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# STUDIES IN REACTIVE EXTRUSION PROCESSING OF BIODEGRADABLE POLYMERIC MATERIALS

Bу

Sunder Balakrishnan

# A DISSERTATION

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#### ABSTRACT

## STUDIES IN REACTIVE EXTRUSION PROCESSING OF BIODEGRADABLE POLYMERIC MATERIALS

#### By

#### Sunder Balakrishnan

Various reaction chemistries such as Polymerization, Polymer cross-linking and Reactive grafting were investigated in twin-screw extruders. Poly (1,4-dioxan-2-one) (PPDX) was manufactured in melt by the continuous polymerization of 1.4-dioxan-2-one (PDX) monomer in a twin-screw extruder using Aluminum tri-sec butoxide (ATSB) initiator. Good and accurate control over molecular weight was obtained by controlling the ratio of monomer to initiator. A screw configuration consisting of only conveying elements was used for the polymerization. The polymerization reaction was characterized by a monomer-polymer dynamic equilibrium, above the melting temperature of the polymer, limiting the equilibrium conversion to 78-percent. Near complete (~100-percent) conversion was obtained on co-polymerizing PDX monomer with a few mol-percent (around 8-percent) Caprolactone (CL) monomer in a twin-screw extruder using ATSB initiator. The co-polymers exhibited improved thermal stability with reduction in glass transition temperature. The extruder was modeled as an Axial Dispersed Plug Flow Reactor for the polymerization of CL monomer using Residence Time Distribution (RTD) Analysis. The model provided a good fit to the experimental RTD and conversion data.

Aliphatic and aliphatic-aromatic co-polyesters, namely Polycaprolactone (PCL) and Poly butylenes (adipate-co-terephthalate) (Ecoflex) were cross-linked in a twin-screw extruder using radical initiator to form micro-gel reinforced biodegradable polyesters. Cross-linked Ecoflex was further extrusion blended with talc to form blends suitable to be blown into films. A screw configuration consisting of conveying and kneading elements was found to be effective in dispersion of the talc particles (5-10 microns) in the polyester matrix. While the rates of crystallization increased for the talc filled polyester blends, overall crystallinity reduced. Mechanical, tear and puncture properties of films made using the talc filled polyester blends were comparable to linear low density Polyethylene (LDPE).

Ecoflex-Thermoplastic Starch (TPS) graft co-polymers were continuously manufactured in melt with maleic acid catalyst using a twin-screw co-rotating extruder. The graft co-polymer was completely extractable in Dichloromethane and formed transparent films on solvent casting. Regular corn-starch was maleated in a twin-screw extruder using maleic anhydride or maleic acid, glycerol plasticizer and optional radical initiator. Confirmation of reactivity of maleic acid onto the starch backbone was confirmed by Fourier Transformed Infra Red (FTIR) Spectroscopy. The Maleated Thermoplastic Starch (MTPS) samples were easier to process than TPS and exhibited lower intrinsic viscosity values. Graft co-polymers of Ecoflex and cross-linked Ecoflex with MTPS were continuously manufactured in a twin-screw extruder. Mechanical, tear and puncture properties of films made using the graft co-polymers were comparable to LDPE. All the above-mentioned reactive extrusion technologies used in the synthesis of novel biodegradable polymeric materials find use in single-use plastics applications.

# Sri Seshadri Swamigal Thunai

Dedicated to

My Parents

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I.

# TABLE OF ABBREVIATIONS

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ATSB	Aluminum tri-sec butoxide	
CL	Caprolactone	
FTIR	Fourier Transformed Infra Red Spectroscopy	
LEcoflex	Cross-linked Ecoflex	
LPCL	Cross-linked PCL	
MTPS	Maleated Thermoplastic Starch	
PCL	Poly (ε-caprolactone)	
PCL-co-	Poly (ε-caprolactone)-co- Poly (1,4-dioxan-2-one)	
PPDX		
PDX	1,4-dioxan-2-one	
PFR	Plug Flow Reactor	
PHB	Poly hydroxy butyrate	
PHBV	Poly hydroxy (butyrate-co-valerate)	
PLA	Poly (D,L, or DL-lactide)	
PPDX	Poly (1,4-dioxan-2-one)	
ROP	Ring Opening Polymerization	
Chapter 2		
CMR	CL mass rate	
DEG	Diethylene glycol	
DSC	Differential Scanning Calorimetry	



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DP	Degree of Polymerization	
GMA	Glycidyl methacrylate	
ISR	Initiator Solution mass rate	
КОН	Potassium hydroxide	
MHS	Mark-Houwink-Sakurada	
MMR	Monomer Mass Rate	
PET	Polyethylene terephthalate	
PMR	PDX mass rate	
PVC	Poly vinyl chloride	
REX-PPDX	Reactive Extruded Poly (1,4-dioxan-2-one)	
RPM	Revolutions per minute	
RTD	Residence Time Distribution	
SAN	Styrene Acrylonitrile copolymer	
SEC	Size Exclusion Chromatography	
TGA	Thermal Gravimetric Analysis	
TSE	Twin-screw extruder	
Х	Monomer conversion	
Chapter 3		
ESEM	Environmental Scanning Electron Microscopy	
LLDPE	Linear low density polyethylene	
Luperox	2,5-Bis (tert-butylperoxy)-2,5-dimethylhexane	
101		
THF	Tetrahydrofuran	

Chapter 4	
DCM	Dichloromethane
DMSO	Dimethyl sulfoxide
DSR	Destructurized starch
EAA	Poly (ethylene-co-acrylic acid)
Ecoflex	Poly butylene (adipate-co-terephthalate)
EVOH	Polyethylene-vinyl alcohol
MA	Maleic anhydride
SAXS	Small angle X-Ray Scattering
TPS	Thermoplastic Starch
WAXS	Wide angle X-Ray Scattering

Chapter 1

### **INTRODUCTION**

### **1.1 RATIONALE**

During the last century, a tremendous advance in the field of materials has been made with the introduction of plastics. In today's world, life without plastics is incomprehensible. While plastics are strong, lightweight, inexpensive and easily processable, they are not readily broken down by the natural elements in the environment. This is of particular concern when plastics are used in single-use disposable packaging and consumer goods. Thus, new products have to be designed and engineered from "conception to reincarnation" incorporating a holistic "life cycle thinking approach". This has opened up new market opportunities for developing biodegradable and biobased products as the next generation of sustainable materials that meets ecological and economic requirements (1-3).

The use of annually renewable biomass as opposed to petrochemicals as the feedstocks for the production of polymers, chemicals and fuel needs to be understood from a global carbon cycle basis. Clearly, petrochemical feedstocks are also natural. Their fossil resources are formed from biomass over geological time frames. However, the rate at which biomass is converted to fossil resources are in total imbalance with the rate at which it is consumed. The use of annually renewable biomass to produce polymer materials, chemicals, and fuel as an adjunct to fossil resources, would begin to move the rate of carbon dioxide fixation more in balance with the rate at which it is released. Furthermore, if we manage our biomass resources effectively by making sure that we plant more biomass than we utilize, we can begin to start reversing the carbon dioxide fixation move towards a net balance between carbon dioxide fixation/sequestration and release due to consumption (4).

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 polymers, natural polymers and degradable polymers. These include natural polymers like starch, cellulose, proteins, synthetic biodegradable polymers like poly ( $\varepsilon$ -caprolactone) (PCL), poly (D, L, or DL-lactide) (PLA), poly hydroxy butyrate (PHB), poly hydroxy (butyrate-*co*-valerate) (PHBV), poly (1, 4-dioxan-2-one) (PPDX) and their modified versions. Along with the above mentioned polymers, the entire portfolio of biodegradable plastics are used in a variety of applications ranging from packaging films, cutlery items such as spoons, knives, forks etc., biodegradable packaging foams and many more.

Extruders are the most common machines in the Plastics Processing Industry. Extruders have been used, in the traditional sense, to transform solid plastic into uniform melt, for delivery to the next stage of processing. Various reactors (Batch, PFR, CSTR or a combination of these) have been used to conduct chemical reactions that include polymerizations, polymer functionalization, reactive grafting etc. The concept of using extruders as reactors is novel and unique and is termed as "*Reactive Extrusion*". More specifically, *reactive extrusion* refers to the process of conducting chemical reactions during the melt extrusion process. There are reports (5-10) in the literature on reactive extrusion processes. The reaction times needed to achieve near complete conversion need to be well within the residence times available in extrusion operations (typically less than 5 minutes). The advantage of using extruders to conduct reactions is as follows:

- Fast and continuous process
- Efficient devolatilization capability through the vent port.
- Modular in design and hence easy to scale up.

Based on the above rationale, the overall goal is to study and evaluate three different reaction chemistries such as Ring Opening Polymerization, Polymer cross-linking and Reactive grafting of synthetic biodegradable and natural polymers in extruders. This novel reactively extruded biodegradable biobased polymeric materials and blends find use in biodegradable plastics technology for film applications.

