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## ENGINEERING AND MODELING OF COMPATIBILIZED BIO-BASED POLYMER BLENDS USING REACTIVE EXTRUSION

presented by

**GUOREN CHENG** 

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## ENGINEERING AND MODELING OF COMPATIBILIZED BIO-BASED POLYMER BLENDS USING REACTIVE EXTRUSION

By

Guoren Cheng

## A DISSERTATION

Submitted to Michigan State University In partial fulfillment of the requirements for the degree of

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#### ABSTRACT

### ENGINEERING AND MODELING OF COMPATIBILIZED BIO-BASED POLYMER BLENDS USING REACTIVE EXTRUSION

By

#### Guoren Cheng

Two bio-based polymers, cellulose acetate (CA) and starch, were selected in this study to prepare compatibilized polymer blends. These blends were prepared by adding a reactive copolymer—poly (styrene-*co*-maleic anhydride (SMA)), generating graft copolymer of a CA-SMA or a Starch-SMA copolymer in situ by reactive extrusion to act as compatibilizer. In order to improve the compatibility of the blends, different grades of SMA having various molecular weights and various maleic anhydride contents were studied.

The grafting reaction (e.g. reactant concentration, temperature and catalyst concentrations), morphology and the mechanical properties of CA/SMA blends were investigated under both solution and melt conditions. We observed that a third order kinetic model of the grafting reaction parameters gave adequate fit and could be used to describe the compatibility of the blends under different reaction conditions. The morphology and the mechanical properties of CA/SMA blends having different compositions were also studied. Our results indicate that it is possible to prepare compatible CA/SMA blends having high tensile properties and good moisture resistance, which should make such blends suitable for a wide range of commercial applications. Furthermore, the preparation process itself was studied and optimized. Our results indicate that if the blends contain more than 15 wt% high molecular SMA, the extrusion proceeds smoothly without the need to add any plasticizer. Generally, the tensile strength

was inversely proportional to the SMA content and the highest tensile strength was obtained when a minimum amount of SMA was used.

The relationship between the morphology of the blends and the extent of grafting reactivity was also studied. In the melt, the phase dispersion affects the grafting reaction via increasing the interface area while the grafting reaction affects the phase dispersion by reducing the interfacial tension. Additionally, shear rate, interfacial tension, temperature and composition as well as the injection molding conditions further impact the compatibility of the blends and were used to optimize the injection process.

In starch/SMA blend, the addition of glycerol as a plasticizer greatly improves the processability due to grafting of glycerol onto SMA as well as additional cross-linking between starch, SMA and glycerol. This modified starch/SMA blend was blended with poly (butylene adipate-*co*-terephthalate) (Ecoflex) and the resulting compatible blend was blown into films. Such blends of Ecoflex and modified starch exhibit good mechanical properties, excellent processability, low cost (compared with Ecoflex and starch blend), and are biodegradable.

In the last part of this thesis, vinyltrimethoxysilane was used as a grafting agent to prepare organic-inorganic hybrids based on Ecoflex and Magnesium Silicate Hydroxide (Talc). The grafting reactions of this silane were studied in relation to the mechanic properties of the blends. Copyright by

# **GUOREN CHENG**

Dedicated to

My parents and my wife

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## TABLE OF ABBREVIATIONS

Chapter 1	
СА	Cellulose acetate
SMA	Poly (styrene-co-maleic anhydride)
Ecoflex	Poly (butylene adipate-co-terephthalate)
Talc	Magnesium Silicate Hydroxide
PCL	Poly (ε-caprolactone)
PLA	Poly (lactic acid)
РНЕ	Poly (hydroxyester)
РНЕЕ	Poly (hydroxyesterether)
DOP	Dioctylphthalate
DEP	Diethylphthalate
T <sub>m</sub>	Melting Temperature
Chapter 2	
MA	Maleic anhydride
DS	Degree of substitution
Mw	Weight average molecular weight
$\overline{M_n}$	Number average molecular weight
Tg	Glass transition temperature
DMAP	4-Dimethylaminopyridine

DMF	N,N-Dimethylformamide
fsma	Weight grafting conversion of SMA
M <sub>i</sub>	Molecular weight of i <sup>th</sup> SMA chain
C <sub>i</sub>	Mole concentration of the i <sup>th</sup> SMA chain after reaction
$C_i^0$	Initial mole concentration of the i <sup>th</sup> SMA chain
α <sub>ung</sub>	Fraction of un-grafted SMA chains that have the same chance to graft compared to the grafted chains
V <sub>s</sub>	Fraction of interfacial volume in total volume between two phases
V <sub>0</sub>	Volume of the solution
N	Number of SMA droplet
S <sub>k</sub>	Surface area of k <sup>th</sup> droplet
$\delta_k$	Depth of the interfacial penetration of k <sup>th</sup> droplet
$\overline{R}$	Average SMA droplet radius
K <sub>0</sub>	Reaction constant
E	Activation energy
R'	Gas constannt
Т	Reaction temperature
С-он	Concentration of OH group
С <sub>-МА</sub>	Concentration of MA group
C <sub>DMAP</sub>	Concentration of DMAP

<i>C</i> <sup>0</sup>	Initial mole concentration of SMA
PDI	Polydispersity index
f'sma	Modified SMA grafting conversion
Chapter 3	
L/D	Length to diameter ratio of extruder
D	Diameter of extruder
FTIR	Fourier transformed infrared spectroscopy
Chapter 4	
$\Delta G_m$	Gibbs energy of mixing
V <sub>A</sub>	Actual volume of polymer A
V <sub>B</sub>	Actual volume of polymer B
¢ <sub>A</sub>	Volume fraction of polymer A
\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$\$	Volume fraction of polymer B
B <sub>AB</sub>	Binary interaction energy
$\overline{V}_A$	Molar volume of polymer A
$\overline{V}_B$	Molar volume of polymer B
$\Delta \overline{H}_m$	Mixing enthalpy at unit volume
$\Delta \overline{S}_m$	Mixing entropy at unit volume
Р	Properties of polymer blend
P <sub>A</sub>	Properties of polymer A

P <sub>B</sub>	Properties of polymer B
w <sub>A</sub>	Weight fractions of polymer A
w <sub>B</sub>	Weight fractions of polymer B
$\Delta P^E(w)$	Excess term of properties
Са	Capillary number
η <sub>m</sub>	Polymer matrix viscosity
Ŷ	Shear rate
R	Radius of disperse phase size
σ	Interfacial tension
t	Processing time
Ca <sub>c</sub>	Critical Capillary Number
R <sub>c</sub>	Radius of disperse phase size at critical state
f	A constant of droplet breakup rate
φ	Volume fraction of the dispersed phase
Pc	Probability that collision of the particles will be followed by their fusion
λ	Ratio of the viscosities of the dispersed phase and matrix
С	Concentration of the compatibilizer
k	A constant of interfacial tension change with compatibilizer concentration
$\sigma_s$	Interfacial tension under saturate compatibilizer concentration
С <sub>он-ма</sub>	Mole concentration of half-ester bonds
Ė	Volume flow rate in the extruder
L	

t <sub>res</sub>	Extruder residence time
$\sigma_0$	Interfacial tension without compatibilizer
R <sub>cs</sub>	Radius of disperse phase droplet at critical state under saturate compatibilizer
<i>R<sub>c0</sub></i>	Radius of disperse phase droplet at critical state with out compatibilizer
Chapter 5	
TPS	Thermoplastic Starch
Chapter 6	
PBS	Poly(butylene succinate)
Lupersol 101	2,5-Bis(tert-butylperoxy)-2,5 dimethylhexane
VTMOS	Vinyl-trimethoxysilane
VMDMOS	vinyl-methyl-dimethoxysilane

#### **Chapter 1. INTRODUCTION**

#### **1.1 RATIONALE**

Plastics play a very important role in today's life. While plastics are convenient, strong, light-weight, inexpensive and easily processable, they are not readily broken down in the environment. This is of particular concern when plastics are used in single-use disposable packaging and consumer goods. It causes a serious issue of environmental pollution. Another important concern of plastics is that most general plastics are petrochemical-based and, hence, are derived from a non-renewable resource. Thus, two concepts: bio-based and biodegradable are introduced into new products design. The impacts of raw material resources and the disposal of end products must be factored into the design phase of any new products. This has opened up new market opportunities for developing biodegradable and bio-based products from annually renewable resources as the next generation of sustainable materials that meets ecological and economic requirements (1 - 5).

The advantage of using annually renewable biomass as the feedstock for the production of polymers, chemicals and fuel, needs to be understood from a global carbon cycle basis. Crude oil is pumped out of the ground and is made into gasoline, diesel and a variety of synthetic materials by the chemical industry. These polymers, chemicals and fuels are used by manufacturers, cars and trucks, which upon their disposal and

decomposition release  $CO_2$  into the atmosphere. The problem is that this release of  $CO_2$  takes only a few years whereby plants and trees capture  $CO_2$  through photosynthesis and fossilized it over geological timeframes (millions of years). Consequently, the geological carbon cycling process for petrochemical feedstock is out of balance leading to unsustainable development (Figure1-1). Thus, it is desirable to use annually renewable crops like corn, soy and wheat as the carbon source for polymers, chemicals and fuels. This approach will ensure that the rate of  $CO_2$  capture by photosynthesis is equal to that of  $CO_2$  release by burning and decomposition. It is important to note that although the Kyoto Protocols hasn't been ratified by the US, Sustainable development is our responsibility to society. Furthermore, if we manage our biomass resources effectively by ensuring that we plant more biomass than we utilize, we can begin to reverse the carbon dioxide rate equation and move toward a net balance between  $CO_2$  fixation/sequestration and release.



#### Figure 1-1 Global carbon cycling

Environmental regulations, societal concerns, and a growing environmental awareness throughout the world have triggered a paradigm shift in industry to develop products and processes compatible with the environment. In this regard, there is an interest in developing and evaluating materials based on recyclable, natural and degradable polymers. These include natural polymers like starch, cellulose and proteins, or synthetic biodegradable polymers like poly (ε-caprolactone) (PCL), poly (D, L, or DLlactide) (PLA), poly (butylene adipate-*co*-terephthalate) (PBAT), poly (hydroxy esters) (PHE), poly (hydroxy ester ethers) (PHEE) and their modified versions. Biodegradable plastics derived from these polymers are currently being used in a variety of applications ranging from packaging films, cutlery items (spoons, knives, forks etc.), biodegradable packaging foams and more.

Although bio-based and biodegradable polymers have been commercialized for over 20 years, this niche market is beset with a variety of roadblocks led by high prices and poor processability. Indeed, natural polymers such as starch, cellulose and proteins, are widely available and are generally comparable in cost to petrochemical based polymer, however, their processability is much poorer. Synthetic biodegradable polymers, on the other hand, have good processability but they are much higher in price. A practical way to reduce the cost and improve the processability is by blending. Blending has emerged as a major tool to obtain new polymeric materials with desired properties by mixing two or more existing polymers. The study of polymer blends has therefore developed rapidly in recent years (6-10). Blends of synthetic, biodegradable polymers with low cost, environmentally friendly fillers or natural products were previously prepared and studied from polymers like PCL, PLA and PBAT that were blended with starch, calcium carbonate or talc (11-15). Unfortunately, simple mixing leads to poor blends due to incompatibility. Thus, it is necessary to add a compatibilizing agent in order to improve the preparation process as well as enhance the physical properties of the blends. Processing natural polymers and their derivatives by adding a plasticizer or using a reactive process are described in the literature as common methods to process polymers to form bio-based polymer blends (16-20).

Extruders are traditionally used to transform a solid plastic into a uniform melt for delivery to the next stage of processing. Various physical processes, such as devolatilization and blending, have also been carried out in extruders. During the last three decades, the direction of polymer R&D has been changing gradually from pursuing new polymers to filling some of the performance gaps in the diversity of existing plastic

materials via modifying, reactive blending, reinforcing and other methods that improve properties. Using extruders as continuous flow reactors to modify polymers (enhancing thermal properties, improving mechanical or adhesive properties via introducing certain chemical changes) is termed as "*Reactive Extrusion*" (20 - 30). More specifically, *reactive extrusion* refers to the process of conducting chemical reactions during the melt extrusion process. Discrete processes can be carried out in specific modular segments of a twin-screw extruder, whose screw configuration can be tailored to meet the desired objective. The reaction needs to be achieved within the residence times available in extrusion operations. Advantages of using extruders to conduct reactions are listed below:

- Fast and continuous process
- Solvent free melt process
- Control over residence time
- Integration of other extrusion 'streams' along with the polymerization process
- Efficient devolatilization capability through the vent port
- Modular in design; easy to scale up

Interest in environmentally friendly materials has stimulated fast development of biodegradable packaging films and foams. However the study of bio-based engineering plastics is rare. Glasser, Wolfgang G (31) discussed converting woody biomass into a variety of thermoplastic and thermosetting materials, and into regenerated fiber and hydrogel products ; Grafting by copolymerization of  $\varepsilon$ -caprolactone and lactic acid onto cellulose diacetate at the residual hydroxyl positions to obtain thermoplastic was studied by Teramoto, Yoshikuni et.al (32); A bio-composite using cellulose acetate and natural fiber (coconut, ramie) with triacetine (TA) as a plasticizer were combined in a melting

process by Lee, Sang Hwan and his co-workers(33).

#### **1.2 PROPOSED GOALS**

The target of this study is to prepare compatible bio-based polymer blends by blending natural polymers (cellulose acetate(CA), starch) with synthetic polymers that have a high number of functional groups (styrene maleic anhydride copolymer(SMA)). Grafting SMA onto CA to form grafting co-polymers, which act as compatibilizers, can be done in situ by reactive extrusion. The graft co-polymer improves the properties of the CA/SMA bio-based polymer blends by reducing the interfacial tension and improving the phase dispersion. Possible target applications of these bio-based polymer blends are in structural materials such as, automobile parts, furniture and tools. The study further deals with improvement of the mechanical properties; cost reduction, and the optimization of process conditions and components.

This study also focuses on improving the compatibilization of bio-based polymers with synthetic biodegradable polymers by reactive blending. The goal is to prepare materials with good properties and to lower the cost associated with bio-based or biodegradable materials. Specifically, the target application for a thermoplastic starch and SMA blend is biodegradable packaging films. Such compositions were prepared by grafting thermoplastic starch and SMA onto biodegradable polyester. The blends thus prepared can be used as low cost biodegradable materials.

#### **1.3 SPECIFIC OBJECTIVES**

#### **1.3.1 Problem Statement**

Cellulose esters are one important family of modified natural polymers. Cellulose acetate is of particular commercial importance. Cellulose acetate is used as a sustainable material in many areas and products (e.g. textiles and fibers, spectacle frames, tools handles) due to its toughness and high gloss. However it has a very narrow processing window due to the close proximity of its melting temperature to its decomposition temperature. Between 28 and 44% phthalate ester plasticizer (e.g. DOP and DEP) is added to enable processing. Unfortunately adding a plasticizer reduces the mechanical properties and in the case of phthalate ester plasticizers can have detrimental health effects. Such plasticizers are suspected cancer causing materials and are prohibited by European Union and California legislation.

Starch, an anhydroglucose polymer derived from plants, offers a structural platform for the manufacture of sustainable, biodegradable packaging material. Starch granules, however, exhibit hydrophilic properties and strong inter-molecular associations via hydrogen bonding due to the hydroxyl groups on the granule surface. The strong hydrogen bonding association and crystallization lead to poor thermal processing because the melting temperature  $(T_m)$  is higher than the thermal decomposition temperature. Thus, degradation sets in before thermal melting. The process properties of plasticized starch are also very poor. It is also incompatible with biodegradable synthetic polymers due to its strong intermolecular associations.

Adding inorganic filler to synthetic biodegradable polymer can lower the cost. However, simply adding inorganic filler significantly reduces the tensile properties of the blend due to incompatibility.

