of the effects of molecular weight and grafted MA of PLA-*g*-MA on the reactive compatibilization of TPCS/PLA blends

PLA-g-MA with different  $M_n$  and/or grafted MA content were used as a reactive polymer (binary blends of PLA-g-MA with TPCS at a ratio of 70/30 by weight) and as a reactive compatibilizer (ternary blends of PLA/TPCS/PLA-g-MA where the total amount of PLA and PLA-g-MA were 70 wt% and TPCS content was 30 wt%). The reactive blending was performed using a vertical mini co-rotating TSE. As a consequence of maleation, PLA-g-MA with higher grafted MA concent had lower  $M_n$ , broader PI, and lower IV. Overall, PLA-g-MA samples had higher  $T_{cc}$  values than PLA resin, but values of  $T_g$ ,  $T_m$ , and crystallinity and thermal stability  $(T_o, T_{max}, T_e)$  were closer to the PLA resin; except for some compositions having lower  $T_g$  value or higher  $T_m$  value, and lower  $T_{d5}$  values than the PLA resin. Additional information is presented in Chapter 6.

The presence of a new FTIR-ATR peak attributed to the carboxyl groups of hydrolyzed anhydrides remained after esterification of anhydride groups of PLA-*g*-MA and hydroxyl groups of starch, which suggested that PLA-*g*-MA interacted with TPCS. Change of thermal stability, decrease of  $T_{cc}$ , and double-melting peaks were observed in the reactive binary blends compared to PLA and the physical TPCS/PLA blend. There were no significant differences in loss modulus or  $T_g$  of PLA (observed from DMA), but the  $T_gs$  of glycerol and starch shifted up to higher temperatures compared to the physical TPCS/PLA blend. Higher grafted MA in the PLA-*g*-MA used provided better distribution and smaller domains of TPCS in the PLA continuous phase, but a few big TPCS domains appeared and could act as stress concentrators, which deteriorated the tensile properties of the reactive blends. Large TPCS domains were observed when PLA-*g*-MA having grafted MA not less than 0.40 wt% and  $M_n$  not higher than 50 kDa was used.

The optimum grafted MA and the minimum  $M_n$  of PLA-g-MA providing better tensile properties were further investigated from the reactive ternary blends. As also found in the reactive binary blends, increasing grafted MA content offered better dispersion and smaller domain size of TPCS, but a broader distribution of TPCS domain size was observed with a high content of PLA-g-MA. The lower the  $M_n$  of PLA-g-MA used, the lower distribution and the bigger were the sizes of the TPCS domains. The highest elongation at break was achieved when 30 wt% TPCS was blended with 70 wt% of PLA having 0.1 wt% of grafted MA and  $M_n$  of PLA-g-MA not lower than 45 kDa.

Finally, the boundary of PLA maleation and its molecular weight stability obtained from the third phase and the specification of PLA-g-MA suitable to be used as reactive compatibilizers or reactive polymers observed from the fourth phase ( $\geq 0.1$  wt% grafted MA with  $M_n$  of  $\geq 45$ kDa) were used as the cut point in the RSM design to produce the optimum PLA-g-MA. The boundary of PLA-g-MA specification is shown in Figure 7.1a, where the curved area at the bottom is indicative of PLA-g-MA having grafted MA less than 0.1 wt%, the curved area at the top is indicative of PLA-g-MA having  $M_n$  less than 45 kDa, and the curved area in the middle is in-spec PLA-g-MA ( $\geq 0.1$  wt% grafted MA with  $M_n$  of  $\geq 45$  kDa). The boundary of PLA maleation and its molecular weight stability still contains PLA-g-MA having  $M_n$  less than 45 kDa (curved area at the top) (Figure 7.1b). The  $M_n$  and grafted MA content of PLA-g-MA after framing by both boundaries are L101 of 0.425-0.61 wt%, MA content of 0.2-4.5 wt% and at TSE screw speed of 20 rpm, the predicted PLA-g-MA will contain grafted MA of around 0.2-0.475 wt% and  $M_n$  of around 47.5-60 kDa. The PI value did not apply in the boundary since  $M_n$  is a major concern.