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#### **1.2 PROPOSED GOALS**

This study targeted the design and engineering of a new process for the extrusion polymerization of 1, 4-dioxan-2-one (PDX) monomer, the co-polymerization of PDX monomer with ε-caprolactone (CL) monomer and the characterization of the resulting polymers. It further deals with the reactive extrusion cross-linking and characterization of biodegradable polyesters such as PCL (aliphatic polyester formed by the Ring Opening Polymerization [ROP] of CL monomer) and Ecoflex (aliphatic-aromatic co-polyester based on the monomers adipic acid, terephthalic acid and 1, 4-butane diol). It finally targets the synthesis of Ecoflex-starch graft copolymers by reactive extrusion processing and the subsequent characterization of the graft copolymers. Specifically, the study focused on the following:

- Reactive extrusion Ring Opening Polymerization (ROP) of PDX and copolymerization with CL monomer.
- Reactive extrusion cross-linking of PCL and Ecoflex.
- Ecoflex-Starch graft copolymers by reactive extrusion processing.

### **1.3 SPECIFIC OBJECTIVES**

- Reactive extrusion Polymerization of PDX and co-polymerization with CL monomer.
  - Bulk (solvent-free) homo-polymerization of PDX monomer and co-polymerization with CL monomer using Aluminum tri-sec butoxide (ATSB) as a catalyst in a batch reactor.
  - Development of an extrusion polymerization process to synthesize three-arm PPDX and Poly (ɛ-caprolactone)-co-Poly (1, 4-dioxan-2-one) (PCL-co-PPDX) using ATSB as a catalyst.
  - Characterization of PPDX and PCL-co-PPDX polymers produced by the bulk extrusion polymerization process-Molecular weight, Thermal Analysis.
  - Modeling reactive extrusion polymerization of CL monomer in a BAKER PERKIN extruder as an axially dispersed Plug Flow model.
- Reactive extrusion cross-linking of PCL and Ecoflex.
  - Development of an extrusion process to cross-link PCL and Ecoflex using free radical initiation chemistry.

- Characterization of the cross-linked PCL (LPCL) and cross-linked Ecoflex (LEcoflex) - Gel fraction and Thermal Analysis.
- Reactive extrusion blending of Ecoflex and their crosslinked versions with talc.
- Characterization of the blends- Thermal analysis and mechanical properties of blown films.

### • Ecoflex-starch graft copolymers by reactive extrusion processing.

- Ecoflex-starch graft copolymers by reactive extrusion processing using maleic acid as a trans-esterification catalyst.
- Characterization of the graft copolymers- Soxhlet extraction, Fourier Transformed Infra Red Spectroscopy (FTIR) analysis, Thermal Analysis and Mechanical Properties of films.
- Development of an extrusion process to maleate starch in a twin-screw extruder using maleic anhydride or maleic acid to form maleated thermoplastic starch (MTPS).
- Characterization of MTPS- Fourier Transformed Infra Red Spectroscopy (FTIR), Thermal Analysis and Intrinsic viscosity measurements.

- Reactive blends of PCL and Ecoflex with MTPS in extruders.
- Characterization of the blends- Soxhlet extraction, Thermal Analysis, FTIR Analysis and Mechanical Properties of films.

#### **1.4 STRUCTURE OF THESIS**

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

Chapter 2 deals with the bulk extrusion polymerization of PDX monomer and the copolymerization of PDX monomer with CL monomer to produce high molecular weight PPDX and PCL-co-PPDX polymer. Chapter 2 also deals with particular reference to screw configuration, residence time requirements, molecular weight of the polymer produced, thermal analysis and modeling experiments. Chapter 3 explains the reactive extrusion modification of biodegradable polyesters by cross-linking. Characterization methodologies with particular reference to gel fraction and Percent Crystallinity are discussed. Chapter 3 also deals with blends of the biodegradable polyesters and their cross-linked versions with talc for blown film applications. Chapter 4 deals with synthesis and characterization of Ecoflex-starch graft copolymers. Chapter 4 also deals with the synthesis of Maleated Thermoplastic Starch (MTPS) and Ecoflex/MTPS graft copolymers by reactive extrusion, and its subsequent characterization using Thermal analysis, FTIR, and mechanical property measurements. Summary and Conclusions are outlined in Chapter 5 and Recommendations for future work are discussed in Chapter 6.

Chapter 2

### **BULK EXTRUSION POLYMERIZATION OF 1, 4-DIOXAN-2-ONE**

### **2.1** INTRODUCTION

1, 4-dioxan-2-one (PDX) is a six-member lactone that is conveniently prepared by the oxidative cyclization of diethylene glycol (DEG) (11). Figure 2-1 represents the oxidative cyclization of DEG to PDX with the competing dehydration reactions. PDX is a useful momomer and co-monomer for the synthesis of biodegradable aliphatic polyesters. Polymerization occurs by a consecutive ROP to give high molecular weight polymer. The high polarity and reactivity of PDX make this lactone a useful chemical intermediate and solvent



# Figure 2-1: Oxidative cyclization of DEG to PDX and competing dehydration

reactions

The properties of PDX are listed in Table 2-1.

Table 2-1: Properties of PDX monomer

Melting Point	27ºC
Boiling Point	212-214 <sup>0</sup> C @ 760mm Hg
Density @ RT	1.≟6 g/ml
Flash Point	255°F; 123°C
Molecular Weight C <sub>4</sub> H <sub>6</sub> O <sub>3</sub>	102.09
The chemical reactivity, solvent properties, and high flash point make PDX useful in several applications. The patent literature contains multiple uses for PDX; Table 2-2 summarizes patented uses for PDX.

The structure of PDX monomer is depicted in Figure 2-2.



Figure 2-2: PDX monomer

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	U.S. Patent	Assignee	Application
	Number		
	2,631,989	Am. Cyan.	Solvent for Acrylonitrile Polymerization
	(1953)		
	3,280,065	Dow	Latex Stabilization
	(1966)		
	3,631,189	Eastman	PDX salts Useful Stabilizers For Halogen
ŀ	(1971)		Containing Polymers (i.e., PVC)
	2,803,646	Jefferson	PDX Ether-Esters Plasticizers and Lube Additives
	(1957)	Chem. Co.	
Γ	3,268,310	Dow	PPDX Controlled Dustiness and Improved Ignition
	(1966)		of Charcoal Briquettes
	3,294,743	GAF	Epoxy Ether Resin PDX Compositions
	(1966)		
	3,351,485	Dow	Preserving Wood By PDX Impregnation
	(1967)		
	3,264,182	Dow	A Process for the Preservation of Specimens of the
	(1966)		Animal Kingdom

## Table 2-2: Patented PDX end uses

The primary reactivity site on the PDX molecule is the ester carbonyl. The carbonyl is reactive toward nucleophiles such as water, alcohols, and amines. These nucleophiles are known to react with PDX to afford the corresponding ring opened product (Refer Figure 2-3).



Figure 2-3: Reactivity of PDX monomer

**Reaction** of PDX with excess alcohol catalyzed by strong acid produces the **corre**sponding ester ether. This final reaction product proceeds through the intermediate **hydroxyl** ester (12). Ring opening polymerization (ROP) of PDX monomer gives poly (pdioxanone) (PPDX), a biodegradable thermoplastic poly (ester-alt-ether). Both in vivo and in vitro, PPDX has good biodegradability. PPDX can degrade in vivo, and the degrading products of each step are in accord with the normal metabolites of the body. Most of them are excreted via the respiratory tract, and the reminder is extracted via the alimentary tract (13). The hydrolytic degradation of PPDX is a consequence of the **breaking** of the ester bonds in every repeating unit of PPDX. This is generally studied in a phosphate buffer solution of pH 7.4 and a temperature of 37<sup>o</sup>C. It is reported that the increase in degree of crystallinity in the beginning of hydrolysis may be attributed to the ester bond breaking first in the amorphous region and then in the crystalline region (14-16). Nishida et al. have also demonstrated that PPDX is decomposed to carbon dioxide and water by microorganisms isolated from natural environments (17).

#### 2.1.1 Mechanism of Polymerization of PDX monomer

The ROP of lactones and lactides has been thoroughly investigated during the last 40 years, due to its versatility in producing a variety of polymers in a controlled manner. There are two main reasons for studying the polymerization of cyclic esters. The primary reason is to exploit the potential of synthetic polymer chemistry to prepare a variety of polymers with control of the major variables affecting polymer properties. A second reason for studying ROP is to enable various advanced macromolecules, including hormopolymers with well-defined structures or end groups, to be prepared, as well as co-polymers with different architectures, e.g., block, graft, or star co-polymers (18).

ROP of lactones begins by addition of the lactone to the initiator. Chain **Propagation** continues by consecutive addition of lactone to the end of the growing **Polymer** chain. Chain propagation is described in Figure 2-4.

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**Figure 2-4: Chain Propagation in Lactone Polymerization** 

Each macromolecule formed generally contains one chain end terminated with a functional group originating from the termination reaction and one terminus end capped with a functional group originating from the initiator. Using different catalysts or initiators, the nature of the functional groups can be varied to fit the desired application. Moreover, the ROP can be performed either as a bulk polymerization, or in solution, emulsion, or dispersion (19-23). Depending on the initiator, the polymerization proceeds according to three different major reaction mechanisms, *viz.*, cationic, anionic, or "coordination-insertion" mechanisms (18).