#### 1.3.2 Objectives of this study

I. In CA processing, use synthetic polymers in place of monomeric plasticizer, eliminate leaching, improve processing window and reduce environmental consequence.

II. Improve the compatibility of CA and synthetic polymer by choosing functionalized synthetic polymer (Styrene maleic anhydride (SMA)) and proper catalyst to introduce grafting reaction between the components in reactive extrusion, generating in-situ grafting copolymer as the compatibilizer.

III. Study factors affecting the reactivity and phase dispersion of CA/SMA polymer blend, optimize the mechanical properties by changing the component contents and injection molding conditions. The following detail objectives are included:

A. Study the reactive kinetics of cellulose acetate and SMA in solution

B. Study the grafting reaction in the reactive extruder

C. Analyze the relationship between compatibility and the reactivity

D. Maximize the bio-based component without affecting the process properties

E. Optimize the mechanical properties by changing the process conditions

IV. Prepare a starch semi-ester by reactive extrusion of thermoplastic starch and SMA, improve the compatibility of thermoplastic starch and a commercialized biodegradable synthetic polyester (Poly (butylene adipate-*co*-terephthalate)) (Ecoflex), and improve the mechanical and biodegradable properties of the blend blown films.

V. Prepare organic-inorganic hybrid polymer blends (Ecoflex/Talc) which apply to blown film, introduce a functional silane as a grafting agent in this organic-inorganic blend to improve the compatibility and tensile properties.

#### **1.4 ORGANIZATION OF THE THESIS**

The thesis is composed of seven chapters, each of which individually addresses the work that has been done in relation to the specific objectives outlined below.

**Chapter 2** deals with the CA/SMA grafting reaction in DMF solution. The grafting conversion of SMA at different time, concentration, temperature and MA content are measured, analyzed and compared with a theoretical analysis..

**Chapter 3** describes the preparation of CA/SMA polymer blends by reactive extrusion and characterizes the grafting reaction in melt conditions. Different SMA compositions and different grades of SMA were used. This chapter also deals with the studies of properties and processing conditions.

**Chapter 4** studies the phase dispersion of CA/SMA polymer blends in a reactive extrusion process. The relationship between grafting reaction and phase dispersion are characterized by experimental and theoretical methods.

**Chapter 5** discusses the preparation of thermoplastic starch and SMA grafting polymer blends. The grafting reactivities at different amounts of SMA are characterized. One such polymer blend is mixed with a biodegradable plastic (Ecoflex) and the blown film process is characterized.

**Chapter 6** introduces a method to prepare biodegradable, organic-inorganic hybrid blend. Here, the biodegradable polyester (e.g. Ecoflex) and an inorganic filler (e.g. talc) are mixed using a functional silane as the grafting agent. The mixture is blown into films and the tensile properties are studied.

The conclusions and recommendations for future work are discussed in chapter 7.

### **Chapter 2. STUDY OF THE GRAFTING REACTION OF CELLULOSE ACETATE AND STYRENE-MALEIC ANHYDRIDE IN SOLUTION**

#### **2.1. INTRODUCTION**

Grafting reactions provide a method for preparing new polymeric materials with desirable and improved properties. Grafting a monomer or a mixture of monomers onto the backbone of an existing polymer for the purpose of improving various properties has been done by free radical, anionic, cationic or a condensation mechanism (34-38). Most graft polymerization processes, irrespective of the initiation process, produce mixtures of graft copolymers, and homo-polymers

Grafting a monomer or a functionalized polymer (ex. styrene, acrylamide, caprolactone, nylon66) onto cellulose or cellulose acetate has been studied in solvent or by extrusion processes (39-43). The availability of more functionalized and/or modified polymers provides new opportunities for the production of graft copolymers and their alloys by coupling two reactive polymers. Maleic anhydride (MA) -modified polyolefins and random copolymers of maleic anhydride with some vinyl monomers are one family of reactive polymers (44-45). The reactivity is provided by the anhydride. Extensive work has been done on grafting anhydride groups on one polymer and amine groups on another polymer to form compatibilized blends via reactive extrusion (46). Polymers containing hydroxyl groups are another family of reactive polymers. The reaction between the anhydride and the hydroxyl is another choice for the production of graft copolymers to form compatibilized blends. Many natural polymers and their derivatives are an important source of hydroxyl-bearing reactive polymers.

Cellulose acetate (Degree of substitution (DS): 2.45) is one of the most commercially important cellulose derivatives. It is a tough material with excellent optical clarity. However, it is well known that cellulose acetate has poor dimensional stability under high humidity and at elevated temperature. Additionally, this polymer is relatively expensive, it is characterized by a very limited compatibility with other synthetic polymers, and it requires high processing temperature.

Styrene-maleic anhydride copolymer has gained attention because it is commercially available. The grafting reaction between CA and SMA can add new properties to cellulose acetate by forming compatibilized blends and the incorporation of hydrophobic SMA can help further improve the dimensional stability of CA.

#### **2.2 EXPERIMENTAL**

#### 2.2.1 Materials

Cellulose Acetate (DS: 2.45,  $\overline{M_w}$ : 103,000,  $\overline{M_n}$ : 46,000,  $Tg=187^{\circ}$ C, Tm=232<sup>o</sup>C) was provided by Eastman Chemical Company. High Molecular weight Styrene maleic anhydride random copolymers (SMA132: 4.75 wt % maleic anhydride,  $\overline{M_w}$ : 274,000,  $\overline{M_n}$ : 136,000; SMA232: 7.08 wt % maleic anhydride,  $\overline{M_w}$ : 249,000,  $\overline{M_n}$ : 126,000; SMA332: 12.2% maleic anhydride,  $\overline{M_w}$ :193,000,  $\overline{M_n}$ : 100,000) were provided by Nova Chemical Company. The structural units of CA and SMA232 are shown in Figure2-1 and Figure2-2. The catalyst 4-Dimethylaminopyridine (DMAP), solvents anhydrous grade N,N-Dimethylformamide (DMF, 99%) and Toluene (anhydrous) were purchased from Sigma-Aldrich, Inc.



Figure 2-1 Cellulose acetate (DS=2.5)



Figure 2-2 Poly (styrene-co-maleic anhydride) SMA232

In this study the grafting reaction of CA with SMA happens between the hydroxyl and anhydride groups in the presence of catalyst to form a half ester (Figure 2-3). In this particular polymers system, each polymer has a large number of reactive groups available for interactions: 85 hydroxyls on CA and 90 anhydrides on SMA232 as can be calculated from the number average molecular weights of these polymers.



CA-SMA grafted copolymer

Figure 2-3 Grafting reaction between CA and SMA232

#### 2.2.2 Grafting reaction

Grafting reactions were carried out in DMF solution in a glass batch reactor with stirring. Cellulose acetate was vacuum dried overnight at 90-100°C. The DMAP catalyst was added after the polymer solution reached a stable temperature and the reaction was allowed to proceed for hours at this temperature. The solutions were then cooled to room temperature and the product was precipitated by washing with large excess (three-times by volume) of water. The precipitate was further washed with excess of hot water to remove residual DMF and any traces of the catalyst. The precipitates were then dried at room temperature overnight and then at 50°C under full vacuum. Each sample was weighed and kept under dry conditions. This procedure was used for different polymer concentrations, temperature, catalyst amounts and grades of SMA (with different MA content).

#### 2.2.3 Soxhlet extraction

Information on the grafting conversion of SMA (wt %) was obtained by soxhlet extraction with toluene for 48 hrs. Elemental analysis of the extractable material (obtained by C,H,N elemental analysis) showed the presence of less than 2% of CA in the extractable fraction. Therefore, only free SMA was extracted. Percentage conversion of SMA was obtained from the mass balance.

#### **2.3 THEORETICAL STUDY**

The grafting conversion of SMA can be written as:
$$f_{SMA} = 1 - \left(\frac{\sum M_i C_i}{\sum M_i C_i^0}\right)_{SMA}$$
(2-1)

 $f_{SMA}$  is the weight grafting conversion of SMA

 $M_i$  is the molecular weight of i<sup>th</sup> SMA chain

 $C_i$  is the mole concentration of the i<sup>th</sup> SMA chain after reaction

 $C_i^{0}$  is the initial mole concentration of the i<sup>th</sup> SMA chain

Thus, the SMA conversion rate can be written as:

$$\frac{\partial f_{SMA}}{\partial t} = -\left(\frac{\sum M_i \partial C_i}{\partial t} \right)_{SMA}$$
(2-2)

In the Batch reactor, the i<sup>th</sup> SMA chain conversion rate can be expressed as:

$$-\left(\frac{\partial C_{i}}{\partial t}\right)_{SMA} = \left(\frac{\alpha_{ung}M_{i}C_{i}}{\sum M_{i}C_{i}^{0} - (1 - \alpha_{ung})\sum M_{i}C_{i}}\right)_{SMA}V_{s}r_{MA}$$
(2-3)

 $\alpha_{_{ung}}$  is the fraction of un-grafted SMA chains that have the same probability to

graft compared to the grafted chains, and  $\frac{\alpha_{ung}M_iC_i}{\sum M_iC_i^0 - (1 - \alpha_{ung})\sum M_iC_i}$  is the

coefficient of the consumption of i<sup>th</sup> SMA chain in the grafting reaction.

$$V_{s} = \sum_{k=1}^{N} S_{k} \delta_{k} / V_{0}$$
 (2-4)

 $V_s$  is the fraction of interfacial volume in total volume between two phases

 $V_0$  is the total volume of the solution

N is the total numbers of SMA droplet

 $S_k$  is the surface area of k<sup>th</sup> droplet

 $\delta_k$  is the depth of the interfacial penetration of k<sup>th</sup> droplet

We assume that  $\delta_k$  does not change with the size of the droplet as it is only

related to free volumes and the interfacial tension.

Thus, at a given volume fraction of SMA,

$$V_s \propto 1/\overline{R}$$
 (2-5)

where,  $\overline{R}$  is the average SMA droplet radius.

 $r_{MA}$  is the reaction rate of MA functional group in SMA and it can be written as:

$$r_{MA} = -\frac{\partial C_{-MA}}{\partial t} = K_0 \exp(-E/R'T)C_{-OH}C_{-MA}C_{DMAP}$$
(2-6)

 $K_0$  is the reaction constant

*E* is the activation energy

R is the gas constant

T is the reaction temperature

 $C_{-OH}$  is the concentration of OH group

 $C_{-MA}$  is the concentration of MA group

 $C_{DMAP}$  is the concentration of DMAP

Substituting equation 2-3 into equation 2-2, we get:

$$-\frac{\partial f_{SMA}}{\partial t} = \left(\frac{\alpha_{ung} \sum M_i^2 C_i}{(\sum M_i C_i^0 - (1 - \alpha_{ung}) \sum M_i C_i) \sum M_i C_i^0}\right)_{SMA} V_s r_{MA}$$
(2-7)

When the grafting reaction is performed at low concentrations in solution, SMA polymer chains are "stretched" and all the reactive groups have similar probability to react.

 $\alpha_{ung} = 1$  and  $V_s$  is a constant.

Thus, we can simplify equation 2-7 and rewrite it as in equation 2-8.

$$-\frac{\partial f_{SMA}}{\partial t} = \left(\frac{\sum M_i^2 C_i}{\left(\sum M_i C_i^0\right)^2}\right)_{SMA} V_s r_{MA}$$
(2-8)

The weight average molecular weight  $\overline{M_w}$  and the number average molecular weight  $\overline{M_n}$  can be written as:

$$\overline{M}_{w} = \frac{\sum M_{i}^{2}C_{i}}{\sum M_{i}C_{i}}$$
(2-9)  
$$\overline{M}_{n} = \frac{\sum M_{i}C_{i}}{\sum C_{i}}$$
(2-10)

And the polydispersity index (PDI) can be expressed as:

$$PDI = \overline{M_w} / \overline{M_n}$$
 (2-11)

Equation 2-8 can be modified to equation 2-12 from equations 2-1, 2-9, 2-10, 2-

(2-10)

11;

$$-\frac{\partial f_{SMA}}{\partial t} = \left(\frac{\sum M_{i}^{2}C_{i}}{(\sum M_{i}C_{i}^{0})^{2}}\right)_{SMA}V_{s}r_{MA}$$

$$= \left(\frac{\sum M_{i}^{2}C_{i}}{\sum M_{i}C_{i}} \times \sum M_{i}C_{i}\right)_{SMA}V_{s}r_{MA}$$

$$= \left(\overline{M_{w}} \times (1 - f_{SMA})/(\sum M_{i}C_{i}^{0})\right)_{SMA}V_{s}r_{MA}$$

$$= \left((1 - f_{SMA}) \times \frac{\overline{M_{w}}}{\overline{M_{w}}^{0}} \times \frac{\overline{M_{w}}^{0}}{(\sum M_{i}C_{i}^{0}) \sum C_{i}^{0}} \times \sum C_{i}^{0}\right)_{SMA}V_{s}r_{MA}$$

$$= \left((1 - f_{SMA}) \times \frac{\overline{M_{w}}}{\overline{M_{w}}^{0}} \times \frac{PDI^{0}}{C^{0}}\right)_{SMA}V_{s}r_{MA}$$

$$= \left((1 - f_{SMA}) \times \frac{\overline{M_{w}}}{\overline{M_{w}}^{0}} \times \frac{PDI^{0}}{C^{0}}\right)_{SMA}V_{s}r_{MA}$$

In the CA-SMA232 grafting reactions, the consumption of -OH and -MA groups are negligible since the average grafted linkage is less than 2.5 even when the SMA grafting conversion goes to 80% as was shown by a theoretical study done by Nie, Li (47). Accordingly, Nie concluded from the molecular weight measurement results of SMA232, that the molecular weight distribution is very close to the Schulz distribution, and the PDI is 1.98. From this distribution, we can draw the relationship between the change of the weight average molecular weight and the graft conversion of SMA as shown in equation 2-13.

$$\left(\frac{M_w}{M_w^{0}}\right)_{SMA} = \left(1 - f_{SMA}\right)^{0.5}$$
(2-13)

Then, we solve the differential equation 2-12 with these initial conditions:  $f_{SMA} = 0$  at t = 0, and we get equation 2-14.

$$(1 - f_{SMA})^{-0.5} - 1 = \frac{PDI^0}{C^0} K_0 \exp(-E/R'T) C_{-OH} C_{-MA} C_{DMAP} V_s t \qquad (2-14)$$

Finally, by setting  $f'_{SMA} = (1 - f_{SMA})^{-0.5} - 1$  the modified SMA grafting

conversion is given by equation 2-15:

$$f'_{SMA} = (1 - f_{SMA})^{-0.5} - 1 = \frac{PDI^0}{C^0} K_0 \exp(-E/R'T) C_{-OH} C_{-MA} C_{DMAP} V_s t \qquad (2-15)$$

In this equation, the term  $\frac{C_{-MA}}{C^0}$  is a constant related to a specific SMA grade.

## **2.4 RESULTS AND ANALYSIS**

## 2.4.1 The SMA grafting conversion vs. time at different CA/SMA232 concentrations

The grafting rate of SMA232 was studied in three different polymer concentrations under constant temperature and fixed catalyst concentration. From the fitting curves we can see that  $f'_{SMA}$  is linearly proportional to the reaction time for all three concentrations. It is further observed that at high polymer concentrations, the R<sup>2</sup> value of the trend line decreased. Apparently, at higher concentration  $\alpha_{ung}$  is not equal to 1 and, therefore a variable coefficient must be considered under these conditions.

We can also observe that the slopes of each fitted line (at 14g/100ml, 11g/100ml and 8g/100ml) are also linearly proportional to the polymer concentration as predicted from equation 2-15.