**Figure 7.1** Contour profilers of predicted PLA-*g*-MA: a) boundary was set from PLA-*g*-MA specification; b) boundary was set from PLA maleation and molecular weight stability;

### 7.2 Overall conclusions

Cassava starch can be used to produce thermoplastic starch and blended with PLA to improve processability and to reduce the water sensitivity of TPCS; meanwhile improving the crystallinity and  $T_{max}$  and k of PLA. However, as PLA/TPCS is an incompatible and immiscible blend, it requires the use of compatibilizer. To maintain the attribute of producing a biobased biodegradable material, PLA was functionalized with MA using free-radical melt grafting performed in an extruder. A DOE indicated that the amounts of L101 and MA have significant effect on the grafting of MA and the final molecular weight of PLA-*g*-MA, whereas TSE screw speed had a significant effect only on the molecular weight of PLA-*g*-MA. Molecular weight and tensile properties of the binary and tertiary reactive blends. The optimum reactive blend of 30 wt% TPCS and 70 wt% of PLA having 0.1 wt% of grafted MA and  $M_n$  of PLA-*g*-MA with a 45 kDa exhibits the highest elongation at break. Finally, the optimum conditions for production of PLA-*g*-MA with the desirable property were predicted.

#### 7.3 **Recommendations for future work**

The recommendations for future work are mainly centered on the third and fourth phases of this work since the first and second phase had already been improved as previously mentioned.

# 7.3.1 Phase III: Functionalization of PLA and evaluation of the effects of process variables on PLA-g-MA

#### Improving homogeneity and purity of PLA-g-MA

The lack of homogeneity of grafted sites onto the PLA-g-MA led to a high variation of grafted MA as found by FTIR and titration results. Either lack of homogeneity or impurities obtained during grafting (discoloration, oligomeric end-grafting, and unreacted MA) reduce the property of PLA-g-MA when used as a compatibilizer. These problems arise mainly due to the complexity of the grafting and the side reactions from grafting and thermal extrusion, and generally occur with any kind of maleated polymers. The homogeneity of grafting may be improved by adjusting the premixing method before feeding a mixture of polymer/MA/peroxide initiator in a TSE. In this research, due to the limitation of the TSE, the mixtures were manually premixed before feeding.

Actually the recommended technique for free-radical grafting by reactive extrusion is that the peroxide initiator and MA should be injected onto the molten polymer to enhance mixing and dispersion [1-2]. MA could be pumped into the extruder in the form of molten MA or mixed with a peroxide initiator in a non-reactive solvent. The incorporation of a vacuum system at the last stage of extrusion helps remove volatile lower molecular weight components from the product. Those techniques could reduce discoloration (yellowness) and/or improve the degree of grafting with high molecular weight as mentioned elsewhere [1-2].

Other techniques to improve the degree of grafting and to reduce the impurities use chemical agents. The use of coagent monomers (*e.g.* methacrylic monomers, styrene) and/or the concept of nanoreactors could be applied to minimize side reactions and improve the degree of grafting as previously shown [3-4]. Research in this area is still evolving.

Improving the stability of PLA-g-MA during storage and investigation of grafting/molecular weight stability during storage including the photo-degradation of PLA-g-MA

The result from Coutinho and Ferreira showed that oxidation reactions occur during freeradical grafting of rubber containing diene and propylene [5]. The results of this work showed that the reduction in  $M_n$  and increase of *PI* of PLA-*g*-MA during storage was related to the initial concentration of MA and L101.  $M_n$  and *PI* values of PLA-*g*-MA were the most stable when a high concentration of L101 and a low concentration of MA were used (2 wt% MA and 0.65 wt% of L101). Therefore, reactive extrusion under a nitrogen atmosphere, using a vacuum system attached at the last stage of the extruder and use of the optimum concentrations of monomer and peroxide initiator could reduce or eliminate instability of PLA-*g*-MA's  $M_n$  during storage.

Previous research demonstrated that selecting a suitable initiator was preferable in controlling oxidation to using antioxidants since the antioxidants also lowered the degree of grafting [5]. When producing PP-g-MA, it was shown that PP-g-MA was photo-oxidized, and that the use of antioxidant can protect against photo-oxidation of PP but not PP-g-MA [6]. As a consequence, the deterioration of maleated polymers may limit the use and properties of the polymer matrix. Thus, an investigation of processing conditions on stability of molecular weight and grafted MA during storage and photo-degradation of PLA-g-MA should be conducted.

# 7.3.2 Phase IV: Investigation of the effects of molecular weight and grafted MA of PLA-*g* MA on reactive compatibilization of TPCS/PLA blends

#### Evaluation of properties of the reactive TPCS/PLA blends

This work was conducted to determine the effects of molecular weight and grafted MA content of PLA-g-MA and the compatibility and the thermo-mechanical properties of the reactive TPCS/PLA blends. The next step for future work should deal with the morphology stability of the reactive blend after fabrication into a film/sheet, and evaluation of the water sensitivity and permeability to gases and vapor, especially water. It should also include an assessment of the stability and biodegradability of the final sample, and the assessment of migrants from the reactive films. Finally, the entire information should be combined to evaluate the potential applications for this reactive material before upscale production.

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