The cationic ROP involves the formation of a positively charged species, which is subsequently attacked by a monomer. The attack results in ring opening of the positively charged species through an  $S_N$ 2-type process. Figure 2-5 depicts the reaction mechanism.



**Figure 2-5: Cationic ROP Reaction Mechanism** 

Anionic ROP of cyclic ester monomers takes place by the nucleophilic attack of a negatively charged initiator on the carbonyl carbon or on the carbon atom adjacent to the acyl oxygen, resulting in linear polyester. The propagating species is negatively charged and is counter balanced with a positive ion. Depending on the nature of the ionic propagating chain end and the solvent, the reacting complex varies from completely ionic to almost covalent. Figure 2-6 demonstrates the reaction mechanisms for the ROP of a **Cyclic** ester by anionic initiation.



Figure 2-6: Anionic ROP Reaction Mechanism

In the case of reaction by coordination-insertion mechanism, the propagation is thought to proceed by coordination of the monomer to the active species, followed by insertion of the monomer into the metal-oxygen bond by rearrangement of the electrons. Figure 2-7 depicts a schematic for the coordination-insertion mechanism.



**Figure 2-7: Coordination-Insertion Reaction Mechanism** 

The growing chain remains attached to the metal through an alkoxide bond during the propagation. The reaction is terminated by hydrolysis forming a hydroxyl end group. It has been shown that the ROP of PDX to form PPDX polymer proceeds via the

coordination-insertion mechanism (24). Figure 2-8 represents the coordination-insertion polymerization mechanism to form high molecular weight PPDX chains.



Figure 2-8: Coordination-Insertion Mechanism in the formation of PPDX polymer

Lactone polymerization can be accompanied by two common side reactions; intermolecular and intramolecular trans-esterification. These two reactions are illustrated in Figure 2-9 for PPDX. Intermolecular trans-esterification occurs when the hydroxyl end group undergoes trans-esterification with a different polymer chain. This process broadens the molecular weight distribution of the polymer until the equilibrium value of two is reached. Intramolecular trans-esterification produces cyclics, by 'back biting' of the hydroxyl end onto the same polymer chain. This reaction is of utmost importance, for if the concentration of cyclics becomes too high, polymer properties and processing may be adversely affected. The focus of this work was on the bulk extrusion ROP of PDX monomer using aluminum alkoxides initiators, specifically aluminum tri-sec butoxide.



Intramolecular



Figure 2-9: Intermolecular and Intramolecular trans-esterification of PPDX

## 2.1.2 Lactone Polymerization Catalysts

There are numerous catalysts available in patents for the polymerization of lactones. Union Carbide had several broad-based cyclic ester polymerization patents, which are valid, but expired (25). GAF was first to patent polymerization catalysts specific for PDX polymerization. These patents fall into two classes: 1) Alkyl, alkoxy, and hydrido aluminum catalysts (26); 2) Alkyl, alkoxy, and halide complexes of group IIB transition

metals (27). These catalysts showed good activity between 0 and  $45^{\circ}$ C at catalyst concentrations of around 0.01 mole%. Dow patented the use of 1, 3-diketone complexes of iron, titanium, and zinc catalysts specifically tailored for PDX polymerization (28). Unlike the earlier case, the activities of these catalysts were low requiring about 0.2-0.5 wt-%. Polymerization temperatures also ranged from 60-90<sup>0</sup>C and gave low molecular weight PPDX polymers (< 5000 g/mol). Eastman Kodak (29) also patented the use of tin (IV) complexes to produce low MW PPDX polymers. Ethicon has the largest number of PDX/PPDX patents on polymerization, processing and fabrication. Ethicon's focus is primarily on the medical device market. Ethicon's earlier patent literature described PDX polymerization in the bulk below the melting temperature of PPDX polymer (30). Recently, Ethicon's patents are focused on PDX melt polymerization, which allows the preparation of a wide range of copolymers and gives uniform molecular weight distribution (31-35). More recently, there has been considerable work in using zinc-based catalysts, specifically Zn-L-lactate, in the bulk polymerization of PDX to form PPDX polymer. While the highest molecular weights were obtained at 100°C, long reaction times between 8 to 14 days were required to obtain optimum results (36). Nishida et al. (37) investigated the PDX polymerization in bulk with Sn (II) ethylhexanoate or triethylaluminum over a range of 60-180°C. More recently, Raquez et al. have studied PDX melt polymerization, as initiated by aluminum triisopropoxide (Al (O'Pr) 3) and compared to the ROP promoted by tin (II) octoate (24). Nishida et al. have conducted the enzymatic polymerization of PDX monomer with 5-wt% immobilized lipase CA. The polymerization was carried out at 60°C for 15 hours and the highest molecular weight obtained was 41,000 g/mol (38).

#### 2.1.3 Kinetics of PDX Polymerization

PDX bulk polymerization kinetics has been investigated in a wide variety of conditions using different catalysts as explained above. It has been shown that zinc lactate initiated polymerizations are relatively slow when compared to Sn (II)-ethylhexanoate  $(Sn (Oct)_2)$ . However, it has the advantage that it does not catalyze backbiting degradation even at reaction times of 14 days. Also, zinc chloride was shown to be less effective for the polymerization as compared to zinc lactate and zinc bromide. Yet, for any preparative application, zinc lactate has two advantages: Firstly, the lactate anion is part of the human metabolism in contract to the bromide ion, and secondly, zinc lactate is less hygroscopic, and thus more stable on storage than zinc bromide. Kricheldorf et al. also found that bulk polymerizations of PDX at 100<sup>o</sup>C with zinc lactate, as a catalyst never exceeded 80% yield (26). Although the polymerization rates using the three abovementioned initiators were distinctly different, the equilibrium monomer conversions were almost the same at each temperature. The equilibrium conversions decreased in a similar manner with increasing polymerization temperature. These results indicate that no matter which initiator is used for the polymerization, the conversion of PDX monomer always converges to a thermodynamic equilibrium. The kinetics of propagation for an equilibrium polymerization system is generally expressed as follows in equation (2.1).

$$\ln\left(\frac{\left[M\right]_{0}-\left[M\right]_{e}}{\left[M\right]_{t}-\left[M\right]_{e}}\right)=k_{app}t$$
(2.1)

In the equation shown above,  $[M]_0$  is the initial monomer concentration,  $[M]_e$  is the equilibrium monomer concentration,  $[M]_e$  is the actual monomer concentration at time t

and  $k_{app}$  is the apparent rate constant. In all cases, a linear time dependence of  $\ln\{\{[M]_0 - [M]_e\} / \{[M]_r - [M]_e\}\}\$  is observed after an induction period close to 6 minutes. This induction period could be attributed to the formation of active initiating species.

When the polymerization was conducted in the presence of aluminum triisopropoxide (Al ( $O^{i}Pr$ )<sub>3</sub>), for similar initial monomer to initiator ratios, the polymerization is faster. Also, PDX conversion, for example, increases from 60% to 80% when Sn (Oct)<sub>2</sub> is replaced by Al ( $O^{i}Pr$ )<sub>3</sub> for an initial monomer to initiator ratio of 100. Even here, it has been determined that the time dependence of polymer conversion passes through a maximum before leveling off at the equilibrium monomer concentration. Table 2-3 compares the effect of using Sn (Oct)<sub>2</sub> and Al ( $O^{i}Pr$ )<sub>3</sub> on the yield of PPDX obtained in bulk at 100<sup>0</sup>C.

## Table 2-3: Influence of the nature of the initiator on the yield of PPDX obtained in

Entry	Initiator	[DX]	Polymerization time (min)	Polymerization yield (%)
		0/metal		
1	Al $(O^{i}Pr)_{3}$	1000	270	80
2	Sn (Oct) <sub>2</sub>	100	270	60
3	Al (O <sup>i</sup> Pr) <sub>3</sub>	300	270	84
4	Sn (Oct) <sub>2</sub>	300	270	71
5	Al (O <sup>1</sup> Pr) <sub>3</sub>	1000	375	70

## bulk at 100<sup>o</sup>C.

Furthermore, kinetic experiments on PDX polymerization initiated by Al (O<sup>i</sup>Pr) <sub>3</sub> have been conducted at 80°C and 100°C for various monomer to initiator ratios. It has been determined that for an initial  $[PDX]_0$ / [Al] ratio of 600 at 100°C, the time dependence of monomer conversion passes through a maximum after about 7 min, and then the monomer conversion decreases and levels of at a value close to the equilibrium monomer conversion at about 12 min. Moreover, it has also been shown that at 80°C, as the initial monomer to initiator ratio increases, the time taken for the conversion to reach the equilibrium value also increases. It has also been noted that a linear time dependence of  $ln\{\{[M]_0 - [M]_e, \}[[M]_e - [M]_e\}\}$  is observed after an induction period close to 6 min. This linearity attests that the bulk polymerization kinetics of PDX monomer initiated by Al (O<sup>i</sup>Pr) <sub>3</sub> is first order in monomer in the overall range of monomer conversions investigated. Such a linear dependence also indicates that the number of growing chains does not appreciably change during polymerization. From the slope of these linear

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relationships, the values have been determined to be 0.293, 0.144 and 0.104 min<sup>-1</sup> for initial monomer to initiator ratios of 200, 400 and 600 respectively at 80<sup>o</sup>C (39). Figure 2-10 shows the effect of polymerization temperature on the equilibrium monomer conversion for a  $[PDX]_0$  / [AI] ratio of 600 and a polymerization time of 14 hours. It is evident from the figure that equilibrium monomer conversions decrease with increasing temperature.