8g/100ml DMF			11g/100ml DMF			14g/100ml DMF		
time	f <sub>sma</sub>	f' <sub>sma</sub>	time	f <sub>sma</sub>	$f'_{SMA}$	time	f <sub>sma</sub>	f' <sub>sma</sub>
hrs	%		hrs	%		hrs	%	
0.5	0.27	0.17	0.5	0.3	0.20	1	0.33	0.22
1	0.4	0.29	1	0.45	0.35	2	0.46	0.36
1.5	0.51	0.43	1.5	0.56	0.51	3	0.54	0.47
2	0.58	0.54	2	0.66	0.71	4.5	0.63	0.64
2.5	0.64	0.67	2.5	0.74	0.96	5.9	0.72	0.89
3	0.69	0.80						

Table 2-1  $f_{SMA}$  vs. reaction time at different CA/SMA concentrations\*

\*CA:SMA232=1:1, DMAP=0.5g/100ml, T=110<sup>°</sup>C





Figure 2-4  $f'_{SMA}$  vs. time fitting curve at 8g/100ml concentration



Figure 2-5  $f'_{SMA}$  vs. time fitting curve at 11g/100ml concentration



Figure 2-6  $f'_{SMA}$  vs. time fitting curve at 14g/100ml concentration

## 2.4.2 The SMA grafting conversion vs. the concentration of DMAP

Using a constant polymer concentration of 11g/100ml the grafting reaction was studied under four different DMAP concentrations. It is apparent from Figure 2-7 that  $f'_{SMA}$  is a linear function of DMAP concentrations confirming a third order reaction kinetics. Furthermore, it is apparent that when the DMAP concentration approaches zero,

 $f'_{SMA}$  becomes a very small negative number indicating that without a catalyst the grafting reaction does not occur. This dependence on the catalyst will also be confirmed under melting conditions.

DMAP concentration	$f_{SMA}$	f' <sub>SMA</sub>
g/100ml	%	
0.135	0.34	0.23
0.27	0.51	0.43
0.45	0.66	0.71
0.54	0.73	0.92

Table 2-2  $f_{SMA}$  vs. DMAP concentrations\*

\*CA:SMA232=1:1, 11g/100ml, T=110<sup>o</sup>C, t=2hrs



Figure 2-7  $f'_{SMA}$  vs. DMAP concentration fitting curve

## 2.4.3 The SMA grafting conversion vs. temperature

The SMA grafting conversion as a function of temperatures was also studied while keeping all other variables constant. The data indicate that the relationship between modified grafting conversion and reaction temperature follows Arrhenius law and the average activation energy can be calculated to be : E = 15567 KJ / Kmol

Т	T 1/T		f <sub>sma</sub>	$f'_{SMA}$	$\ln(1/f'_{SMA})$
С	K	1/K	%		
91	364	0.0027	0.43	0.32	0.489
100	373	0.00268	0.58	0.54	0.265
110	383	0.00261	0.66	0.71	0.146
125	398	0.00251	0.73	0.92	0.034

Table 2-3  $f_{SMA}$  vs. temperatures\*

<sup>\*</sup>CA:SMA232=1:1, 11g/100ml, DMAP=0.5g/100ml, t=2hrs



Figure 2-8  $\ln(1/f'_{SMA})$  vs. 1/T fitting curve

## 2.4.4 The SMA grafting conversion vs. MA content in SMA

As discussed before,  $\frac{C_{-MA}}{C_0}$  is only related to the grade of SMA, more particularly, to the

MA content in SMA. Here, SMA132 and SMA232 with different MA contents were used. It is expected according to equation 2-15 that  $f'_{SMA}$  will be a linear function of MA contents as shown in Figure 2-9.

SMA grade	MA%	f <sub>SMA</sub>	$f'_{SMA}$
		%	
SMA132	4.74%	0.56	0.51
SMA232	7.08%	0.66	0.71

Table 2-4  $f_{SMA}$  vs. MA content\*

\*CA:SMA=1:1, 11g/100ml, T=110<sup>o</sup>C, t=2hrs, DMAP=0.5g/100ml



Figure 2-9  $f'_{SMA}$  vs. MA contents fitting curve

# 2.4.5 Calculate reaction constant $K_0$ from the SMA conversion value in solution The reaction constant (K0) can be calculated from equation 2-15 using the following conditions: $T=100^{\circ}C$ , t = 2hrs, CA/SMA232=1:1, solution concentration of 11g/100ml, and DMAP concentration of 0.5g/100ml. At $f_{SMA}=0.58$ we can assume a dilute solution conditions, so, $V_s=1$ .

Thus, using Equation 2-15:

$$f'_{SMA} = (1 - f_{SMA})^{-0.5} - 1 = \frac{PDI^0}{C^0} K_0 \exp(-E/R'T) C_{-OH} C_{-MA} C_{DMAP} V_s t$$

$$C^{0} = 5.5g/100ml \div \overline{M}_{n(SMA)} = 5.5 \times 10^{-4} mol/L$$

$$C_{-OH} = 5.5g/100ml \div \overline{M}_{n(CA)} \times N_{-OH} = 0.102mol/L, N_{-OH} \text{ is the number of}$$

-OH groups in the CA chain with a given number average molecular weight.

$$C_{-MA} = C^0 \times N_{-MA} = 0.0495 mol / L$$
,  $N_{-MA}$  is the number of -MA groups in

the SMA chain with a given number average molecular weight.

$$C_{DMAP} = 0.5g / 100ml \div M_{n(DMAP)} = 0.0409mol / L$$
  
T=373.15 K  
t =120 min

We can calculate  $K_0$  from the equation 2-15:

$$K_0 = 1.195L^2 / mol^2 \min$$

## **2.5 CONCLUSIONS**

The CA/SMA grafting reaction in dilute solutions can adequately be described by equation 2-15. Our data clearly indicate that the modified SMA conversion  $f'_{SMA}$  is proportional to the CA concentration as predicted. Furthermore, grafting reaction is also linearly proportional to the MA content of SMA and the catalyst. Finally, the results show that the relationship between the reaction constant and the temperature follows Arrhenius Law, with an activation energy of 15,567 KJ / Kmol.

However, it should be noted that as the polymers concentration is increased, some phase separation can occur, which will then impact the effective reaction volume and the probability of the un-grafted chain and the grafted chain to react.

## Chapter 3. STUDY OF THE GRAFTING REACTIVITY AND PROPERTIES OF CA/SMA POLYMER BLENDS PREPARED BY REACTIVE EXTRUSION

#### **3.1 INTRODUCTION**

Grafting provides a method to improve the compatibility of polymer blends to achieve desirable properties. It is based on the formation of compatibilizer at the interface between the two polymers phases (48). Maleic anhydride (MA) has been widely used as one such compatibilizer because it has two distinct functional groups; an anhydride group that can undergo a condensation reaction with polymers containing amine or alcohol groups and a double bond, which can be copolymerized onto the backbone of polymers such as styrene, ethylene and propylene (49-52). From an environmental concerns point of view and sustainable development considerations, it is preferable to use natural polymers such as starch, cellulose and their derivatives (53). Many natural products and their derivatives (after chemical modification) are an important source of hydroxylbearing reactive polymers, but their processing and mechanical properties are often poor. Grafting a functional synthetic polymer with maleic anhydride groups onto natural polymers provides an important method of improving the properties of a natural polymer while meeting environmental requirements (54, 55).

Cellulose acetate is one of the commercially available cellulose derivatives. It is a tough material with excellent optical clarity, however, due to its poor processability high concentrations of plasticizer is necessary during processing. Although grafting synthetic

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polymers such as styrene or acrylamide onto cellulose or cellulose acetate has been studied in the past, these studies show that the reactivity of the grafted polymers is poor and their properties have not improved significantly (56-60). Grafting SMA onto CA in DMF solution using DMAP as catalyst was studied by Nie, Li (61). Who showed that with a proper catalyst, high SMA grafting conversion could be obtained.

In this study, an extruder was used as a continuous flow reactor to perform in situ the grafting reactions and blending simultaneously. Such continuous process is advantageous over reactions in dilute solutions as it provides good mixing, excellent temperature control and obvious economic benefits (62). As is shown below, it was apparent that successful grafting greatly improved the processability, enhanced the mechanical properties and improved the water resistance of the modified CA polymers. These improvements were realized only when DMAP catalyst was present. In the absence of the catalyst, almost no grafting reaction occurred and no significant changes were observed in the properties.

#### **3.2 EXPERIMENTAL**

## 3.2.1 Materials

Cellulose Acetate (DS: 2.45,  $\overline{M_w}$ : 103,000,  $\overline{M_n}$ : 46,000,  $Tg=187^{\circ}$ C, Tm=232

<sup>o</sup>C) was provided by Eastman Chemical Company. High molecular weight Styrene maleic anhydride random copolymers (SMA232: 7.08 wt % maleic anhydride,  $\overline{M_w}$ : 249,000,  $\overline{M_n}$  : 126,000; Tm=232 °C ,SMA332: 12.2% maleic anhydride,  $\overline{M_w}$  :193,000,  $\overline{M_n}$  : 100,000, Tm=232 °C) was provided by Nova Chemical Company; low molecular weight SMA(SMA3000P, 25 mol% maleic anhydride,  $\overline{M_w}$ :9,500,  $\overline{M_n}$ : 3,800,

Tg=125°C) was supplied by Sartomer Company Inc. The catalyst, 4-

Dimethylaminopyridine (DMAP) was purchased from Sigma-Aldrich, Inc. Dioctyl phthalate (DOP) was provided by Spectrum Chemical Mfg. Corp., and ethyl acetate was purchased from EMD Chemical Inc.

## 3.2.2 Reactive extrusion of CA/SMA

All the extrusions were run in a Century ZSK-30 twin screw extruder. This equipment consists of an extruder driver with a speed control gearbox; a twin-screw, co-rotating screw with a screw diameter of 30 mm and an L/D (Length to Diameter ratio) of 40, fed by accurate single-screw feeders. CA was dried in a ventilated oven at 100 °C for 24 hr. prior to feeding it into the extruder. The catalyst, DMAP, was dispersed in CA at a ratio of 1000:1 (CA:DMAP) and the mixture was then crushed using a mortar and a pestle until a uniform mixture was obtained. This master batch was then mixed with the balance of the CA powder and the required amount of SMA resin.

The screw configuration used (Figure 3-1) is divided into 3 sections; section 1 of 12.5D distance followed by section 2 of 15.5D distance and finally section 3 with 12D distance. The vent port was kept open to remove vapor and catalyst.



Figure 3-1 Screw configuration used for the synthesis of CA-SMA copolymers

The temperatures in the extruder zones were set up to reach the required melting temperature of CA and SMA. For all mixtures the temperature profile during the extrusion was set at 15/145/200/235/245/250/250/250/255/245/235°C from the feed throat to the die, with a melt temperature of 235°C-246°C. The feeder for mixture material was set to between .50-2.20. This setting was calibrated to14.7-16.0 lb/hr for different mixtures required to maintain the main motor torque at 50-60%. The screw speed was maintained at 150 rpm.

The CA/SMA232 blends with various percentage of SMA (30/70, 50/50, 70/30, 85/20, 85/15) were processed by extrusion. When the SMA content decreased, the torque and the melting pressure increased due to the very high viscosity of CA Thus, the feed rate was reduced in order to maintain a constant torque. At 10wt% SMA, the melting

pressure became very high and the extruder was shut off automatically due to blockage at the die.

CA/SMA blends with a ratio of 70/30 were processed for different grades of SMA (ex. SMA3000P, SMA232, SMA332) and different amounts of catalyst (0.01%, 0.05%, 0.1%). The catalyst concentration did not significantly affect the extrusion process. When CA/SMA3000P was processed, the melting pressure and torque were very high leading to the very weak and brittle materials due to poor mixing. When 20% DOP (wt% of CA) was added the pressure and torque dropped and mixing improved significantly.

The extrudate was cooled by water, pelletized into resin and dried in a ventilated oven at 70  $^{\circ}$ C for 24 hrs.

## 3.2.3 Soxhlet extraction and Fourier transformed infrared spectroscopy (FTIR) test

The CA/SMA polymer blend to be tested was grounded into a powder. The powder was Soxhlet extracted with ethyl acetate as the solvent for 48 hrs. When pure CA was Soxhlet extracted under identical conditions, less than 2% were extracted.

The conversion of SMA grafted onto CA was calculated by the mass balance.

The materials which remained in the thimble and casts made from the extracted solution were analyzed by FTIR to confirm the grafting reaction.

FTIR analysis: For solid materials, a 1% sample was mixed with 99% KBr powder and pressed using a pellet maker to a fine transparent disk. This disk was directly put into the sample holder in the FTIR to obtain the spectrum. A background scan was obtained with the pure KBr pellet and this spectrum was subtracted from the sample spectrum in order to eliminate interference from atmospheric moisture and CO<sub>2</sub>. FTIR of all the extracted materials were obtained by first solvent casting thin films of the samples and then placing these films directly in the sample chamber to obtain the FTIR spectrum.

## 3.2.4 Injection mold

The reacted blends were injection molded into tensile bars (ASTM D638 type 1) using a Cincinnati Milacron injection molder. The zone temperature profile, pressure, shot velocity and mold temperature was changed to study their effects on the tensile properties. The general set is shown below.

<b>Temperature profile</b> :	(All temperatures are in	°F)
------------------------------	--------------------------	-----

	Nozzle	Zone 1	Zone 2	Zone 3	Mold
Set	500	490	480	480	150
Temperature					
Actual	501	490	480	480	150
temperature					

## The pressure setting profile was:

Fill pressure: 1300 psi

Hold pressure: 1000 psi

Pack pressure: 1200 psi

## **Timer conditions:**

Inject high: 5 sec

Pack: 3 sec

Hold: 2 sec Cooling: 35 sec Extruder delay: 16 sec Open dwell: 1 sec Shot size: 1.0 in Shot velocity: 2.0 in/s Cushion: 0.25 in Transfer position: 0.5 in

## **3.2.5 Tensile properties test**

The tensile properties (e.g. tensile strength, elongation, Young's modulus) were tested in a UTS machine following the ASTM D638 standard. The tensile bars were conditioned at 50%RH, 23°C for 40hrs. The cross head speed was set at 0.2 in/min, the load cell capacity was 1000 lbs. At least 5 specimens were tested for each sample.

## **3.2.6 Izod impact test**

The tensile bars were cut into  $2.4 \times 0.5 \times 0.125$  inches. A TMI notch cutter and impact tester were used in notching and Izod impact test following the ASTM D256A standard.

## **3.2.7 Moisture absorption test**

The ground CA/SMA232/DMAP (70/30/0.01) and CA/SMA232 (70/30) polymer blend powders were dried in a ventilated oven at 100 °C for 24 hrs, 10g of each blend

powder was put in a desiccator (diameter 30 cm) for 24 hrs, which was adjusted to 90% relative humidity by filling with saturated barium chloride solution at 25 °C. After equilibrium moisture was achieved, the powder was weighed again.

## **3.3 RESULTS AND ANALYSIS**

## 3.3.1 Grafting reaction results

The SMA grafting conversion is calculated from the mass balance of the Soxhlet extraction data, the results are shown in Table 3-1.

Materials(weight percentage)	SMA conversion
CA/SMA3000P/DMAP(70/30/0.01)	39.4%
CA/DOP/SMA3000P/DMAP(56/14/30/0.01)	>46.7%
CA/SMA232/DMAP(30/70/0.01)	32.3%
CA/SMA232/DMAP(50/50/0.01)	41.3%
CA/SMA232/DMAP(70/30/0.01)	68.%
CA/SMA232/DMAP(80/20/0.01)	32.3%
CA/SMA232/DMAP(85/15/0.01)	23.8%
CA/SMA232(70/30)	7%
CA/SMA332/DMAP(20/80/0.01)	21.8%
CA/SMA332/DMAP(30/70/0.01)	32.5%
CA/SMA332/DMAP(50/50/0.01)	41.9%
CA/SMA332/DMAP(50/50/0.05)	77.7%
CA/SMA332/DMAP(70/30/0.01)	54.2%
CA/SMA332/DMAP(85/15/0.01)	26.2%
CA/SMA332(30/70)	0.0%

## Table 3-1 SMA grafting conversion in CA/SMA blends

The FTIR results are shown in Figure 3-2, Figure 3-3 and Figure 3-4.

Figure 3-2 shows pure CA, the material remaining in the thimble, and the film

cast from the extracted solution of the CA/SMA3000P/DMAP (70/30/0.01) blend.

Figure 3-3 shows the FTIR spectrum of the material remaining in the thimble from the extraction of CA/SMA232/DMAP (50/50/0.01) blend.

Figure 3-4 shows the FTIR spectrum of the material remaining in the thimble form the extraction of CA/SMA232 (70/30) blend compared with pure CA.



Figure 3-2 FTIR spectrum of CA/ SMA3000P blend after extraction



Figure 3-3 FTIR spectrum of CA/SMA232/DMAP (50/50/0.05) after extraction



Figure 3-4 FTIR spectrum of CA/SMA232 (70/30) after extraction

The Soxhlet extraction data indicate a very low grafting reaction in the absence of the catalyst.

The Soxhlet extraction data also show that adding catalyst improves the reaction significantly. Adding a plasticizer to the CA/SMA3000P blend increases the conversion of SMA since it improves the processability of the blend, reduces the matrix phase viscosity, increases the SMA phase dispersion, and increases the reactivity.

The phase dispersion effects on grafting can also be observed by comparing the composition of CA/SMA232 at 70/30, 80/20 and 85/15 proportions. The SMA conversion drops due to poor processability and lower phase dispersion. However, when the SMA content increases from 30% to 50% and then 70%, SMA grafting conversion is reduced due to a lower concentration of CA in the blend.

Furthermore, when more DMAP is added, higher grafting conversion of SMA is observed comparing with a composition of CA/SMA332 (50/50) at 0.01% and 0.05% DMAP respectively.

It is observed that SMA332 has a better compatibility with CA because than the other grades of SMA used. Apparently, SMA332 has a closer viscosity and solubility parameter to CA. Since the original compatibility affects the SMA phase size, it further affects the grafting reactivity. Under the same conditions, CA/SMA332 has a higher grafting conversion than CA/SMA232 except at the 70/30 blend level.

It is observed from the FTIR data (Figure 3-2 ) of a sample composition of CA/SMA3000P/DMAP (70/30/0.01) after Soxhlet extraction, that it still contain the benzene group (around 700 cm<sup>-1</sup>), the ester C=O group (peak frequency that was shifted

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from 1754.7 cm<sup>-1</sup> to 1731.1 cm<sup>-1</sup>) and greatly lower content of the hydroxyl group (around  $3500 \text{ cm}^{-1}$ ). Similar results are also observed from Figure 3-3.

All these results indicate that SMA has been grafted onto CA. We can only observe the most significant anhydride peak (1778 cm<sup>-1</sup>) and benzene group peak (700 cm<sup>-1</sup>) from the FTIR of the cast film prepared from extracted solution. It is apparent that only free SMA and a very few short chain CA which were grafted onto SMA have been extracted.

In the samples with lower grafting (CA/SMA232 without catalyst) we cannot identify the benzene group (Figure 3-4), the shift of the ester C=O group is small, and the hydroxyl group peak value has almost the same intensity. It is apparent from these data that the grafting conversion was very low in the CA/SMA232 blend without catalyst and that almost all the free SMA232 was extracted.

#### 3.3.2 Properties of CA/SMA blend

#### **3.3.2.1 Properties test results**

The tensile properties and Izod impact strength of highly grafted CA/SMA232 (70/30/0.01) blend at different content SMA and a lower grafted CA/SMA232 (70/30) sample were tested and are compared in Table 3-2.

Table 3-3 shows the mechanical properties for the different compositions of CA/SMA.

# Table 3-2 The properties and phenomena comparison between compatibilized and

properties	CA/SMA232/DMAP	CA/SMA232
Graft percent	>60%	<7%
Tensile strength	9800 psi	6400psi
Tensile strength (after 2 month)	9700psi	5900psi
Tensile modulus	480 kpsi	560 kpsi
Tensile modulus (after 2 month)	480 kpsi	480 kpsi
Elongation	2.52%	1.22%
Moisture absorption	0.7%	2.97%
(at 90% RH, 24hrs)		
Acetone solution(10g/100ml)	Uniform solution, gray color	a layer of CA precipitated in bottom after 24 hr

# incompatibilized CA/SMA233/DMAP (70/30)

Table 3-3 Mechanica	properties of CA/SMA	blend at different compositions
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Materials	Tensile strength	Moudulus	Elongation	Izod impact strength
	psi	(kpsi)	(%)	ft.lb/in
CA/SMA232(70/30)	6400±400	560±20	1.21±0.13	0.31±0.05
CA/SMA232/DMAP(50/50/0.01	5500±350	480±40	1.19±0.17	0.86±0.05
CA/SMA232/DMAP(70/30/0.01	9600±450	470±30	$2.52 \pm 0.26$	$1.47{\pm}0.10$
CA/SMA232/DMAP(85/15/0.01	12500±900	700±20	2.81±0.21	$2.12{\pm}0.09$
CA/SMA332/DMAP(70/30/0.01	9200±420	470±10	2.31±0.24	$1.23 \pm 0.15$
SMA232*	7100	500	1.8	
SMA332*	7500	540	1.7	
CA(plasticized)*	3840-7540	220-320	16-25	2.6-6.59

\*data was provided by the producer

These results show that in a CA/SMA blend without the catalyst, the grafting between CA and SMA is very low yielding an incompatible blend with very poor mechanical properties. When the catalyst DMAP is added, the mechanical properties of the blends are greatly improved indicating high grafting reactions. Also, the moisture absorption is reduced significantly due to the grafting reaction. The grafted polymer blend can form a clear uniform solution in acetone compared with the un-grafted polymer blend which does not yields a clear solution at these concentrations. This is because the grafted CA-SMA copolymer acts as a compatibilizer to form a strong interfacial adhesion between two incompatible polymers, thus, improving the mechanical properties and the moisture resistance. The CA/SMA blend with higher CA content gives higher mechanical properties due to CA having higher mechanical properties. The grafted polymer blend has higher properties than plasticized CA and pure SMA (properties given by the supplier).

#### **3.3.2.2 Injection mold conditions studying results**

The effects of injection molding conditions on the tensile properties are analyzed by unbalanced Fractional Factor Design Analysis using an SAS program. The four factors: fill pressure (A), set temperature (B), shot velocity (C) and mold temperature (D) were studied in this design.

Sample	Fill pressure (psi)	Nozzle temperature ( <sup>o</sup> F)	Shot velocity (in/sec)	Mold temperature ( <sup>0</sup> F)	Tensile strengt h (psi)	Tensile Modulus (kpsi)	Elongation (%)
1	1300	518	1.5	100	8300	520	1.76
2	1300	518	1.5	100	9040	480	2.17
3	1300	490	1	100	8660	480	2.05
4	1000	490	0.5	130	8500	430	2.11
5	1000	490	0.5	130	8380	430	2.15
6	1000	490	0.5	100	9100	470	2.31
7	1000	490	0.5	100	8350	470	2.06
8	1000	490	2	130	10500	450	2.97
9	1000	490	2	130	9900	450	2.69

#### injection conditions

The results show that the Shot velocity (factor C) and the Mold temperature (factor D) have significant effects on tensile strength and elongation. At a higher mold temperature and higher shot velocity, the tensile strength and the elongation are much higher. Apparently, the higher shot velocity and higher mold temperature make the polymer blend cooling more uniformly and the residual stress is reduced under these conditions. The Fill Pressure (factors A) and the Nozzle temperature (factor B) do not have significant effects on the tensile strength, tensile modulus or the elongation at break. The interaction of the Shot velocity (factor C) and the Mold temperature (factor D) has a significant effect on the tensile modulus but no significant effect on the tensile modulus.

## **3.4 CONCLUSIONS**

It is concluded that high grafting reaction of SMA onto CA can be obtained only when a catalyst (DMAP) is present. Without this catalyst, the grafting reactivity of CA/SMA blends is very low and incompatible CA/SMA blends with very poor mechanical properties are produced.

The grafting reaction improves the phase dispersion due to reduced interfacial tension and increased interfacial adhesion between the two phases. The mechanical properties of these compatible blends are improved and are comparable to glass fiber reinforced ABS and other engineering thermoplastics. These high mechanical properties make CA/SMA polymer blends useful, sustainable materials.

At specified grade SMA and catalyst concentration and temperature, the SMA conversion is affected by two factors: the proportion of CA/SMA and its processability. In the case of CA/SMA3000P blend, adding plasticizer can improve the reactivity of the blend by reducing the viscosity of the CA phase. The highest mechanical properties were observed at 15% SMA, which is the highest CA content processable without plasticizer.

The injection molding conditions were studied in order to optimize the tensile properties of the CA/SMA blends. A lower fill time and a higher mold temperature can improve the tensile properties due to uniform cooling.

## Chapter 4: COMPATIBILIZATION STUDY OF CA/SMA BLEND

## 4.1 INTRODUCTION

## 4.1.1 Polymer Blend

The development of new multiphase polymeric materials often involves the blending of two or more polymers. The combination of the favorable properties of different polymers is usually the goal of blending. In polymer blends the required properties can be easily achieved by the careful selection of the component polymers and their blend ratios (63, 64).

Polymer blends can be broadly classified into three types: miscible blends, immiscible but compatible blends, and incompatible blends. When the free energy of mixing is negative the blend is a miscible blend. According to Flory-Huggins's theory, the free energy for mixing of two polymers A and B in the homogenous state can be expressed as:

$$\frac{\Delta G_m}{V_A + V_B} = B_{AB}\phi_A\phi_B + RT[\frac{\phi_A \ln \phi_A}{\overline{V}_A} + \frac{\phi_B \ln \phi_B}{\overline{V}_B}]$$
(4-1)

 $\Delta G_m$ : Gibbs free energy of mixing

 $V_A, V_B$ : actual volume of polymer A and B

 $\phi_A, \phi_B$ : volume fraction of polymer A and B

 $B_{AB}$ : binary interaction energy

 $\overline{V}_A$ ,  $\overline{V}_B$ : molar volume of polymer A and B

$$\Delta \overline{H}_m = B_{AB} \phi_A \phi_B$$
,  $\Delta \overline{H}_m$  is mixing enthalpy at unit volume

$$\Delta \overline{S}_m = -R[\frac{\phi_A \ln \phi_A}{\overline{V}_A} + \frac{\phi_B \ln \phi_B}{\overline{V}_B}], \ \Delta \overline{S}_m \text{ is mixing entropy at unit volume.}$$

In miscible blends, this miscibility of the two polymers results in a single glass transition temperature  $(T_g)$  for the blend, which is composition dependent, as per the Fox-Flory theory. The Fox relationship for a two-component blend (65) is explained in equation as follows:

$$\frac{1}{T_g} = \frac{w_A}{T_{gA}} + \frac{w_B}{T_{gB}}$$
(4-2)

Here  $T_{g_A}$  and  $T_{gB}$  are the glass transition temperatures of the polymer A and B, and  $w_A$  and  $w_B$  are the weight fractions of polymer A and B in the blend respectively. The mechanical properties of miscible blend can be predicted by the equation:

$$P = w_A P_A + w_B P_B \tag{4-3}$$

 $P, P_A, P_B$  is the properties of polymer blend, polymer A and polymer B respectively.

Due to the low combinatorial entropy of mixing of high molecular weight polymers, the miscible polymer blends can only be attained when there are some kind of specific intermolecular interactions, such as hydrogen bonding and  $\pi$ -bonding, so that mixing enthalpies are negative (exothermal). But most of the binary polymer blends are not thermodynamically miscible giving rise to a two-phase system which is mostly characterized by coarse and unstable phase morphology and poor interfacial adhesion between the phases. This strongly affects the mechanical/physical properties of the finished product. The interaction between the polymer pairs at the molecular level has been defined by the term "*compatibility*". Compatibility is treated as a relative term and can be defined by a compatibility number as explained in the following equation.

## $N_c = (Experimental Probe size)/(Domain sizes of phases)$

The experimental probe size can be taken as the scale of resolution of an instrumental technique. The domain size is the average dimension of the dispersed phase in the blend. Thus, when  $N_c \rightarrow \infty$ , the system is compatible and when  $N_c \rightarrow 0$ , the system is incompatible (66, 67, 68).

Most incompatible blends show phase separation. The phases, however, vary in amount, size, sharpness of their interfaces, and degree of continuity. The type of morphology depends upon several factors, the most important being the composition and the viscosities of each component.

Figure 4-1 shows the effect of those two parameters on the morphology of the blend. The component, which is in higher proportion or is less viscous, tends to form the continuous phase (69).



Volume ratio A/B

## Figure 4-1 Effect of composition and viscosity on phase morphology

## 4.1.2. Compatibilization

Simple blending of immiscible blends does not generally give a material with desired characteristics because of the high interfacial tension existing between the two phases.

In general, the properties of two component polymer mixtures can be described by the equation:

 $P = w_A P_A + w_B P_B + \Delta P^E(w) \qquad (4-4)$ 

In equation 4-4,  $\Delta P^{\mathcal{E}}(w)$  is an excess term, which is dependent on the composition under consideration. The compatibilization achieved results in positive

values of  $\Delta P^E(w)$ , which means that the properties of the polymer combination are better than the volume arithmetic average of the constituents' properties (70). There are various routes for obtaining this effect of compatibilization.

Compatibilization is most often based on the use of suitable block or graft copolymers which are located at the interface between the phases of an immiscible blend and act as an emulsifying agent. In the past, much attention has been paid to the synthesis of block and graft copolymers as potential compatibilizers which were subsequently added to an immiscible blend. However, this strategy cannot be applied for all kinds of blends and, moreover, the synthesis is most often very expensive. For these reasons, most current interest is now directed to a method called 'reactive' compatibilization. This is based on the in situ formation of a block or graft copolymer at the interface between the blend phases as a result of chemical reactions during melt-mixing. In most cases, the two components of a binary blend do not have the appropriate reactive groups for the formation of a copolymer at the interface and, as a consequence, functionalization is required. Functionalization of the blend components is a widely applied strategy for reactive compatibilization. In recent years, research has been performed to realize functionalization of different types of polymers and to obtain insight into the reactivity of different functional groups and hence to obtain the desired compatibilization effect (71). Another method of reactive compatibilization is based on the addition of a reactive polymer to the blend as a third component. It is necessary that this reactive polymer is miscible with one of the blend components and reactive with the other blend component. A reactive polymer which fulfils these conditions can only be found for a limited number of binary blends.

Recently, increasing efforts have been directed towards in situ compatibilization of immiscible polymer blends by reactive extrusion (72-77). Instead of synthesizing the compatibilizers in a separate step, these are created in situ during extrusion through interfacial reactions between the respective functionalized polymers. From a technological point of view, a one-step reactive extrusion process is easier to control for cost-effective generation of compatible blends from initially immiscible polymers. In this study, CA-SMA grafting copolymer was synthesized in situ by reactive extrusion and acted as a compatibilizer of the CA/SMA blend.