Figure 2-10: Effect of Polymerization Temperature on the monomer conversion reached at equilibrium for a monomer to initiator ratio of 600 and a polymerization

time of 14 h.

Thus, PDX polymerization leaves high amounts of unreacted monomer due to a low ceiling temperature. The micro reversibility model can adequately describe such monomer-polymer equilibrium. According to the model, all growing chains  $(M_n^* and M_{n+1}^*)$  are capable of depolymerizing until they reach a constant equilibrium monomer concentration as explained by equation (2.2) and (2.3).

$$M_n^* + M \xrightarrow{k_p} M_{n+1}^* \tag{2.2}$$

$$M_{n+1}^* \xrightarrow{k_d} M_n^* + M \tag{2.3}$$

Where  $k_p$  and  $k_{dp}$  correspond to the propagation rate constant and the depolymerization rate constant respectively. US 5,717,059 describe a method for removing the PDX monomer from previously solidified polymerizing mixture without any adverse degradation reactions to form high molecular weight polymers. However, the time for removing the unreacted monomer from the polymerizing mixture is in the order of hours. Thermally stabilized PPDX polymers have also been prepared by end-capping the extremity of PPDX in the melt. However, after end-capping of the PPDX extremity by a **chemical** agent such as pyromellitic anhydride, the reacting mixture still contains a large **armount** of unreacted monomer, which has to be removed from PPDX and recycled, **making the process economically unattractive (US No 5,652,331).** 

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#### 2.1.4 Thermodynamics of Polymerization

In order for a polymerization reaction to yield high molecular weight polymer at a given temperature and pressure, the monomer-polymer equilibrium must be favorable to drive the reaction forward and the reaction must be mechanistically feasible (40). All reactions are generally characterized by a thermodynamic equilibrium as explained above in equations (2.2) and (2.3). This equilibrium is characterized by equilibrium constant, which to a first approximation is equal to the inverse equilibrium monomer concentration as explained in equation (2.4) and equation (2.5).

$$K = \frac{\left[M_{n+1}^{*}\right]}{\left(\left[M_{n}^{*}\right]\left[M\right]_{e}\right)} \approx \frac{1}{\left[M\right]_{e}}$$
(2.4)

$$\ln[M]_{e} = \frac{\Delta G}{RT} = \frac{\Delta H^{0}}{RT} - \frac{\Delta S^{0}}{R}$$
(2.5)

Equation (2.5) discloses the connection between the equilibrium monomer concentration and the free enthalpy of polymerization as the driving force of the polymerization. For standard conditions (initial monomer concentration equal to 1M) and for a certain critical temperature, the equilibrium constant may be 1 and hence the equilibrium monomer concentration is 1M. Under these conditions, no polymer is obtained. From a thermodynamic point of view, the critical temperature is defined as the ceiling temperature (T<sub>c</sub>) with both  $\Delta$ H and  $\Delta$ S<0 (and as the floor temperature, T<sub>f</sub> for both  $\Delta$ H and  $\Delta$ S>0). For every polymer system, above T<sub>c</sub> polymerization is impossible and propagation occurs only if concentration of monomer is greater than the equilibrium monomer concentration at a given temperature (41). Monomer-polymer equilibrium is not the only equilibrium observed in ROP. There is a second equilibrium to be considered, ring chain equilibrium.

$$M_n^* \leftrightarrow M_{n-x}^* + R_x \tag{2.6}$$

As indicated by equation (2.6) the equilibrium constant of a certain cyclic  $R_x$  with degree of polymerization x is to a first approximation equal to the equilibrium concentration of the respective cycle. According to Jacobson and Stockmayer (42), the equilibrium constant is determined by and is proportional to the degree of polymerization to the -2.5 power and indicated by equations (2.7) and (2.8).

$$K_{x} = \left[M_{n-x}^{*}\right] \left[R_{x}^{*}\right] / \left[M_{n}^{*}\right] \approx \left[R_{x}\right] = \left[\frac{3}{(2N)}\right]^{\frac{2}{3}} \cdot \frac{1}{(2N_{x})} \cdot \left(\frac{1}{< r_{x}^{2} >}\right)^{\frac{3}{2}}$$
(2.7)

$$K_x \approx \frac{1}{x^{5/2}}$$
 (2.8)

with  $[R_x]$  being the equilibrium concentration of the cyclic oligomers with degree of polymerization x, N the number of bonds of the oligomers, and  $\langle r_x^2 \rangle$  the mean square radius of gyration of a polymer segment with degree of polymerization x.

Thermodynamic data for small and medium sized lactones show that the entropy change during polymerization is negative. Thus, the driving force for polymerization is the negative change of entropy. The ROP of highly strained three-and four-membered rings is a favorable reaction- the driving force being the release of angular strain (Bayer's strain). The presence of substituents at the ring carbons further increases the strain and thus increases the exothermicity of the reaction. In medium sized rings, such as a 7membered ring, the relief of intramolecular crowding (transannular strain) is the driving force. The  $\Delta G_p^0$  values for  $\beta$ -propiolactone,  $\gamma$ -butyrolactone,  $\delta$ -valerolactone,

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ε-caprolactone, and α,α-dimethyl-β-propiolactone have been reported as -60.2, +12.6, -8, -12.8, and -84.02 kJ/mol, respectively. The  $\Delta G_p^0$  is positive for γ-butyrolactone, indicating that the ROP of γ-lactone is thermodynamically unfavorable because of the stability of the 5-membered ring (43,44). However, by use of drastic reaction conditions, polymerization may be carried out. For example, poly (γ-butyrolactone) of M<sub>n</sub> 35,000 g/mol could be prepared under a pressure of 20,000 atm at 160<sup>o</sup>C (45,46).

ROP of lactones begins by addition of the lactone to the initiator. Chain propagation continues by consecutive addition of lactone to the end of the growing polymer chain. The conformational strain of six member ring cyclic esters, such as PDX, differs from other six member heterocyclic rings not containing a carbonyl group such as tetrahydropyran or 1,4-dioxane etc. These cyclic ethers do not undergo ROP due to the stability of the ring conformation adopted as explained above. With six member ring lactones, ring strain is induced from the planar configuration of the ester group. In addition, this ring strain twists the planar ester group, causing resonance destabilization (47). Both these factors result in the polymerizability of six member ring lactones such as PDX.

There is limited work done on the thermodynamics of PDX polymerization. The equilibrium monomer concentration is related to temperature using Dainton's equation as shown below.

$$R\ln[M]_{e} = R\ln\left(\frac{k_{dp}}{k_{p}}\right) = \frac{\Delta H_{p}}{T} - \Delta S_{p}^{0}$$
(2.9)

In equation (2.9),  $\Delta H_p$  is the enthalpy of polymerization under the prevailing experimental conditions,  $\Delta S_p^0$  is the entropy change at the standard state

 $([M]_e = 1 mol/L)$  and R is the perfect gas constant. By doing a linear regression analysis and plotting  $R \ln[M]_e vs \frac{1}{T}$ , the enthalpy of polymerization is determined to be -14.1

KJ/ mole and the entropy of polymerization is determined to be -45.3 J/ mole.K. The enthalpy of polymerization reported is less negative than that reported for L-lactide. This may be attributed to less ring strain for the non-substituted ether-ester PDX ring than for the substituted diester L-lactide ring (39). The thermodynamic parameters mean that PDX polymerization has a less negative free energy than that for L-lactide. These values are in quite good agreement, with the values reported by Nishida et al. (38). The precipitation of the polymer in the low temperature bulk polymerization of PDX profoundly influences the monomer polymer equilibrium. For example, polymerization of trioxane to polyacetal at or above the T<sub>m</sub> of polyacetal is equilibrium limited to less than 50%. To drive the reaction, polyacetal is prepared in molten trioxane. Under the polymerization conditions, polyacetal precipitates from the molten trioxane. Chain growth proceeds both in the liquid phase and in the crystalline phase. The precipitation of polyacetal from solution shifts the trioxane-polyacetal equilibrium, allowing complete conversion of monomer to polymer. Similarly, the PDX to PPDX equilibrium is shifted by the precipitation of **PPDX** from solution.