## 4.1.3. Theoretical study of compatibilization

The morphology of polymer blends and their interrelations with compatibilizers has been mostly studied experimentally (78, 79, 80), and less attention has been paid to the theoretical analysis of the phase structure development at mixing. Tang and Huang (81) tried to describe the effect of a compatibilizer on the size of dispersed droplets in polymer blends, but only the droplet break was studied in their work. This approach is justified only for blends containing very small fractions of the dispersed phase due to coalescence. Milner and Xi (82) considered the effect of a compatibilizer on both breakup and coalescence of dispersed droplets and draw a conclusion that the compatibilizer decreases the interfacial tension slightly and does not affect the breakup of the droplets. This conclusion is in strong disagreement with the experimental results of other studies. Recently, the balance of breakup and coalescence of dispersed droplets in polymer blends containing a compatibilizer was analyzed by I. Fortelny and A. Zivny (83). The formula for dispersed droplet size in the steady state was drawn in assumed

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interfacial copolymer states. I. Aravind et.al describe a simple theoretical analysis of an ethylene-polypropylene-diene terpolymer (EPDM)/poly(trimethylene terephalate) system using poly(ethylene-co-propylene-co-maleic anhydride) (EPM)-g-MA as compatibilizer and compared it with experimental results (84).

In this study, the compatibilizer CA-SMA was generated in situ. The concentration of compatibilizer is determined by the grafting reactivity. The grafting reactivity was affected by phase dispersion. On the other hand, the phase dispersion was improved by the grafting co-polymer generated in situ. A formula was derived between disperse phase size and reactivity and further used to explain the experimental results.

### **4.2 EXPERIMENTAL**

## 4.2.1 Transmission Electron Microscopy (TEM)

Morphology of CA/SMA blend was examined by TEM with samples that were freshly fractured. Samples with thickness of the 90-150 nm were prepared using a 3 mm MICRO STAR diamond knife. The samples were examined by A JEOL 100CX TEM at very short time (around 15 seconds) under 10 KV potential. Since the contrast between CA and SMA phase is high, no staining is required. The number average particle size was calculated. The TEM was done on the CA/SMA232 blends under different extrusion passes, different catalyst amounts (0, 0.01%, 0.05%, 0.1%) and varied CA/SMA332 blends. The TEM pictures and the comparison of SMA particle size are shown in the following figures. The section is perpendicular to the flow direction for all TEM pictures.

## **4.2 RESULTS AND ANALYSIS**

The TEM pictures of CA/SMA blend at various passes, catalyst amounts and SMA grades are shown in Figure 4-2 to Figure 4-9. The lighter area is CA phase due to the loss of material in the CA phase under the electron beam. The darker area is the SMA phase.



Figure 4-2 TEM of CA/SMA232(70/30) after 1 extrusion pass



Figure 4-3 TEM of CA/SMA232(70/30) after 2 extrusion passes


Figure 4-4 TEM of CA/SMA232 (70/30) after 3 extrusion passes



Figure 4-5 TEM of CA/SMA232/DMAP (70/30/0.01) after 1 extrusion pass



Figure 4-6 TEM of CA/SMA232/DMAP (70/30/0.05) after 3 extrusion passes



Figure 4-7 TEM of CA/SMA232/DMAP (70/30/0.1) after 3 extrusion passes



Figure 4-8 TEM of CA/SMA332 (70/30) after 1 extrusion pass



Figure 4-9 TEM of CA/SMA332/DMAP (70/30/0.01) after 1 extrusion pass

The number average diameter of the SMA droplet was measured and calculated from the TEM picture, the results are shown in Figure 4-10.



Figure 4-10 Number average diameter of SMA (µm) in CA/ SMA blend

From the results we can see the SMA phase size in the CA/SMA232 blend became smaller with increased extrusion passes. In Figure 4-2, Figure 4-3 and Figure 4-4, the size reduction from 1 extrusion pass to 2 extrusion passes is much sharper than the reduction from 2 extrusion passes to 3 extrusion passes. The data show that the phase dispersion was improved significantly after increased initial mixing time, but when the phase size reached a specific level, additional mixing had little effect.

When the catalyst was added more grafting occurred and the phase dispersion improved. This can be observed by comparing Figure 4-2 and Figure 4-5 for CA/SMA232 blend, and comparing Figure 4-8 and Figure 4-9 for CA/SMA332 blend. This is caused by the grafting reaction generated CA-SMA co-polymer at the interface and consequent reduction in the interfacial tension resulting in improved phase dispersion. When Figure 4-6 and Figure 4-7 are compared it can be seen that higher catalyst content gave higher phase dispersion due to higher grafting conversion.

It can also be seen that the phase dispersion in the CA/SMA332 blend is improved compared with that of the CA/SMA232 blend, due to the increased MA content of SMA332. The lower molecular weight and the higher MA content make it more compatible with CA because its solubility parameter is closer to that of CA.

#### **4.4 THEORETICAL STUDY**

# 4.4.1 The disperse phase droplet breakup under shear rate

Morphology analysis for in-situ forming grafting copolymer used as compatibilizer has not been studied before. In the first step, we will analyze the breakup of dispersed droplets under shear rate in the extruder without considering coalescence.

The Capillary number was introduced by Taylor (98) as:

$$Ca = \frac{\eta_m \dot{\gamma} R}{\sigma} \tag{4-5}$$

Where  $\eta_m$  is the matrix viscosity,  $\dot{\gamma}$  is the shear rate, R is radius of disperse phase size,  $\sigma$  is interfacial tension.

The droplet breakup rate was expressed by the Equation 4-6 (83):

$$-\left(\frac{dR}{dt}\right)_b = f(Ca - Ca_c)R \tag{4-6}$$

Where f is a function of rheological property of the matrix and dispersed phase.

 $Ca_c$  is critical Capillary Number, which is the value the breakup stopped

We assume at the critical Capillary Number, the droplet size is at steady state  $R_c$ , and

$$Ca_{c} = \frac{\eta_{m} \dot{\gamma} R_{c}}{\sigma}$$
(4-7)

Then we rearrange equation 4-6 as:

$$-\left(\frac{dR}{dt}\right)_b = \frac{f\eta_m \dot{\gamma}}{\sigma} R(R - R_c) \qquad (4-8)$$

We solve the equation for CA/SMA blend at a constant composition using the following assumptions:

 $Ca_c$  is only dependent on the blend system.

 $\dot{\gamma}$  is a constant at a specified process condition

 $\sigma$  does not change without grafting reaction

$$\ln \frac{R}{R-R_c} = \frac{f\eta_m \dot{\gamma} R_c}{\sigma} t \qquad (4-9)$$

At  $t = \infty$ ,  $R = R_c$ .  $R_c$  was measured from CA/SMA blend cast film from the dilute

solution, the value is  $1.14 \,\mu\text{m}$ .

In CA/SMA232 system without catalyst, the experimental results are shown in

Table 4-1, the curve of  $\ln \frac{R}{R-R_c}$  vs. extrusion passes is drawn in Figure 4-11.

Sample #	Passes	Phase size(diameter, µm)	
1	1	2.88	
2	2	2.36	
3	3	2.32	

Table 4-1 Dispersed phase size of CA/SMA232 at different passes



Figure 4-11 ln  $\frac{R}{R-R_c}$  vs. extrusion passes of CA/SMA232

The curve is close to a straight line showing that the assumptions are reasonable and  $\frac{f\eta_m \dot{r}R_c}{\sigma}$  is close to a constant. It also indicates that the effect of coalescence is insignificant and the droplet breakup dominated in the extrusion process. But in the 3<sup>rd</sup> extrusion pass, the radius of dispersed phase droplet is larger than we predicted from the data. This is caused by the onset of coalescence when the phase size approaches the critical size.

When the volume fraction of dispersed phase is increased, the action of coalescence must be taken into account. The rate of coalescence can be written as (83):

$$\left(\frac{dR}{dt}\right)_c = \frac{4}{\pi}\dot{\gamma}\phi P_c R \tag{4-10}$$

Where  $\dot{\gamma}$  is shear rate,  $\phi$  is volume fraction of the dispersed phase, Pc is the probability that collision of the particles will be followed by their fusion. It is a function of  $\sigma$  and R, and can be expressed as (83):

$$P_{c} = \exp\{-\frac{9Ca^{2}R^{2}}{8h_{c}^{2}(1+3C/\lambda)}\}$$
(4-11)

Where  $\lambda = \eta_d / \eta_m$  is the ratio of the viscosities of the dispersed phase and matrix,

C is a function of the mobility of the interface, Ca is capillary number,  $h_c$  is specific distance between two disperse phase droplets fusion. The critical dispersed phase size can be solved by the following Equation 4-12. At this state, the rate of breakup and rate of coalescence are equal.

$$-\left(\frac{dR}{dt}\right)_{b} = \left(\frac{dR}{dt}\right)_{c} \tag{4-12}$$

The phenomenon of coalescence has not been studied in detail in this work.

# 4.4.2 The effect of compatibilizer on the interfacial tension

The compatibilizer reduced the interfacial tension, and then improved the phase dispersion. The relation of interfacial tension and the compatibilizer concentration can be expressed as:

$$-\frac{d\sigma}{dc} = k(\sigma - \sigma_s) \tag{4-13}$$

Where c is the concentration of the compatibilizer

k is a constant related to the chemical properties of the compatibilizer

 $\sigma_s$  is interfacial tension under saturate compatibilizer concentration

In the CA/SMA blend system, the concentration of semi-ester *OH-MA* was used as concentration of compatibilizer, then:

$$\frac{-d\sigma}{\sigma - \sigma_s} = kdc = kdC_{OH-MA} \tag{4-14}$$

We solve the differential equation using the initial condition,

$$\sigma = \sigma_0$$
 at  $c = 0$  to get:  
 $\sigma = \sigma_s + (\sigma_0 - \sigma_s) \exp(-kC_{OH-MA})$ 
(4-15)

Here both  $\sigma$  and  $C_{OH-MA}$  are function of time.

#### 4.4.3 The morphology of in situ compatibilized CA/SMA in reactive extrusion

In the CA/SMA blend system, the compatibilizer (grafting copolymer) was generated in situ during reactive extrusion. The grafting copolymer reduced the interfacial tension between the two phases, which increased the dispersed phase (SMA phase) droplet breakup speed. The droplet breakup gave more interfacial area (reaction area) to improve the rate of generation of grafting copolymer.

The reactive extruder can be modeled as a PFR reactor, so the *OH-MA* generating rate can expressed as:

$$\frac{\dot{F}dC_{OH-MA}}{dV} = V_s K_0 \exp(\frac{-E}{R'T}) C_{-OH} C_{-MA} C_{DMAP}$$
(4-16)

Where  $\dot{F}$  is a CA/SMA polymer blend volume flow rate in the extruder, V is the total volume of the extruder, and  $V_s$  is coefficient of effective reaction volume and is a function of the SMA phase size:  $V_s \propto \frac{1}{R}$ 

Since  $\dot{F}$  was set to a constant in the extrusion, equation 4-16 can be rearranged using the extrusion residence time  $t_{res}$ :

$$t_{res} = V / \dot{F}, \text{ we got:}$$

$$\frac{dC_{OH-MA}}{dt} = V_s K_0 \exp(\frac{-E}{R'T}) C_{-OH} C_{-MA} C_{DMAP}$$
(4-17)

Substitute equation 4-14 by equation 4-17:

$$\frac{-d\sigma}{\sigma - \sigma_s} = kdC_{OH-MA} = kV_sK_0 \exp(\frac{-E}{R'T})C_{-OH}C_{-MA}C_{DMAP}dt \quad (4-18)$$

When it is solved as before we get:

$$\sigma = \sigma_s + (\sigma_0 - \sigma_s) \exp(-k \int_0^t V_s K_0 \exp(\frac{-E}{R'T}) C_{-OH} C_{-MA} C_{DMAP} dt) \quad (4-19)$$

By substituting equation 4-19 to 4-8, the droplet break can be rewritten as

$$-\left(\frac{dR}{dt}\right)_{b} = f\eta_{m}\dot{\gamma}R(R-R_{c})/(\sigma_{s}+(\sigma_{0}-\sigma_{s})\exp(-k\int_{0}^{t}V_{s}K_{0}\exp(\frac{-E}{R'T})C_{-OH}C_{-MA}C_{DMAP}dt))$$

$$(4-20)$$

Here Vs is a function of R;  $R_c$  is a function of  $\sigma$ .

1

For CA/SMA blending in reactive extrusion, the following assumptions are used to solve the differential equation 4-20:

1) The dispersed phase size is much larger than the critical size, so droplet breakup dominates in the extrusion, thus the action of coalescence is negligible. 2) For a specified blend system (ex. CA/SMA232/DMAP), f is only a function of rheological property of the matrix and dispersed phase, we can assume the grafting does not change the rheological property significantly, so f is a constant.

3)  $R_c$  is only a function of concentration of compatibilizer for a specific system. It can be written as:

$$R_c \propto \frac{k'}{C_{OH-MA}} \qquad (C_{OH-MA} \neq 0)$$

Where k is a constant.

4) For a specified CA/SMA system, the concentration of -OH, -MA group and catalyst DMAP are constants due to the reacted group is less than 3% even when the grafting conversion of SMA is about 90%.

5) In equation 4-13, k and  $\sigma_s$  is a constant for the CA-SMA grafting copolymer compatibilizer.

We use the data of CA/SMA without catalyst to solve out the value of  $\sigma_{\scriptscriptstyle 0}$  .

$$\frac{f\eta_m \dot{\gamma}}{\sigma_0} = \frac{\ln \frac{R_1}{R_1 - R_{c0}} - \ln \frac{R_2}{R_2 - R_{c0}}}{-R_{c0}t_{res}}$$
(4-21)

We assume the critical Capillary number  $Ca_c$  is a constant for a specified system,

so we can drive:

$$\frac{\eta_m \dot{\gamma} R_{c0}}{\sigma_0} = \frac{\eta_m \dot{\gamma} R_{cs}}{\sigma_s} \tag{4-22}$$

Then,

$$\sigma_s = \sigma_0 R_{cs} / R_{c0} \tag{4-23}$$

The  $R_c$  values at different compatibilizer concentrations can be attained by measuring the phase size in the solvent cast films of a specified grafting conversion polymer blend. SEM pictures of four CA/SMA blend cast films at different SMA grafting conversion are shown in Figure 4-12.



\*bar length is 1 micron

# Figure 4-12 the TEM picture of CA/SMA232 cast film at different grafting conversions

(a) 
$$f_{SMA} = 0.26$$
 (b)  $f_{SMA} = 0.39$  (c)  $f_{SMA} = 0.51$  (d)  $f_{SMA} = 0.74$ 

<b>f</b> sma	<b>Ѓ</b> ЅМА	1/f <sup>°</sup> SMA	particle diameter(µm)
0.29	0.19	5.35	0.18
0.36	0.25	4.00	0.15
0.51	0.43	2.33	0.09
0.74	0.96	1.04	0.06

Table 4-2 The SMA particle size of cast film at different grafting conversion

According to equation 2-15, the concentration of the grafting bond MA-OH is proportional to the value  $f'_{SMA}$ . The relationship of particle size and the modified grafting conversion was drawn in Figure 4-13. From the figure we can draw the following formula:

$$R_c = 0.01405 + 0.01445 / f'_{SMA}$$
 (f'<sub>SMA</sub>  $\neq 0$ ) (4-24)

This also confirms the assumption that the critical phase size is inversely proportional to the concentration of the grafting bonds.

L



Figure 4-13 Fit of SMA phase diameter ( $\mu$ m) vs. 1/  $f'_{SMA}$  (cast films)

Here the state  $f'_{SMA}$ =2.2 (which  $f_{SMA}$ =0.9 is the highest grafting conversion we

can attain) was used as saturate compatibilizer concentration.

 $R_{cs}$ =0.0206  $\mu$ m.

 $R_{c0}$  was measured in the cast film of un-grafted CA/SMA blends. the value is

1.14µm.