#### 2.1.5 Molecular Weight and Molecular Weight Distribution

The two main polymerization parameters that determine the molecular weight of the PPDX polymer are initiator concentration and monomer to polymer conversion. The total

initiator concentration determines the number of polymer chains for a given polymerization reaction. The number of monomer units in each polymer chain is then determined by the conversion of monomer to polymer. Therefore, the two-polymerization parameters that determine the molecular weight of the PDX polymer is; initiator concentration and the monomer to polymer conversion. Equation (2.10) shown below provides the number average molecular weight as a function of the initiator concentration and conversion of monomer to polymer.

$$M_n = [\%Conv.*PDX(moles)/ Initiator(moles)]*102.09$$
(2.10)

While equation (2.10) predicts the number average molecular weight, it does not predict molecular weight distribution, which is determined by specific polymerization conditions (48).

Kricheldorf et al. polymerized PDX monomer using zinc lactate catalyst and determined that 100<sup>o</sup>C was the optimum temperature for polymerization to obtain a high molecular weight. Moreover, up to a monomer to initiator ratio of 4000, highest viscosity values were obtained at the longest reaction times. These results again demonstrate that zinc lactate is a relatively inefficient catalyst, but it has the advantage that it does not catalyze backbiting degradation. When zinc chloride was used as the catalyst, the molecular weight obtained at a monomer to initiator ratio of 2000 was significantly lower than the value obtained with zinc lactate (36).

Nishida et al. polymerized PDX at  $80^{\circ}$ C and determined that the number and weight average molecular weights increased linearly with conversion. These results suggest that this process is a living mechanism (37,49). However, since the polymerization is an equilibrium polymerization, the polydispersity of the polymers

broadened to about 2; the most probable distribution of molecular weights, with increase in conversion. Equilibration and depropagation probably occur by bimolecular transesterification as in the case of  $\varepsilon$ -caprolactone reported by Kowalski et al. (50) and Schindler et al. (51).

Raquez et al. polymerized PDX monomer in bulk using aluminum triisopropoxide as initiator. It was determined that with an increase in the  $[PDX]_0/[AI]$  ratio, the PPDX molecular weight (with reference to polystyrene standards) increases gradually with time. Furthermore, there is a relative increase of  $M_n$  with an increase in the  $[PDX]_0/[AI]$ ratio at constant monomer conversion. As an example,  $M_n$  passes from 6000 g/mol to 11,200 g/mol as the  $[PDX]_0/[AI]$  ratio increases from 400 to 600, respectively. It has also been observed that by using chloroform added with 0.3-wt% of tri-*n*octylmethylammonium chloride (TOAC) as an eluent at 40<sup>0</sup>C; low values of apparent molecular weight are obtained as expressed with reference to polystyrene standards and low polydispersities ( $M_w/M_n < 1.3$ ). This is due to the poor solubility of PPDX in conventional organic solvents, which leads to the formation of very compact coils, characterized by a low hydrodynamic volume compare to highly soluble polystyrene (39).

Nishida et al. also polymerized PDX at  $60^{\circ}$ C for 15 hours with 5 wt% immobilized Lipase CA as an enzymatic catalyst. The product without purification showed multimodal distribution and wide polydispersity. This wide polydispersity is attributable not only to the heterogeneous polymerization but also to the simultaneous degradation process (52,53).

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#### 2.1.6 Extrusion Studies

The traditional use of an extruder is to use heat, pressure, and shear to transform solid plastic into a uniform melt, for delivery to the next stage of processing. This frequently involves mixing in additives such as color concentrates, blending resins together, and incorporating regrind. The extruder accomplishes all this by using a barrel, a hollow tube, containing a screw with helical channels. The screw is generally divided into three sections: (1) the solids conveying section, (2) compression section and (3) the metering or pumping section. The major purpose of the feed section is to convey the plastic pellets forward through the extruder, once they have been fed into the barrel at one end through the hopper and feed port. In the compression section of the screw, the plastic is melted. The depth of the screw channels decreases, building up more pressure on the plastic and forcing the solid against the barrel wall. External heating, as well as internal heating from friction between the plastic and the barrel and especially from the shearing of the plastic itself, causes the plastic to soften and melt. In the metering section of the screw, the channel is again a constant depth. This part of the screw is responsible for delivering molten polymer at a desired and uniform rate to the shaping device (54).

Reactive extrusion refers to the process of conducting chemical reactions during the melt extrusion process. These reactions include polymerization, cross-linking, grafting, chain extension etc. The advantage of using extruders to conduct reactions is as follows:

- Fast and continuous process.
- Reactions can be performed in bulk in the absence of solvent.
- Efficient devolatilization capability through the vent port.

• Modular in design and hence easy to scale up.

However, in any reactive extrusion process, the following parameters are of key importance

- Screw Configuration
- Metering of reactants
- Temperature profile
- Heat transfer requirements.

There are numerous references on grafting reactions conducted in extruders. Specifically, grafting of functional groups like acids, esters and anhydrides have been studied by many researchers (55-57). Cross-linking of polypropylene has been conducted in extruders (58). Cross-linking of biodegradable polyesters will be discussed in detail in the forthcoming chapter. Chain extension of PET and that of polyamides have also been investigated (59,60). Blends of synthetic polymers with natural polymers such as starch and cellulose have been synthesized in twin-screw extruders (61,62). Table 2-4 represents the various reactions performed in co-rotating twin screw extruders (63).

Final Product	Feed Product	Type of reaction
Polyurethane	Polyol + Diisocyanate +	Polyaddition
	Aromatic Diamine	
Polyethylene	Bis (Hydroxyethyl)	Polycondensation
Terephthalate	Terephthalate	
Potassium Aluminate	Clay + alkali solution	Salt formation
Polyarylate	Bisphenol A + Phthalic acids	Polycondensation
Polyoxymethylene	Trioxane + comonomer	Ionic Polymerization
IS Block Copolymer	Isoprene, 1, 3-butadiene +	Ionic block
	styrene	copolymerization
Polyamide (Nylon 6)	Caprolactam	Ionic polymerization
SAN Copolymer	Styrene + Acrylonitrile	Ionic polymerization, free
	prepolymer	radical
Ethylene vinylacetate	Polyethylene + vinylacetate	Radical grafting
Terephthalic acid	Isophthalic acid	Isomerization
Polyalkylmethacrylate	Methacrylate ester	Radical polymerization
Polyols, Amines	Polyurethane scrap	Hydrolysis
Styrene monomer	Polystyrene	Depolymerization
Indoxyl	Phenylglycine	Cyclization

# Table 2-4: Reactions performed in co-rotating twin screw extruders

#### 2.1.6.1 Reactive Extrusion Polymerization

Reactive extrusion polymerization involves polymerizing a liquid/solid monomer or prepolymer within the residence time available in the extruder to form a high molecular weight melt. The economics of using the extruder as a bulk polymerization reactor are favorable when high throughputs and control of molecular weight are realized. This places a limitation on the residence time required to complete the polymerization, which ideally should be less than 5 minutes (64). Researchers have shown that extruders can be used for bulk polymerizations of monomers like methylmethacrylate, styrene, lactam and lactide (65-67). Further, there are various patents in literature describing the polymerization of polyurethanes, polyacetals and polyetherimide in modular twin- screw extruders (68-74). Since different polymerization mechanisms are involved in the extrusion of these polymers, the process schematics and screw configurations vary considerably. The extruder screw configuration can have an effect on yield, molecular weight, molecular weight distribution and product throughput.

Bulk polymerization of CL monomer in a co-rotating twin-screw extruder has been investigated (75-78). Narayan et al. have used a reactive extrusion process for the bulk polymerization of CL monomer using coordination insertion catalysts to form a high molecular weight polymer at high throughputs (79-81). Bulk polymerization of CL monomer using coordination insertion catalysts have been discussed by Young et al (82). Narayan et al. (83) have also discussed bulk polymerization of CL monomer in an extruder in the presence of starch to give a compatibilized blend of PCL, starch and starch-g-PCL polymers. EP 626405 describes the preparation of low molecular weight PCL polymer with M<sub>n</sub> ranging from 35,000 g/mol to 66,000 g/mol at residence times ranging from 6 to 15 minutes respectively. Low cost production and processing methods for biodegradable plastics are of great importance since they enhance the commercial viability and cost-competitiveness of these materials. Reactive extrusion is an attractive route for the polymerization of a cyclic ester monomer, without solvents, to produce high molecular weight biodegradable plastics. There is thus a definite need for an improved bulk polymerization process for economically producing aliphatic ester polymers. Compositions of such polymers that possess improved properties and processability are useful as biodegradable articles, especially films.

#### 2.1.6.2 Screw Configuration

Twin-screw extruders have been used for processing of viscous materials for over a century. They are used for a wide variety of applications and are made in a number of different geometries. The screw configuration used in an extruder depends on the application. There are three fundamental types of screw elements: forwarding, mixing and zoning. The screw configuration is generally limited to the torque handling capability of the screw shafts.

Forwarding elements are used to drive and center mixers and zoning elements. They also forward material past feed, vent, drain and output barrel holes. Forwarding screw elements can be single flighted (monolobal), double flighted (bilobal), or triple flighted (trilobal). Single flighted screws have the largest channel cross-section and are useful when large conveying capacity is required, such as in the feed section when feeding low bulk density materials. Double flighted screws have the second largest channel cross-section. They are used when both good mixing and output is required. Triple flighted screws have the smallest channel cross-section and, consequently, the lowest output capacity. They are useful when high shearing forces are required; triple flighted screws also yield high heat transfer capability (63). Left-handed screw elements are primarily used for sealing purposes. A left handed screw element requires the upstream screw section to be completely filled over a certain distance in order to generate the pressure necessary to override the left handed section. Thus, one can intentionally create a fully filled screw section to obtain complete sealing. This is frequently used just before a vent port where vacuum is being applied.

Mixers will be dispersive, distributive or a combination thereof. They can also be described additionally as having a pressure drop over them (restrictive), no pressure drop (neutral) or a pressure rise over them (forwarding). Common distributive mixers include narrow kneaders, slotted screw flights, vane mixers, turbine mixers, slotted axial flow elements, pin mixers, and the like. Common dispersive mixers include wide kneaders, shaped lobals, radial barrier elements, axial barrier disc elements, large advance flighted solid elements, axial slotted restrictors with OD gaps to the barrels, etc. The strongest of these dispersive mixers capture lobal and other regions from which material may be elongationally acclerated. The most distributive mixers simply divide and recombine materials with material domains remaining intact. Absence of lobal capture is often an advantage for distributive mixing. Figure 2-11 represents the concepts of distributive and dispersive mixing schematically.

## **Dispersive mixing**



Figure 2-11: Dispersive and Distributive Mixing schematic

A sequence could be described for a strong dispersive mixer of where material leaving gentle screw channels to be captured in a lobal pool from which it experiences elongational acceleration/extensional flow/stretching and mixing, entering an overflight region. Usually, when this condition is met, a productive elongational mixing condition will also exist around the intermesh and apex regions (84).

Zoning elements are used to separate two sub-processes, such as a vacuum vent from upstream screws, an injection/mixing sub-process from upstream and downstream screws, ensuring the maximum size of a particle that can pass a given barrel point, and the like. Most zoning elements also serve as forwarding or mixing elements. A typical screw configuration in an extruder consists of conveying and kneading elements. Conveying or forwarding elements are represented by a set of two numbers as X/Y where X is the pitch of the element and Y, the axial length, both in millimeters (mm). Reverse flighted elements are represented as X/Y LH. Kneading or Mixing blocks are represented as KB X/Y/Z where X is an angle that represents the degree of stagger, Y is the number of kneading block elements and Z is the pitch in mm. Additionally, they may be reverse staggered and represented as KB X/Y/Z LH (79). A typical screw configuration consisting of conveying and kneading elements is shown in Figure 2-12.



**Figure 2-12: Conventional screw configuration** 

## 2.1.6.3 Residence Time Distribution

The idea of using the distribution of residence times in the analysis of chemical reactor performance was apparently first proposed in a pioneering paper by MacMullin and Weber. However, the concept did not appear to be used extensively until the early 1950's, when Danckwerts gave organizational structure to the subject by defining most of the distributions of interest. In an ideal plug flow reactor, all the atoms of material leaving the reactor have been inside it for exactly the same amount of time. This time that the atoms spend in the reactor is called the *residence time* of the atoms in the reactor. The *residence time distribution (RTD)* of a reactor is characteristic of the mixing that occurs in the chemical reactor. There is no axial mixing in a plug-flow reactor, and this omission is reflected in the RTD, which is exhibited, by this class of reactors. The CSTR is thoroughly mixed and possesses a far different kind of RTD than the PFR. Thus, the RTD exhibited by a given reactor yields distinctive clues to the type of mixing occurring within it and is one of the most informative characterizations of the reactor.

The RTD is determined experimentally by injecting an inert chemical, molecule, or atom, called a tracer, into the reactor at some time t = 0 and then measuring the tracer concentration, C, in the effluent stream as a function of time. In addition to being a nonreactive species that is easily detectable, the tracer should have physical properties similar to those of the reacting mixture and be completely soluble in the mixture. It should also not adsorb on the walls or other surfaces in the reactor.

In a pulse input experiment, an amount of tracer  $N_0$  is suddenly injected in one shot into the feed stream entering the reactor in as short a time as possible. The outlet concentration is then measured as a function of time. The effluent concentration-time curve is referred to as the *C curve* in RTD analysis. The quantity E (t) is called the residence time distribution function. It is the function that describes in a quantitive manner how much time different fluid elements have spent in the reactor. It is defined as shown in equation (2.11).

$$E(t) = \frac{C(t)}{\int_{0}^{\infty} C(t)dt}$$
(2.11)

The integral in the denominator is the area under the C curve. The principal difficulties with the pulse technique lie in the problems connected with obtaining a reasonable pulse at a reactor's entrance. The injection must take place over a period, which is very short compared with residence times in various segments of the reactor or reactor system, and there must be a negligible amount of dispersion between the point of injection and the entrance to the reactor system. E (t) is also called the exit-age distribution function. If we regard the "age" of an atom as the time it has resided in the reaction environment, then E (t) concerns the age distribution of the effluent stream. The fraction of the exit stream that has resided in the reactor for a period of time shorter than a given value t is equal to the sum over all times less than t of E (t), or expressed as follows:

$$\int_{0}^{t} E(t)dt = F(t)$$
 (2.12)

F (t) is defined as a cumulative distribution function. Sometimes, the F curve is used in the same manner as the RTD in the modeling of chemical reactors.

No matter what RTD exists for a particular reactor, ideal, or non-ideal, the nominal holding time  $\tau$ , is equal to the mean residence time,  $t_m$ . The mean value of the variable is equal to the first moment of the RTD function, E (t). Thus, the mean residence time is as explained in equation (2.13)
$$t_m = \frac{\int_0^\infty tE(t)dt}{\int_0^\infty E(t)dt} = \int_0^\infty tE(t)dt$$
(2.13)

The second moment commonly used is taken about the mean and is called the variance, or square of the standard deviation. It is defined as follows in equation (2.14)

$$\sigma^{2} = \int_{0}^{\infty} (t - t_{m})^{2} E(t) dt$$
 (2.14)

The magnitude of this moment is an indication of the "spread" of the distribution; the greater the value of this moment, the greater a distribution's spread. The third moment is also taken about the mean and is related to the skewness. The skewness is defined as follows in equation (2.15).

$$s^{3} = \frac{1}{\sigma^{3/2}} \int_{0}^{\infty} (t - t_{m})^{3} E(t) dt$$
 (2.15)

The magnitude of this moment measures the extent that a distribution is skewed in one direction or another with reference to the mean. More recently, on-line measurements of RTD in a twin-screw extruder (TSE) using simple optical techniques have been developed (85). Use of the RTD in screw design can minimize thermal degradation, improve product uniformity and control the residence time of the melt to allocate sufficient time to complete a reaction. The RTD, in combination with the reaction kinetics, can be used with the assumption of segregated flow to provide models for fitting reactive extrusion data without requiring complete understanding of the physical flow conditions (86).

#### 2.1.6.3.1 Extrusion Modeling

Extrusion is one of the most versatile and energy-efficient processes for the manufacture of polymer products, including food, pharmaceuticals and plastics (87). Flow patterns, mixing conditions and Residence Time Distribution (RTD) in any plasticizing and cooking extruder have significant effects on the extent of the thermal and shear treatment provided to the extradites, and the extent of conversion and chemical reactions of the biopolymers (88). Flow in the extruder has been modeled at various levels of sophistication. A review of the basic features of extrusion models is available (89) and it would appear that one could predict the gross features of the relationships among design and performance variables with reasonable success. The major failures of simple extruder models lie in two areas. Most models introduce simplifying assumptions with respect to heat transfer between the extruder surfaces and the melt, and these assumptions are probably rarely consistent with typical commercial operation. Furthermore, detailed instrumentation of an extruder, from which heat transfer coefficients might be obtained, is rarely carried out and/or reported. The other major factor in the failure of simple extruder models lies in the variety of screw designs. Simple extruder models include simplification with respect to screw geometry, and the nearly infinite variability of detailed geometrical parameters makes it impossible to consider more than a small fraction of possible designs. Nevertheless, such models are useful for indicating how the major variables are related, and so provide a rational basis upon which one may estimate performance limits of a specific piece of equipment. In addition, such models should

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provide some rational guidelines for scale-up from a small laboratory extruder-reactor to a larger commercial system (90).

The flow behavior of the twin-screw extruder (TSE) is also not well understood, but is generally believed to fall between a CSTR (complete mixing) and a PFR (no axial mixing). As explained in the earlier paragraph, model configurations such as PFR, CSTR, PFR+CSTR, CSTR in series, and PFR+CSTR in series have been proposed for the flow profile in a single-screw extruder. Few models have been proposed for the TSE because its flow profiles are much more complex. Bounie (91) used Fourier functions and multivariable optimization techniques to predict a pulse response from several flow models, and reported that the model of PFR + nCSTR gave the best fit to the experimental data. Giudici et al. modeled industrial nylon-6, 6-polycondensation processes in a twin-screw extruder reactor (92). Michaeli et al. (93) have developed an extruder design based on a model that describes the mechanism of conveying, heat transfer, and reaction in a co-rotating twin-screw extruder. The developed model has been tested in practice on the production of homopolymers (nylon 6 and polystyrene) and a copolymer (nylon 6 block copolymer). Zhang et al. (94) investigated the 'living' free radical polymerization of butyl acrylate and styrene using a tubular reactor model. Residence time distribution effects on polymer properties are studied by varying the Peclet no (Pe,) to show the degree of back mixing that adversely affects polymer properties. Polymerization of CL monomer has been studied in a co-rotating extruder and modeled using kinetic and rheological data (78).