Using by these data, we can simplify the equation 4-21 as:

$$\frac{f\eta_m \dot{\gamma}}{\sigma_0} = \frac{1.816}{R_{c0} t_{res}} \tag{4-25}$$

The equation 4-20 can be simplified by using the above results and assumptions:

$$-\left(\frac{dR}{dt}\right)_{b} = \frac{1.816R(R-R_{c})}{R_{c0}t_{res}} / \left(\frac{R_{cs}}{R_{c0}} + \left(1 - \frac{R_{cs}}{R_{c0}}\right)\exp\left(-\int_{0}^{t} \frac{C'}{R}dt\right)\right) \quad (4-26)$$

Here C' is a constant related with copolymer generating rate and chemical properties of the copolymer in the blend system. We assume at critical phase size under

saturated compatibilizer concentration, the polymer blend is perfectly mixed, and the effective volume parameter equals 1.

$$V_s = 1$$
, at  $R = R_{cs}$ 

Then 
$$V_s = R_{cs} / R$$

So we can drive the formula for C'

$$C' = kK_0 R_{cs} \exp(\frac{-E}{R'T}) C_{-OH} C_{-MA} C_{DMAP}$$
(4-27)

We can calculate the grafting conversion for CA/SMA232/DMAP (wt%, 70/30/0.01) in the extrusion process by equation 2-15.

$$f'_{SMA} = (1 - f_{SMA})^{-0.5} - 1 = \frac{PDI^0}{C^0} K_0 \exp(-E/R'T) C_{-OH} C_{-MA} C_{DMAP} V_s t \quad (2-15)$$

The initial concentration of SMA in the CA/SMA melting blend is:

$$C^{0} = w_{SMA} \times \rho_{CA/SMA} \div \overline{M}_{n(SMA)} = w_{SMA} \times 1.14 kg / L \div \overline{M}_{n(SMA)} = 0.0027 mol / L$$

 $w_{SMA}$  is the weight percentage of SMA,  $\rho_{CA/SMA}$  is the density of the polymer blend in melting condition,  $\overline{M}_{n(SMA)}$  is the number average molecular weight of SMA.

The concentration of -OH group can be written as:

 $C_{-OH} = \rho_{CA} \div \overline{M}_{n(CA)} \times N_{-OH} = 1.20 kg / L \div \overline{M}_{n(CA)} \times N_{-OH} = 2.217 mol / L$  $\rho_{CA}$  is the density of the CA in melting condition,  $\overline{M}_{n(CA)}$  is the number average

molecular weight of CA.  $N_{-OH}$  is the number of -OH groups in a CA chain which has the number average molecular weight.

The concentration of -MA group can be expressed as:

1

$$C_{-MA} = \rho_{SMA} \div \overline{M}_{n(SMA)} \times N_{-MA} = 1.08 kg / L \div \overline{M}_{n(SMA)} \times N_{-MA} = 0.972 mol / L$$

 $\rho_{SMA}$  is the density of the SMA in melting condition,  $N_{-MA}$  is the number of – MA groups in a SMA chain which has the number average molecular weight.

At 250  $^{\circ}C$ , we assume the concentration of DMAP vapor distributed in the void volume of the polymer blend is much larger than the concentration of DMAP vapor penetrated into the polymer matrix in the melting condition. We can, therefore, neglect the DMAP penetrated into the polymer matrix. According to the measurement of the expansion ratio between room temperature and melting condition, the expansion ratio is:

$$r_{ex} = (\overline{V}_{melt} - \overline{V}_{cold}) / \overline{V}_{melt}$$
 is about 0.008, where  $\overline{V}_{melt}$  is the specific volume of

CA/SMA polymer blend in melting condition, and  $\overline{V}_{coldt}$  is the specific volume of CA/SMA polymer blend in room temperature under high pressure (1300psi). We assume the expanded volume is close to the void volume in the melting condition.

$$C_{DMAP} = wt\% DMAP \times 1.14 kg / L \div Mn_{DMAP} \div r_{ex} = 0.117 mol / L$$
  
 $T = 523.15 K (250^{\circ}C)$ 

$$t = t_{res} = 4 min$$

- L

From the equation 2-15 and 4-26, we can apply numerical method to integrate the value of dispersed phase size and SMA grafting conversion by fitting the k value and use the following initial conditions:

$$R=R_0=2mm$$
,  $f_{SMA}=0$  At  $t=0$ 

The SMA phase size and grafting conversion vs. time are shown in Figure 4-14 and Figure 4-15.

Dispersed phase size vs.time



Figure 4-14 SMA phase size vs. time for CA/SMA232/DMAP (70/30/0.01)





Figure 4-15 SMA conversion vs. time for CA/SMA232/DMAP (70/30/0.01)

When we set the k value to equate the simulation result of SMA droplet radius to that of the measuring value  $(0.505 \mu m)$ , the simulation SMA grafting conversion result is

42% and the measuring value is 68%. The difference is derived from the approximations in the assumptions that were made.

# **4.5 CONCLUSIONS**

1. It is reasonable to describe the relationship between phase dispersion and grafting conversion in reactive extrusion of polymer blend by using equation 4-26, the grafting reaction generates a co-polymer acting as a compatibilizer, reduces interfacial tension, and hence improves the droplet breakup rate.

2. From the theoretical study of phase dispersion and the experimental study, we draw the same conclusions for the relationships between dispersed phase size and grafting conversion. Without reaction, the phase size was reduced with more extrusion runs. When the phase size is close to the critical size, coalescence begins. At the critical size, the breakup rate and the coalescence rate are in balance, and the droplet stabilized. When catalyst is added, the grafting copolymer is formed during reactive extrusion. This copolymer can reduce the interfacial tension and further reduce the critical size of the blend system. In the CA/SMA blend system, the relationship between the critical size and concentration of *OH-MA* bonds (which can be expressed by  $f'_{SMA}$ ) is inversely proportional. Hence the grafting reaction can improve the droplet breakup speed and shift the balance of critical state to a small phase size.

3. Theoretical study shows that in-situ generation of compatibilizer is an effective way to compatibilize polymer blends due to increased reactivity during phase dispersion, and subsequent grafting of copolymers to improve the phase dispersion.

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# Chapter 5: STUDY OF THE GRAFTING REACTION BETWEEN THERMOPLASTIC STARCH AND SMA VIA REACTIVE EXTRUSION

#### **5.1 INTRODUCTION**

#### 5.1.1 Starch and thermoplastic starch

Starch is the second most abundant carbohydrate in plants after cellulose. It is the major storage component of polysaccharide in plants. Principal sources of commercial starch are maize (corn), potato, wheat and cassava (86). Starch is an anhydroglucose polymer and consists of two distinct molecules: amylose and amylopectin which both contain  $\alpha$ -D-glucose units. Amylose is a linear or sparsely branched polymer with a molecular weight in the range of 10<sup>5</sup> to 10<sup>6</sup> g/mol linked primarily by  $\alpha 1 \rightarrow 4$  glucosidic linkages (Figure 5-1). The chains form a spiral-shaped single or double helix (87).



Figure 5-1 Structure of amylose

In contrast, amylopectin is a highly branched polymer with a molecular weight of  $10^7$  to  $10^9$  g/mol. Amylopectin also contains  $\alpha 1 \rightarrow 4$  glucosidic linkages, but in addition it has  $\alpha 1 \rightarrow 6$  glucosidic branching points which occurs every 25-30 glucose units. Figure 5-2 shows the structure of amylopectin.



Figure 5-2 Structure of amylopectin

Thermoplastic starch (TPS) is described as a substantially amorphous starch. TPS is produced from granular starch by employing heat and mechanical energy in the presence of several plasticizers, which do not evaporate substantially during processing at high temperature and pressure. Some common plasticizers used are glycerol, ethylene glycol and polyols. Plasticization of starch in an extruder using a plasticizer breaks the hydrogen bonds and disrupts the granular crystalline structure. It further releases the amorphous polymer chains with  $\alpha 1 \rightarrow 4$  and  $\alpha 1 \rightarrow 6$  linkages.

# 5.1.2 Starch and biodegradable polyester blends

Due to the biodegradable nature of starch, many researchers have attempted to incorporate starch into a variety of materials in order to improve the environmental desirability and reduce the cost of such materials. Starch may be added as an inert filler (88, 89), typically in its native, unmodified, state, which is generally a water insoluble, granular material. Ramsay et al. (90) studied blends of granular starch with Poly (HB-co-HV). The inclusion of 25-wt% of a granular starch was reported to result in a composition with a tensile strength of about 60% that of the original. The authors acknowledged that the use of unmodified granular starch as a particulate filler did not offer any appreciable reinforcement due to the poor adhesion at the polymer granule interface. In such cases, the starch granules will normally behave as any other solid particulate filler and will not improve the mechanical properties of the resulting material. The thermodynamic incompatibility between starch and synthetic polymers leads to the poor performance properties of these blends.

Alternatively, starch that has been plasticized dried, and then ground into a powder may also be added as particulate filler. Examples of patents that disclose the manufacture of "destructurized starch" and blends of "destructurized starch" and other polymers include U.S. Patent 4,673,438 to Wittwer et al.; U.S. Patent 4,095,054 to Lay et al.; U.S. Patent 5,256,711 to Tokiwa et al.; U.S. Patent 5,275,774 to Bahr et al.; U.S. Patent 5,382,611 and U.S. Patent 5,405,564 to Step et al. Lately, there have been considerable publications on the use of thermoplastic starch (TPS) as a component in multi-phase blends (91-95).

Although many researchers have attempted to discover the "perfect" starch/polymer blend that would yield an environmental polymer, the desired mechanical

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properties and comparatively low cost are difficult to achieve. One drawback is that most of the polymers and other mixtures are more expensive than starch, which tends to increase the cost of such polymer blends compared to starch melts. Another drawback is that such starch/polymer blends lead to poor performance properties due to the thermodynamic incompatibility between the starch and the polymer.

#### 5.1.3. Modified starch to improve its compatibility with biodegradable polyesters

Reaction with cyclic dibasic acid anhydrides such as succinic anhydride yields starch esters (96). The same chemistry could be carried out with maleic anhydride to yield the maleate half ester. The reaction schemes are depicted below in Figure 5-3. Treatment of a starch suspension with a cyclic dicarboxylic acid anhydride containing a hydrophobic substituted group yields products with emulsion stabilizing properties (97).



Figure 5-3 Starch reaction with half-esters of dicarboxylic acids

While all of the above work is related to the production of starch esters in batch systems, starches can be acylated during extrusion with cyclic anhydrides in the presence of carbonate buffers to yield the corresponding starch esters. Tomasik et al. (98) reacted corn starches in extruders containing varying amounts of moisture (18, 20 and 30%) with succinic, maleic and phthalic anhydrides. A carbonate buffer, to either pH 8 or pH 9, was added during extrusion. It was demonstrated that extrusion of starch with cyclic anhydrides in an alkaline medium presents a facile method for preparation of anionic starches with hydrophobic base character.

In this study, starch was reacted with low molecular weight, high MA content SMA, in a twin-screw, co-rotating, extruder in the presence of glycerol as plasticizer. The grafting between starch and SMA, glycerol, and SMA and the cross-linking among starch, SMA and glycerol were observed. The TPS/SMA grafting blend was further blended with a biodegradable polyester,r Ecoflex, a polymer designed for blown-film applications, in the melt phase.

#### **5.2 EXPERIMENTAL**

#### 5.2.1 Materials and Equipment

Granular starch was obtained from Cargill, grade SMP 1100, un-modified cornstarch with equilibrium moisture content of about 12 wt%. Ecoflex polyester [poly (butylene adipate-co-terephthalate)] was obtained from BASF. Anhydrous glycerol [2136-03], 99.9% assay was obtained from J.T. Baker. Low molecular weight SMA (SMA3000P, 25 mol% maleic anhydride, Mw:9,500, Mn: 3,800, Tg=125 °C; SMA1000P, 50 mol% maleic anhydride, Mw:4,500, Mn: 2,000, Tg=155 °C; ) was supplied by Sartomer Company Inc, the catalyst 4-dimethylaminopyridine (DMAP) were purchased from Sigma-Aldrich Inc. The structure of SMA1000P and SMA3000P and Ecoflex are show in Figure 5-4, Figure 5-5 and Figure 5-6 respectively. Un-modified corn starch was dried in a vacuum oven at  $120^{\circ}$ C for 48 hrs to reduce the moisture to less than 1wt%. Ecoflex was dried at 70°C for 24 hrs in a ventilated oven. All other materials were used as obtained.



Figure 5-4 Structure of SMA1000P



Figure 5-5 Structure of SMA3000P



**Figure 5-6 Structure of Ecoflex** 

A twin-screw, co-rotating CENTURY extruder having a length: diameter ratio (L/D) of 40:1 and a screw diameter of 30 mm was used for the plasticization as well as the grafting reaction and blending. The extruder was electrically heated and was cooled

using circulating water. The screw elements needed for the screw configuration were also obtained from CENTURY. The auxiliary equipment includes a water bath to cool the extrudate and a pelletizer to cut the extruded strand into small pellets.

#### 5.2.2 Synthesis of TPS/SMA graft copolymers by reactive extrusion

The synthesis of TPS/SMA graft copolymers was accomplished in a twin-screw co-rotating CENTURY extruder using DMAP as a catalyst. Glycerol at 20 wt% (based on TPS) is added as a plasticizer in the extrusion. About 2.5, 5, 10, 20wt% SMA1000P was mixed with starch before feeding. The catalyst DMAP at 0.01wt% percent was ground to a fine powder with 10g starch, and then mixed with 100g starch, finally it was mixed with the balance of the starch. The mixed starch, SMA and DMAP was fed through the main extruder feeder, and the glycerol was heated to 70°C and pumped into a separate feed port. The material was collected in an aluminum pan and ground into powder, then stored in a ventilated oven at 70°C. The extrusion temperature profile was set as 15/95/145/155/160/165/165/165/160/150 °C. For comparison, pure TPS (20%wt glycerol) and TPS/SMA (2.5wt% SMA) without DMAP was also made. The proposed reaction structures for starch and SMA, glycerol and SMA, and cross-linking of starch, SMA and glycerol are shown in Figure 5-7, Figure 5-8 and Figure 5-9.

SMA3000P was applied in the same conditions to compare the results.



Starch

Styrene maleic anhydride



Starch-SMA grafting copolymer

Figure 5-7 Grafting reaction between starch and SMA



Figure 5-8 Grafting reaction between SMA and glycerol



Starch





Starch-SMA-Glycerol coploymer

# Figure 5-9 Cross-linking between starch, SMA and glycerol

# 5.2.3 Soxhlet extraction of TPS/SMA grafting co-polymer

The graft TPS/SMA copolymer powder was extracted using acetone. For comparison, TPS was also extracted with acetone. Approximately 10 grams of the sample

was accurately weighed into a cellulose extraction thimble (33 mm x 94 mm) and placed into the Soxhlet extractor. The extraction was run for 24 hours. After extraction, the thimble together with the sample were removed and dried to constant weight. A mass balance and FTIR analysis were completed for the remaining contents in the thimble and a cast film sample was obtained from the extracted solution.

# 5.2.4 Blending Ecoflex with TPS/SMA by extrusion process

The synthesis of Ecoflex-TPS/SMA graft copolymers was accomplished in the twin-screw co-rotating CENTURY extruder. The polymer blend TPS/SMA was oven dried overnight at  $70^{\circ}$ C, ground to a fine powder, and fed using an external feeder to the feed port of the extruder. Ecoflex was dried in an oven at  $70^{\circ}$ C to remove moisture and fed through the main feeder. The feeder rates were adjusted to obtain a ratio of 70:30 Ecoflex: TPS/SMA. The temperature profile was set at the same processing temperature profile used for blending TPS/SMA. The vent port was kept open to remove steam. The extruded strand was cooled using a water bath and pelletized in line. The pellets were dried in an oven overnight at  $70^{\circ}$ C before being blown into a film.

#### **5.2.5 Fourier Transformed Infrared Spectroscopy**

FTIR analysis was conducted on samples of TPS and TPS/SMA graft copolymers using a Perkin Elmer spectrophotometer. The TPS/SMA copolymer was extracted using acetone in a Soxhlet extraction unit, dried and ground to a fine powder. 1% extracted TPS/SMA was mixed with 99% KBr powder and pressed using a pellet maker to a fine transparent disk. This disk was put directly into the sample holder to obtain the spectrum. A background scan was also conducted with just the KBr pellet, which was subtracted from the total spectrum to obtain the sample spectrum. Films obtained by solvent casting were directly placed into the sample chamber to obtain the FTIR spectrum.