S. Hojabr et al. (95) modeled the melt grafting of glycidyl methacrylate (GMA) onto polyethylene in a co-rotating twin-screw extruder as a modular reactor consisting of

plug flow and axial dispersion reactor cells. There are also sources available in literature where researchers have modeled the conveying elements of a screw as PFR and the kneading blocks as a CSTR (96). Thus, it was suggested to model the bulk extrusion polymerization process of CL monomer by an axial dispersed PFR model using RTD analysis. Moreover, as a regular PFR model represented a good fit of the batch process, it was assumed that an axial dispersed PFR would represent a good fit of the extrusion polymerization process.

The axial dispersed PFR model can be thought off as a PFR superimposed with some degree of back mixing or intermixing. This dispersion coefficient, inversely proportional to  $Pe_r$  can be determined by pulse tracer experiments as described in equation (2.16).

$$\frac{\sigma^2}{t_m^2} = \frac{2}{Pe_r} - \frac{2}{Pe_r^2} \left( 1 - e^{-Pe_r} \right)$$
(2.16)

Here  $\sigma^2$  is the variance and  $t_m$  the mean residence time, evaluated from the experimental RTD data. The cumulative F-curve  $F(\tau)$  can be obtained from equations (2.17) & (2.18).

$$F(\tau) = \frac{C}{C_0} = \frac{1}{2} - \frac{1}{2} erf\left[\frac{1-\tau}{2\sqrt{\tau\left(\frac{De}{uL}\right)}}\right]$$

$$erf(y) = \frac{2}{\sqrt{\Pi}} \int_{0}^{y} \exp(-v^2) dv$$
(2.18)

The predicted F- curve can be compared with the experimental F-curve to find the goodness of fit (97). Knowing the kinetics of the reaction [equations (2.2) and (2.3)], monomer concentration could be calculated by the axial dispersion model using equation (2.19) and compared with the experimental values. In equation (2.19),  $\overline{C}$  is the normalized concentration equal to  $\frac{C}{C_0}$ , where  $C_0$  is the initial concentration of the monomer; z is the normalized length of the extruder equal to  $\frac{X}{L}$ , where L is the total extruder length;  $k_p$  is the forward propagation reaction rate constant in *lit/mol.min*;  $[I]_0$  is the initial concentration of the initiator in *mol/lit*;  $\frac{L}{u}$  is the mean residence time in *min* obtained from the experimental RTD data and  $[C]_e$  is the equilibrium monomer

concentration at a given temperature.

$$\frac{1}{Pe_{r}}\frac{d^{2}\bar{C}}{dz^{2}} - \frac{d\bar{C}}{dz} + \frac{k_{p}[I]_{0}L\bar{C}}{\bar{u}} = \frac{k_{p}[I]_{0}L[C]_{e}}{\bar{u}C_{0}}$$
(2.19)

Equation (2.19) can be solved using the boundary conditions represented in equations (2.20) and (2.21).

$$z = 0; \bar{C} = 1$$
 (2.20)

.....

$$z = 0; \frac{d\bar{C}}{dz} = 0$$
(2.21)

Equation (2.22) shows the solution to the above equation (2.19).

$$\bar{C}(z) = \left(\frac{b}{a}\right) + \exp(m_1 z)[c_1 \cos(m_2 z) + c_2 \sin(m_2 z)]$$
(2.22)

Expressions for the constants a, b,  $m_1$ ,  $m_2$ ,  $c_1$  and  $c_2$  are shown in equations (2.23) through (2.28) respectively.

$$a = \frac{k_p [I]_0 LPe_r}{u}$$
(2.23)

$$b = a \frac{[C]_e}{C_0}$$
(2.24)

$$m_1 = \frac{Pe_r}{2} \tag{2.25}$$

$$m_2 = \frac{\sqrt{4a - Pe_r^2}}{2}$$
(2.26)

$$c_1 = 1 - \left(\frac{b}{a}\right) \tag{2.27}$$

$$c_2 = -c_1 \left(\frac{m_1}{m_2}\right) \tag{2.28}$$

## 2.2 EXPERIMENTAL DETAILS

The process requirements needed to develop an extrusion process to continuously polymerize PDX monomer to form PPDX polymer are as follows:

- Accurate metering of PDX monomer and initiator under an inert atmosphere of nitrogen.
- Adequate length of the extrusion zone to meet residence time requirements needed to convert PDX monomer to PPDX polymer. However, in the case of homo-polymerization of PDX, due to the dynamic chemical equilibrium between the monomer and the polymer above the melting temperature of the polymer, it is not possible to obtain complete conversion. When PDX monomer is copolymerized with a small amount of CL monomer (about 5-10 mol %), the length of the extrusion zone becomes very critical.
- Suitable screw configuration in order to meet residence time requirements, melt pumping needs and mixing requirements.
- Good melt temperature control.
- Reasonable product throughputs of the polymer.

Based on these requirements, a novel extrusion process was developed to continuously polymerize PDX monomer. The details of the polymerization process developed to homo-polymerize PDX monomer and co-polymerize PDX monomer with a few mole% CL monomer in a twin-screw extruder will be outlined in the pages that follow. The characterization of PPDX and PCL-co-PPDX polymers synthesized by the extrusion process is also discussed.

#### 2.2.1 Materials and Equipment

PDX monomer, provided by Shell Chemicals, was purified by vacuum distillation and then dried over molecular sieves before the polymerization. The details of the distillation and the drying step are provided in <u>section 2.2.2</u>. The initiator for polymerization was aluminum tri-sec butoxide (ATSB), obtained from Aldrich Chemicals and used as obtained. A 10 percent (w/w) solution of ATSB in anhydrous toluene (Aldrich Chemicals) was used for initiation of the polymerization. The initiator solution was prepared in a glove bag under an inert atmosphere of nitrogen. Extreme care was taken to prevent the entrainment of ambient moisture in any of the process steps. CL monomer was purchased from Dow Chemicals and was used as obtained. RTD studies were conducted using a fluorescent die, UV-XPBB obtained from LDP Net.

The polymerization of PDX monomer and its co-polymerization with CL monomer was conducted in a Baker Perkins co-rotating Twin Screw (MPC/V-30); 30 mm co-rotating, fully intermeshing screws were mounted in a barrel about 450 mm long. The barrel sections were electrically heated and cooled by circulating water. The two-strand hole die was heated using an external power supply. The screw elements needed were also obtained from Baker Perkins.

#### 2.2.2 PDX monomer purification

All parts of the distillation setup were dried overnight at 110<sup>o</sup>C in a ventilated oven before use. The distillation setup was then put together, purged by three vacuum/nitrogen cycles and filled by a nitrogen flow. The different parts of the distillation setup were held by rubber bands attached via metal wires around the necks. Crude PDX monomer, provided by Shell Chemicals and made by the catalytic dehydrogenation of ethylene glycol using a copper (I/0) catalyst supported on silica particles is a mixture of PDX monomer and linear or cyclic oligomers of PPDX (Shell Oil Company, US Patent). Among the various purification methods available, fractional distillation under reduced pressure has been proven to be the most effective way to obtain pure PDX monomer with high yield (98).

In practice, about 600 g of crude monomer was introduced into a previously ovendried and nitrogen-purged distillation system under nitrogen flow (Refer Figure 2-13).



Figure 2-13: Schematic of Distillation setup

The distilled PDX monomer was recovered like a solid trapped by an ice/water bath (at  $0^{0}$ C). Starting from an initial purity degree of crude monomer of 90% such as determined by <sup>1</sup>H NMR in CDCl<sub>3</sub>, a recovery yield of 95% was obtained.

The residual acid content of the distilled monomer was determined by titration. The titration consists in an acid-base reaction between the PDX monomer and KOH using phenolphthalein as indicator. The medium is methanol at room temperature. An average acid value of 2.3  $mg_{KOH} / g_{PDX}$  characterized the distilled monomer, which is higher than the value required (below  $0.5 mg_{KOH} / g_{PDX}$ ) for typical ring-polymerization of lactones such as CL (40) by reactive extrusion.

In order to reduce the acid value, the PDX monomer was again distilled. The acid value obtained after the second distillation step decreased strongly from 2.3 to 0.33  $mg_{KOH} / g_{PDX}$  allowing us to envision the reactive extrusion polymerization of PDX monomer.