# **5.2.6 Blowing Film**

Films of the Ecoflex-TPS/SMA blend are made using a Killion single-screw blown film unit. The screw diameter was 25.4 mm with an L: D ratio of 25:1. The die inner diameter was 50.8 mm with a die gap size of 1.5 mm. The blown film processing conditions are shown in table 5-1.

Table 5-1: Blown Film Processing Conditions for Ecoflex-TPS/SMA blend

	Die 3	Die 2	Die 1	Adaptor	Clamp Ring	Zone 3	Zone 2	Zone 1
Set (°F)	70	330	350	360	360	360	360	315
Actual ( <sup>°</sup> F)	78	330	350	357	358	338	360	315

Melt ( <sup>°</sup> F)	328
Screw Speed (RPM)	17.0
FPM (ft/min)	8.5
Pressure (psi)	1890

# **5.2.7 Mechanical Property Determination**

Tensile properties of the films were determined using INSTRON Mechanical Testing Equipment fitted with a 100 lb. load cell. The crosshead speed was set at 1 inch per minute. Rectangular film samples,  $4"\times1"$ , were conditioned at  $23^{0}$ C and 50%Relative Humidity for 40 hours before being tested according the ASTM D-882 standard.

# **5.3 RESULTS AND ANALYSIS**

# 5.3.1 Soxhlet extraction and FTIR result

The TPS/SMA blends Soxhlet extraction results are shown in table 5-2. Here TPS was made using 80% starch and 20% glycerol. In all these samples, 0.01% DMAP was added as catalyst except where noted. Sample #5 was a blend of pure starch and SMA with no added glycerol.

		sample	weight	SMA in	weight
SP	SMA content	weight	loss	sample	loss/SMA
		g	g	g	
0	2.5%SMA1000P*	10.0083	0.7203	0.2441	2.887
1	2.5%SMA1000P	10.008	0.8996	0.2441	3.685
2	4.76%SMA1000P	9.49	0.4928	0.4519	1.091
3	10%SMA1000P	10.0455	0.2218	1.0036	0.221
4	20%SMA1000P	9.9763	0.0761	1.9953	0.038
5	50%SMA1000P**	10.0233	4.6095	5.0117	0.92
6	0%SMA1000P	10.6146	0.5429	0	

 Table 5-2 TPS/SMA soxhlet extraction results

\*No DMAP was added in this sample.

**\*\*Pure corn starch without glycerol was used in this SP#5** 

The extraction results are expressed graphically in Figure 5-10. The weight of extracted material based on a 10g sample vs. SMA content is shown.



Extracted material weight vs. SMA content

Figure 5-10 Extracted material weight vs. SMA content

In the Soxhlet extraction of pure TPS with acetone, about 25% glycerol was extracted. Another solvent, THF, was also tested. Using THF about 14% glycerol was extracted. Acetone was, therefore, used in this study.

From the Soxhlet extraction results, it is clear that at 2.5wt% SMA1000P, without DMAP, almost all of the SMA1000P and about 25% of the glycerol has been extracted. With DMAP more material has been extracted. This is due to the faster reaction between SMA and glycerol compared with that of SMA and starch. The SMA/glycerol grafted material can also be extracted. At this SMA level, the reaction between SMA and starch or cross linking between starch/SMA/glycerol is rare, thus the extracted material is greater than the original SMA content. From FTIR results no ester C=O stretch peak,

around  $1730 \text{cm}^{-1}$ , is observed in the Soxhlet residue. However, the C=O peak is observed in the cast film produced from the extraction solvent.

When the SMA content increases to 5%, the grafting reaction between starch and SMA occurs, but the grafting between SMA and glycerol still dominates, thus the extracted material is still greater than the original SMA amount. At 5% SMA content, the ester C=O stretch peak can be observed from both FTIRs (the material in the thimble and in the solvent). When the SMA content increases to 10%, most SMA and SMA/glycerol is grafted onto starch, resulting in only a small amount of SMA/glycerol (about 22 wt% of original SMA) being extracted. The ester C=O peak becomes more significant, and the OH group peak around 3400 cm<sup>-1</sup> is smaller. When the SMA content increases to 20%, very few materials are extracted. Almost all SMA and SMA/glycerol are grafted onto the starch backbone. From the FTIR, we can observe un-reacted maleic anhydride at 1775cm<sup>-1</sup> and 1730cm<sup>-1</sup>. The FTIR results are shown in Figure 5-11, Figure 5-12 and Figure 5-13. Catalyst was added in all TPS/SMA blends shown in these figures.

From the extraction results, it can be observed that about 25% of free glycerol can be extracted with acetone. Free SMA and SMA/glycerol grafted co-polymer can also be extracted. Pure starch, SMA and SMA/glycerol which grafted onto starch remain in the thimble.

Without DMAP, almost no grafting reaction occurs. This can be observed from the sample TPS/SMA (2.5% SMA) without catalyst, the weight loss is equal to the sum of the weight loss in pure TPS and the SMA weight in this sample.

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With DMAP as a catalyst, the reaction of SMA with glycerol occurs first to form SMA/glycerol grafting copolymer. When the SMA concentration increases, the grafting reaction between starch and SMA; starch and SMA/glycerol occurs.

At 20wt% SMA, all SMA, SMA/glycerol is grafted onto the starch back-bone and almost nothing can be extracted with acetone. However, without glycerol as a plasticizer, the grafting conversion of SMA 1000P in the starch/ SMA1000P/DMAP (50/50/0.01) blend is very low. This is due to the high viscosity of the starch phase in the absence of plasticizer and consequent poor dispersion of the SMA phase.



Figure 5-11 FTIR of TPS and TPS/SMA (2.5%wt) after extraction (thimble)



Figure 5-12 FTIR of TPS/SMA (5, 10, 20wt%) after extraction(thimble)



Figure 5-13 FTIR of material extracted from TPS/SMA (10%wt) (solvent)

# 5.3.2 Mechanical properties of Ecoflex and TPS/SMA blends

The TPS/SMA grafting co-polymer with 20wt% SMA1000P was used to blend with Ecoflex at 30/70 wt% ratio to blow film. Compared with the Ecoflex/TPS/MA (70/30/1) blend, the modulus and the machine direction tensile strength improved, but the elongation and transverse direction tensile strength decreased. The properties are poor compared with Ecoflex and an inorganic filler blend (see chapter 6). The mechanical data are shown in Table 5-3:

material	Direction	tensile strength	elogation	modulus
		psi	%	psi
Ecoflex+TPS/SMA	MD	$1120 \pm 30$	$200 \pm 20$	9440 ± 1000
70/30	CD	550 ± 20	$110 \pm 15$	$7920 \pm 140$
Ecoflex+TPS+MA*	MD	980	500	6000
70/29/1	CD	900	350	5000

Table 5-3 The mechanical properties of Ecoflex and TPS/SMA blend

\* Data form the other group member's work

## **5.4 CONCLUSIONS**

1. The grafting reaction between starch, SMA and glycerol occurs with DMAP as a catalyst under reactive extrusion conditions.

2. At lower SMA concentrations (less than 5%), the reaction between glycerol and SMA dominates.

3. With increased SMA concentration, the reaction between starch and SMA, and starch and SMA/glycerol copolymer increases significantly.

4. At 20wt% SMA, almost all SMA and glycerol are grafted or cross-linked onto starch.

5. Grafting SMA onto starch improves the compatibility between Ecoflex and starch to a lesser extent. At higher grafting conversion, the intermolecular attraction between starch, glycerol and SMA becomes stronger thus reducing the compatibility of TPS/SMA and Ecoflex.
# Chapter 6: PREPARING COMPATIBLE ORGANIC-INORGANIC HYBRID BLENDS BY REACTIVE EXTRUSION

#### **6.1 INTRODUCTION**

The main drawback of synthetic biodegradable polymers is their high cost. Adding natural and inorganic fillers such as starch, cellulose, CaCO3, and Talc to reduce the cost has been studied widely. In order to improve the properties of these blends by improving their compatibility, most researchers attempt to graft functionalized groups onto the biodegradable polymer backbones and then react with the filler to generate the co-polymer as the compatibilizer. Typically, functional groups such as isocyanate, amine, anhydride, carboxylic acid, epoxide and oxazoline are introduced through a fast reactive extrusion process, and then combined using their suitably reactive functionalities, such as hydroxyl-isocyanate, amine-anhydride, amine-epoxide, amine-lactam, amine-carboxylic acid and amine-oxazoline (99). Maleic anhydride was first used as a monomer to graft onto non-biodegradable polymers such as polyethylene, polypropylene and other polymers (100, 101) to form a functional group. Earlier results from research conducted by Bhattacharya and co-workers (102 - 112) on maleation of biodegradable polymers such as PCL, PBSA, poly(butylene succinate) (PBS) and Eastar Bio<sup>®</sup> co-polyester; Narayan and co-workers (113, 114) on maleation of PLA, indicated that blends of anhydride functional polymers and starch as a natural filler could lead to products with

useful final properties. Such functionalization of polymer matrices can reduce the interfacial tension, strengthen interfacial adhesion, and minimize coalescence (115). Reactive extrusion techniques have proved to be an effective way to introduce a variety of functional groups onto the surface of natural polymers (116, 117).

Recently, BASF has marketed a novel biodegradable poly (butylene adipate-*co*-terephthalate) trademarked Ecoflex<sup>®</sup> (118). This aliphatic-aromatic (co)polyester is prepared by condensation polymerization from adipic acid, 1,4-butanediol, and more especially terephthalic acid (aromatic ring), designed to reinforce the co-polyester structure. Combination of these biodegradable polymers with cheap inorganic fillers such as Talc also provides a useful way of reducing the cost, and optimizing the properties of biodegradable thermoplastic polyesters (119 – 121).

Developing a melt-blend with satisfactory overall physico-mechanical behavior will depend on the ability to control interfacial tension in order to generate a smalldisperse phase size and strong interfacial adhesion. It is of prime importance to achieve high-performance mechanical properties in the final material.

In this respect, our study aims at reactive melt-blending of Ecoflex with a natural filler through the reactive extrusion process with the ultimate objective of producing blown films with enhanced mechanical properties, In this study, Talc was utilized as the natural filler. Although the basal surface of Talc is composed of a chemically inert magnesium silicate layer, its lateral surface exhibits some hydroxyl functionality. The Ecoflex backbone was reactively modified through free-radical grafting of vinyl-trimethoxysilane or vinyl-methyl- dimethoxysilane. Further, the objective of this study was to chemically react the methoxy (alkoxy) groups of the silane with the hydroxyl

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group of the filler to provide better filler-matrix adhesion and/or a tough, cross-linked matrix with improved mechanical properties and water repellency. Silane-polyester graft copolymers can be melt cast or blown into transparent films with applications in the areas of lawn and leaf compost bags, agricultural mulch films, trash bags, regular carry out retail bags, food packaging etc. US Patent 3,646,155 issued to Scott (122) relates to the cross-linking of polyethylene materials using an organofunctional silane as a cross-linking agent, which is grafted on to the polymer using a peroxide catalyst. The process as described in the patent also leads to a reduction in melt flow of the polymer leading to difficulties in processability in normal equipment and a significant reduction in elongation compared with the base material. Other US patents similar to the above work are US 4,117,195 (123), US 4,413,066 (124), US 4,514,539 (125), US 5,773,145 (126).

The use of trifunctional silanes in enhancing the mechanical properties of thermoset materials has been discussed in the Japanese Patent Application 2003221446 (127); the main intention, however, was to produce highly cross-linked networks. The invention did not relate to the manufacture of films, and also the mechanism of modification was the condensation reaction of end groups, and not a peroxide aided route as discussed in the present work. Laminates using silane-grafted polypropylene and liquid crystal polyesters were discussed in the Japanese patent application 2001239539 (128). Production of fibers from waste polyesters and glass fibers is discussed in the Japanese patent application 2001040528 (129) – but the silane used as a coupling agent operated via a condensation mechanism and not by the peroxide route.

Thermoplastic polyurethanes have been modified using silane grafting agents (130). Their technique, however, was to use a condensation type reaction between an

isocyanate grafting agent and an amino functional silane rather than a free radical peroxide induced grafting which was the aim of the present work. Similar work is reported in the literature (131) where the authors have grafted a vinylsilane on to a silicone rubber using an organic peroxide catalyst to improve compatibility with polyurethane.

DE 10111992 (132) discusses the use of silane grafting on to polyolefins to make compatibilized blends with polyesters in the presence of a silane coupling agent. But in the invention, the focus was on grafting the polyolefin and not the polyester with the organosilane. Furthermore the work did not mention films, and was concerned only with the manufacture of threads.

This present study deals with the improvement of the physico-mechanical properties of these silane-grafted filled polyester films by improving the compatibility between the filler and the polyester. This graft co-polymer helps achieve the aforementioned objective by providing blends in a one-step extrusion process to give films with enhanced tensile strengths up to 6000 psi. The grafting reaction and the mechanical properties of the blown films are discussed in this chapter.

### **6.2 EXPERIMENTAL**

#### 6.2.1 Materials

Ecoflex FBX 7011 was purchased from BASF Corporation, 2,5-Bis(tertbutylperoxy)-2,5 dimethylhexane (Lupersol 101) was provided by Sigma-Aldrich Chemical Company (Milwaukee, WI) and used as received. Talc having a particle size of ca. 6 µm under the trade name Luzenac 20M00S was provided by Luzenac Europe, and

dried at 120°C overnight before use. Vinyl-trimethoxysilane (VTMOS) and vinylmethyl-dimethoxysilane (VMDMOS) were purchased from Gelest, Inc. Dichloromethane was provided by EMA chemicals Inc. The structure of Lupersol 101, VTMOS, VMDMOS and proposed structure of Talc are shown in Figures 6-1, 6-2, 6-3 and 6-4.



2,5-Bis(tert-butylperoxy)-2,5-dimethylhexane

# Figure 6-1 structure of 2,5-Bis(tert-butylperoxy)-2,5 dimethylhexane (lupersol

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#### Figure 6-3 Structure of vinyl-methyl-dimethoxysilane



Figure 6-4 Proposed structure sketch of Talc

#### **6.2.2 Reactive extrusion**

700g of PBAT was hand-mixed with 0.05/0.1/0.2 wt% Lupersol(of PBAT) as a free radical initiator, 0.5/1/2 wt% (of PBAT) VTMOS/VMDMOS, and 300g of Talc, in that order, and fed together to a Century ZSK-30 co-rotating twin screw extruder at a feed rate of approximately 150 g/min. The screw diameter was 30 mm, with a length-to-diameter ratio of 40:1. Barrel and die temperatures were maintained by means of ten electrical/cooling devices as described heretofore. The screw speed was 150 rpm resulting in a mean time residence of about 4-5 minutes. The temperature profile was set as 15/90/135/160/170/175/175/165/160 °C from the feeder barrel to the die. The strand was extruded through a single orifice die having a nozzle opening of 2.7 mm in diameter, cooled in a water-bath, and pelletized downstream. The supposed grafting reaction between Ecoflex, vinyl-trimethoxysilane and Talc is shown in Figures 6-5 and 6-6. Side reactions such as crosslinking of silane will also occur.

To study the grafting reaction between Ecoflex and silane, Ecoflex with 1wt% vinyl-trimethoxylsialne and 0.1wt% Lupersol was extruded by itself at the same temperature profile. In comparison with pure Ecoflex the torque increased by about 20% at the same feed rate.



Figure 6-5 Proposed reaction structure of Ecoflex and Silane



Figure 6-6 Proposed crosslink between Ecoflex, silane and Talc

# 6.2.3 Soxhlet extraction and FTIR test

For comparison, Ecoflex/Talc (70/30) and Ecoflex/Talc/VTMOS/Lupersol (70/30/1/0.1) blends were dried in a vacuum oven at  $70^{\circ}$ C for 24hrs, and Soxhlet extracted with dichloromethane for 24 hrs. Both the material remaining in the thimble

and that extracted in the solvent were analyzed by FTIR. To investigate the grafting reaction between Ecoflex and silane, the Ecoflex/silane/lupersol blend was also analyzed by FTIR.

## 6.2.4 Blowing films

The reactively modified Ecoflex-Talc composites were extruded into films using a Killion single-screw blown film unit. The screw diameter was 25.4 mm with a length-todiameter ratio of 25:1. The die inner diameter was 50.8 mm with a die gap size of 1.5 mm. The blown film processing conditions are shown in Table 6-1. The screw speed was maintained at 15 rpm. Blown film processing was carried out at a pressure of ~ 2500 psi, with a melt temperature around 150°C.

	Die 3	Die 2	Die 1	Adaptor	Clamp Ring	Zone 3	Zone 2	Zone 1
Set ( <sup>o</sup> F)	75	280	300	310	310	330	330	315
Actual (°F)	78	281	300	311	310	318	330	315
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 Table 6-1: Blown Film Processing Conditions for Ecoflex-silane-Talc blends

Melt ( <sup>°</sup> F)	302
Screw Speed (RPM)	15
FPM (ft/min)	7.8
Pressure (psi)	2580

# **6.3 RESULTS AND ANALYSIS**

### 6.3.1 Soxhlet extraction and FTIR results

The Soxhlet extraction results are shown in table 6-2. In the Ecoflex/Talc blend, almost 100% Ecoflex was extracted. There is no grafting in the Ecoflex/Talc blend and the extraction is complete since FTIR analysis shows that the material remaining in the thimble is pure Talc. There are two significant peaks at 1009 cm<sup>-1</sup> and 670 cm<sup>-1</sup> for Talc (Figure 6-7), the peak at 1009 cm<sup>-1</sup> is assigned as Si-O-Si stretch and 670 cm<sup>-1</sup> is assigned as Si-O-Mg stretch. d'Espinose de la Caillerie et al. displayed the same FTIR results for Talc (133).

Extracted data of ecoflex/talc with/without vinyltrimethoxysilane						
samples	weight (g)	materials reamian in thimble (g)	material extracted out (g)	Ecoflex grafting percentage (%)		
Ecoflex/Talc (70/30)	1.851	0.5437	1.3066	-0.01		
Ecoflex/talc/silane/lupersol (69/30/1/0.1)	1.9281	1.1883	0.7391	0.45		

 Table 6-2 The Soxhlet extraction data for Ecoflex/Talc blends



Figure 6-7 FTIR spectrum of Talc

The material extracted by the solvent in the Ecoflex/Talc blend is pure Ecoflex. This has been confirmed by FTIR. The FTIR of Ecoflex is shown in Figure 6-8. The ester C=O and C-O stretch,  $-CH_2$ - group, and *para*-substituted benzene group can be identified at 1710 cm<sup>-1</sup>, 1268(1103-1164) cm<sup>-1</sup>, 2953 cm<sup>-1</sup> and 728 cm<sup>-1</sup>.



Figure 6-8 FTIR spectrum of Ecoflex

In the Ecoflex/Talc/VTMOS/Lupersol blends, only about 55 wt% Ecoflex was extracted. The FTIR of the material remaining in the thimble shows Ecoflex -Talc grafting copolymers were generated. The FTIR results for the material remaining in the thimble compared to pure Ecoflex is shown in Figure 6-9. In this figure, we can observe the Si-O-Si peak shift from 1009 cm<sup>-1</sup> to 968 cm<sup>-1</sup> combined with the ester C-O stretch and Si-O-Mg peak at 667 cm<sup>-1</sup> from Talc. The ester C=O peak at 1715 cm<sup>-1</sup>, parasubstituted benzene peak at 729 cm<sup>-1</sup> and the  $-CH_2$ - peak around 2950 cm<sup>-1</sup> from Ecoflex can also be identified clearly.



Figure 6-9 FTIR spectrum of Ecoflex/silane/Talc after extraction (in thimble) vs. Talc

The cast film made from the extracted solution shows us some interesting results. It is a clear film at the edges and opaque in the center. The FTIRs of the edge of the film and the center of the film are shown in Figure 6-10. Figure 6-11 shows the FTIR results for the center of the cast film compared to pure Ecoflex in the  $600 \text{ cm}^{-1}$  to 1050 cm<sup>-1</sup> range.

The FTIR results show that the edge of the film is identical to pure Ecoflex, but in the center there are two strong peaks at 794 cm<sup>-1</sup> and 1015 cm<sup>-1</sup>. Hjertberg, T. et al. in their study on cross-linking of copolymers of ethylene and vinyltrimethoxysilane pointed

out that wave number around 800 cm<sup>-1</sup> is the peak for the  $-Si-OCH_3$  group and 1030 cm<sup>-1</sup> is the peak for the -Si-O-Si- stretch (134).

The FTIR results confirm that the grafting reaction between Ecoflex and vinyltrimethoxysilane generates the grafting copolymer, and the –Si-O-Si- group shows that the reaction between the -Si-O-CH<sub>3</sub> groups of vinyl-trimethoxysilane to form an –Si-O-Si- structure can also occur.



#### FTIR of material extracted form Ecoflex/ta

Figure 6-10 FTIR spectrum of extracted material from Ecoflex/silane/Talc (solution) (edge and center)





Figure 6-11 FTIR spectrum of extracted material from Ecoflex/Silane/Talc(solution) comparing with Ecoflex

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For further confirmation the reaction between silane and Ecoflex, FTIR was also studied for an Ecoflex/Silane/lupersol (99:1:0.1 at weight) blend. The spectrum of the blend subtracted from the spectrum of pure Ecofelx in the 1050-600<sup>-1</sup> range is shown in Figure 6-12. The peak at 1018 and 796 can be clearly identified although the silane concentration is low (1 wt %).



Figure 6-12 FTIR spectrum of Ecoflex/silane substracted by Ecoflex

#### 6.3.2 Mechanical properties of Ecoflex-silane-Talc blends

Tables 6-3 and 6-4 show the tensile properties in the machine and transverse directions respectively for blown films derived from the *in situ* silane-modified PBAT-Talc composites, and the simple PBAT-Talc melt-blend.

Using VTMOS (Entries 2 - 6, Table 6-3), it was observed that tensile strengths higher than 5000 psi in the machine direction could be achieved in some formulations (Entries 2 & 5, Table 6-3) with elongations at break of 300 - 350%.

Tensile strengths greater than 4000 psi and break elongations in the range of 150 – 300% were obtained from the remaining formulations (Entries 3, 4, & 6, Table 6-3). Thus, higher mechanical properties were obtained using lower concentrations of the free-radical initiator as well as of VTMOS. This is probably due to the fact that low levels of branching would have occurred within the polyester chains due to the presence of the peroxide. Also, the free-radically grafted silane would have induced low levels of branching. The branching in the polyester matrix due to the silane could be due to curing of the methoxy groups with other methoxy groups from the grafted silane as well as curing of the grafted methoxy groups with the lateral hydroxyl groups possessed by the Talc filler. This branching would effectively improve the tensile strength of the resulting composite but result in a decrease in elongations at break due to the formation of a network between the polyester and the filler (which would restrict the elongation of the polymer chains). Higher levels of peroxide or VTMOS would lead to increased branching (or possibly cross-linking) restricting the elongations at break to very low values (150 – 300%).

VMDMOS was used in order to reduce the branching due to the silane within the polyester chains, and to form a more flexible network with improved tensile strengths as well as elongations. VMDMOS is, however, more expensive than VTMOS, and thus not economically feasible. The tensile strengths of the composites obtained using VMDMOS were approximately 4300 psi, with break elongations in the range of 430 – 480% (Entries 7 - 8, Table 6-3).

The tensile properties of the films in the transverse direction displayed a similar trend to those in the machine direction (Table 6-4).

	% Free	Type and (%	Young's	Yield	Tensile	Break
Entry	Radical	Amount of	modulus	Stress	Stress	Elongation
	Initiator	Silane)	(psi)	(psi)	(psi)	(%)
1	-	-	17000	1840	2060	600
2	0.1	VTMOS (0.5)	56850	5800	5800	300
3	0.1	VTMOS (1.0)	54850	4600	4700	230
4	0.1	VTMOS (2.0)	50840	4000	4340	160
5	0.05	VTMOS (1.0)	47000	5100	5100	340
6	0.2	VTMOS (1.0)	49300	4300	4300	270
7	0.1	VMDMOS (1.0)	48000	4250	4300	470
8	0.1	VMDMOS (2.0)	49700	4250	4300	420

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Table 6-3 Tensile Properties (Machine Direction) of blown films derived from the

**PBAT-silane-Talc blends** 

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	% Free	Type and (%	Young's	Yield	Tensile	Break
Entry	Radical	Amount of	modulus	Stress	Stress	Elongation
	Initiator	Silane)	(psi)	(psi)	(psi)	(%)
1	-	-	17200	1400	1500	300
2	0.1	VTMOS (0.5)	50700	3300	3300	270
3	0.1	VTMOS (1.0)	57300	3700	3800	200
4	0.1	VTMOS (2.0)	51600	3200	3300	160
5	0.05	VTMOS (1.0)	47600	3000	3000	170
6	0.2	VTMOS (1.0)	52200	3650	4000	280
7	0.1	VMDMOS (1.0)	51600	3500	3500	430
8	0.1	VMDMOS (2.0)	53600	3700	3800	390

Table 6-4 Tensile Properties (Transverse Direction) of blown films derived from the

**PBAT-silane-Talc blends** 

# 6.4 CONCLUSIONS

1. The grafting reaction between silane functionalized Ecoflex and Talc was characterized by Soxhlet extraction and confirmed by FTIR.

2. The grafting reaction improves the tensile strength and Young's modulus of the organic-inorganic hybrid blend with a corresponding decrease in elongation. The crosslink agents vinyl-trimethoxsilane or vinyl-methyl-dimethoxysilane can be reacted

with Ecoflex and Talc to form a grafting copolymer and improve the compatibility of Ecoflex and Talc with resulting improvement in mechanical properties.

3. The reaction mechanism between Ecoflex, silane and Talc is complicated and more work needs to be done to analyze the relationship between the mechanical properties and the compositions of silane and Lupersol.

#### **Chapter 7: CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK**

#### 7.1 CONCLUSIONS

Using bio-based polymeric materials has a positive affect on the environment. The main drawback of bio-based polymers is their poor processability and hydrophilicity and the main factor affecting the marketability of synthetic biodegradable polymers is their higher cost. The addition of cheap fillers will significantly reduce the cost but physical and processing properties are significantly impaired.

Compatilization is a process that improves the interfacial interaction in polymer phases by reducing the interfacial tension, improving the phase dispersion and reducing the phase separation and hence improving the properties of the polymer blend. In this study, compatiblizing a CA/SMA or an organic-inorganic hybrid blend by introducing chemical reactions between the components has proved to be an effective way to achieve acceptable price and usable properties.

In a CA/SMA bio-based blend the high grafting conversion of SMA was obtained by adding an appropriate catalyst both in solution and reactive extrusion reactions. SMA grafting conversion was characterized by Soxhlet extraction and confirmed by FTIR analysis. A third order reaction was demonstrated by experimental data. The reaction constant and activation energy were also derived from the experimental data. Constant of the second

CA can be easily processed without any added plasticizer by reactive blending high molecular weight SMA (15wt% or higher). The grafting copolymer generated in-situ acts as a compatibilizer to improve the phase dispersion by reducing the interfacial tension thereby improving the mechanical properties. Compatibilized CA/SMA blends with mechanical properties equivalent to commercial engineering plastics (glass fiber reinforced ABS, glass fiber reinforced Nylon 66) were obtained by a one-step reactive extrusion process.

Injection molding conditions were also studied to optimize the tensile properties of the CA/SMA blend. Higher shot velocities and higher mold temperatures can improve the tensile properties due to uniform cooling and should result in better properties for the CA/SMA blends.

The process of CA/SMA compatibilization was also simulated using the model deduced in this work by applying reasonable assumptions and approximations. The simulation results are in agreement with the experimental data. Introducing a grafting reaction to generate a copolymer acting as a compatibilizer improves the phase dispersion. On other hand, better phase dispersion generates more reacted areas, thus improving the grafting rate. The mutually positive effect between phase dispersion and grafting reaction make the CA/SMA grafting system compatibilization rapid.

Adding the inorganic filler Talc to synthetic biodegradable polymer Ecoflex can reduce the cost, improve the Young's modulus, improve barrier properties and improve the blown film process by reducing tackiness.

The use of vinyl-trimethoxysilane or vinyl-methyl-trimethoxysilane as a coupling agent improves the tensile strength by 100%-200% and Young's modulus by more than

200% due to the formation of chemical bonds between Ecoflex, VTMOS or VMTMOS and Talc. A lower cost, higher property biodegradable polymer blend is achieved for blown film applications.

This study aimed at processing compatible blends by introducing grafting reactions between the components proved to be an effective method to achieve the desired properties and to reduce cost thus making it more feasible to use bio-based or biodegradable polymeric materials.

#### **7.2 RECOMMEND FUTURE WORK**

#### 7.2.1 Theoretical expectations for polymer blend properties

In this study, the relationship of phase dispersion and such factors as component composition, interfacial tension, compatibilizer concentration, and shear rate have been characterized and modeled. The theoretical analysis results are close to the experimental results obtained. Theoretical anticipation of the properties of polymer blends will provide valuable insights into the design of a polymer blend with desired properties.

In a miscible polymer blend, the properties can be readily predicted by calculating their volume/weight average properties of the blended polymers. However, most polymer blends are immiscible. To anticipate immiscible polymer blend properties is much more complicated and most studies have been concentrated in the experimental area.

A general model to calculate average molecular weight of the copolymer formed between two poly-disperse reactive polymers has been generated by Lie-Ding Shiau (135) based on Flory's assumptions. Jose.S., et.al (136) have done the theoretical analysis of the tensile properties of Polyamide 12 and polypropylene blend with or without

compatibilizer using Nielsen's first power law model, Nielsen's two-third power law model and the Nicolais–Narkis model. Nielsen's first power law model was found to be the best fit with the experimental data.

To estimate the properties of polymer blends by using its components properties, processing conditions and their microstructures will be a crucial challenge in the study of polymer blends.

## 7.2.2 Compatibilizing biodegradable polyesters

In the biodegradable polymer family we still focus on developing new products with lower cost and good properties. Recently several studies on blends of existing biodegradable polymers were done (137-139). Poly (lactic acid) (PLA) has been commercialized by Natureworks on a large scale (140,000 ton/year). PLA is a completely bio-based and biodegradable polymer with comparable price to petrochemical-based polymers. The application perspectives of PLA are exciting in the biodegradable field. However, PLA has some drawbacks such as low deflection temperature, low melting strength (difficult to blow film), and slow crystallization (requiring long cycle time in molding). To improve these shortages, blending PLA with other biodegradable polyesters has been studied widely (140-142). The crystallization time can be shortened by adding a nucleating agent, but none of these workers show that the deflection temperature and melting strength were improved significantly.

To introduce a new blend of PLA with a high deflection temperature and good melting strength for blown film will dramatically improve the application of PLA and capitalize on its lower price, higher tensile strength and good processability. To blend

Ecoflex with PLA by introducing functional silane as the crosslink agent has been tried. Both the melt strength and deflection temperatures of PLA can be improved at low additive levels. The blend can be used for blown film when more than 70% Ecoflex is added. To lower the content of Ecoflex and investigation of other biodegradable polymers to achieve the object will be very interesting future work.

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