It is very important to reduce the residual water content in the PDX monomer before reactive extrusion. Water present could deactivate the active species in the polymerization by the hydrolysis of the aluminum-alkoxide bond. Thus drying is a very crucial step in the preparation of the PDX monomer for reactive extrusion. All glass parts of the drying setup were dried overnight at 110<sup>o</sup>C in a ventilated oven before use. The drying setup was then put together, purged by three vacuum/nitrogen cycles and filled by nitrogen. The different parts of the drying setup were held by rubber bands attached via metal wires around necks. The monomer (previously melted above its melting temperature) was pumped through a molecular sieves (3A) column using a peristaltic

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pump for at least 72 hr (Refer Figure 2-14). The PDX monomer, after distillation and drying was polymerized by reactive extrusion.



Figure 2-14: Schematic of Drying setup

## 2.2.3 Batch Polymerization Studies

Before conducting extrusion experiments, the polymerizability of PDX and CL monomers were determined in small scale by conducting polymerization experiments in vials. This is also useful in determining the efficiency of the distillation and drying steps. The initiator used for the polymerization is ATSB, which does not require any purification prior to the experiment. The initiator solution in toluene was prepared in a glove bag under an inert atmosphere of nitrogen. 13 ml of anhydrous toluene was mixed

with 1.5 ml (to form a 10% solution) of ATSB. This solution was transferred to an 8 ml vial, again under nitrogen flow. A 10 ml conical bottom thin-walled vial was oven dried and purged with nitrogen prior to the experiment. It was filled with 7 ml monomer and sealed using a screw cap. The vials were heated using an oil bath at 140°C and 160<sup>o</sup>C for the PDX and CL polymerization, respectively. For all the vials, nitrogen was supplied by connecting the nitrogen hose to a syringe needle. Figure 2-15 shows the pictorial representation of the experimental set up.



Figure 2-15: Schematic of Batch polymerization setup

The theoretical degree of polymerization DP for the three-arm polymer is given by equation (2.29) where X is monomer conversion and  $[M]_{0,mol}$  and  $[I]_{0,mol}$  signifies the initial moles of monomer and initiator charged to the reactor respectively.

$$DP_{three-arm} = \frac{[M]_{o.mol}}{[I]_{o.mol}} X$$
(2.29)

Thus the theoretical degree of polymerization of each linear arm of the three-arm polymer is given by equation (2.30)

$$DP_{linear} = \frac{DP_{three-arm}}{3}$$
(2.30)

Following this,  $M_n$  of the three-arm or the linear PCL polymer is given by equation (2.31), where '114' refers to the molar mass of CL monomer and  $M_n$  of the three-arm or the linear PPDX polymer is given by equation (2.32), where '102' refers to the molar mass of PDX monomer.

$$M_{n,three-arm/linear} = 114(DP_{three-arm/linear})g/mol$$
(2.31)

$$M_{n,three-arm/linear} = 102(DP_{three-arm/linear})g/mol$$
(2.32)

The amount of initiator to be added was dependent on the desired molecular weight of the polymer and was determined from equations (2.33) and (2.34) for PCL and PPDX polymers respectively, where  $M_{0,ml}$  is the initial volume of monomer charged to the reactor and  $\rho$  is the density of the monomer.

$$[I]_{0,mol} = \frac{[M]_{0,mol}}{DP_{three-arm}} = \frac{[M]_{0,mol}}{(3M_{n,linear}/114)} = \frac{(\rho M_{0,ml}/114)}{(3M_{n,linear}/114)} = \frac{\rho M_{0,ml}}{3M_{n,linear}}$$
(2.33)

$$[I]_{0,mol} = \frac{[M]_{0,mol}}{DP_{three-arm}} = \frac{[M]_{0,mol}}{(3M_{n,linear}/102)} = \frac{(\rho M_{0,ml}/102)}{(3M_{n,linear}/102)} = \frac{\rho M_{0,ml}}{3M_{n,linear}}$$
(2.34)

Using the molar mass of aluminum tri-sec butoxide (97% purity) as 246 g/mol and the density of the 10% (w/w) initiator solution in toluene as 0.874 g/ml, equations (2.33) and (2.34) can be simplified further to equation (2.35).

$$I_{0,mL} = \frac{([I]_{0,mol})(246 g/mol)}{(0.97)(0.874 g/mL)(0.10)} = 967 \frac{\rho M_{0,mL}}{M_{n,linear}}$$
(2.35)

Equation (2.35) was used to calculate the necessary amount of initiator required to synthesize a three-arm PCL and PPDX polymer with a desired  $M_{n, linear}$  (the number average molecular weight of each arm in the three-arm polymer). The required amount of initiator was withdrawn into a plastic syringe fitted with a 23-gage needle in the glove box. The tip of the syringe needle was capped with a rubber septum, and it was then removed out of the glove box in order to be added to the pre-heated monomer. A stopwatch was started when the initiator was added to the monomer in the reaction vial. The reaction was allowed to proceed for the desired time, following which the vial was removed from the hot bath and placed in liquid nitrogen to stop further reaction. Upon cooling, the contents of the vial were removed for analysis of percent conversion of monomer. The vial was broken to remove the product for analysis in the case of high polymer.

#### 2.2.4 Determination of Extent of Monomer Conversion

The extent of polymerization or the monomer conversion to polymer was determined by a dissolution-precipitation gravimetric method. A known amount,  $w_c$ , of the crude polymer (around 5-10 grams) was dissolved in 50 ml solvent (anhydrous toluene in the case of CL polymerization and 1,1,2,2-tetrachloroethane in the case of PDX polymerization) for 24 hours at room temperature. The solution was then poured into a flask containing about 500 ml of another solvent (heptane in the case of CL polymerization and Petroleum ether (Petroleum distillates,  $30^{\circ}C-60^{\circ}C$ ) in the case of PDX polymerization) to precipitate the polymer and keep the un-reacted monomer in solution. The precipitate was filtered and dried in vacuum oven and weighed,  $w_p$ . By comparison to the starting crude polymer weight, the fractional monomer conversion, X was calculated as explained in equation (2.36).

$$X = \frac{w_p}{w_c}$$
(2.36)

## 2.2.5 Extrusion Polymerization Studies

The molecular architecture of the PPDX polymer produced by the ROP of PDX monomer initiated by ATSB is as shown in Figure 2-16.



Figure 2-16: Three-arm structure of the PPDX polymer produced by reactive extrusion polymerization of PDX monomer.

Due to the expected three-arm nature of the polymer produced, the desired theoretical  $M_n$  of the PPDX polymer is designated as the molecular weight of each individual arm of the three-arm polymer. The relative ratio of the monomer to the initiator determines molecular weight of the polymer produced. Due to limited availability of the PDX monomer and the difficulties associated with repeated distillation and drying operations, the optimal conditions for extrusion (temperature, screw speed and screw configuration) were determined by conducting the polymerization of CL monomer. Table 2-5 shows the processing parameters along with the desired theoretical molecular weights.

RPM	M M R <sup>a)</sup>	ISR <sup>b)</sup>	Theoretical.	Torque
	(g/min)	(g/min)	M <sub>nPCL</sub>	(%)
			(each arm,	
			g/mol) <sup>c</sup>	
130	96	0.41	193,780	61
130	328	0.61	44,400	60
130	482	0.61	65,300	57

Table 2-5: Extrusion Processing Conditions for CL polymerization at 150°C.

a) Mass flow rate of monomer

b) Mass flow rate of initiator solution

c) Theoretical Number average molecular weight (g/mol) of each arm determined

from Equation (2.32)

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Knowing the polymerizability of CL monomer to three different molecular weights, the synthesis of REX-PPDX by extrusion polymerization of PDX monomer using ATSB initiator in a twin-screw co-rotating extruder was conducted. Specifically, the polymerization was conducted at three different temperatures for three molecular weights. The monomer and initiator flow rates required for a given desired theoretical molecular weight was calculated as shown from equation (2.29) through equation (2.35). A peristaltic pump with MASTERFLEX tubing (Pharmed 06485-15) was used to meter the PDX monomer to the extruder feed zone. The PDX monomer was heated using a heating mantle and the temperature of the monomer maintained at around 35<sup>o</sup>C to enable facile pumping of the monomer into the extruder. Nishida et al have explained the density of the monomer as a function of temperature (37). The initiator solution was pumped using a MASTERFLEX pump with Master flex tubing (06412-14). The extrusion processing conditions for the synthesis of REX-PPDX is shown in Table 2-6. The overall process schematic is shown in Figure 2-17.



Figure 2-17: Process schematic for REX-PPDX production

The pumps were each calibrated over the desired flow rate range in order to accurately control the process by adjusting the ratio of the monomer to the initiator. (Refer Figure 2-18 and Figure 2-19). The PPDX homo polymer was collected in aluminum pans and air-cooled.



Figure 2-18: PDX monomer pump calibration curve (PDX monomer maintained

between 32-35<sup>o</sup>C)



Figure 2-19: ATSB initiator solution calibration curve

## Table 2-6: Polymerization of PDX monomer by Reactive Extrusion: Determination

T <sub>poly</sub>	M M R <sup>a)</sup>	ISR <sup>b)</sup>	Theoretical	Torque
(°C)	(g/min)	(g/min)	M <sub>n</sub> PPDX	(%)
			(each arm,	
			g/mol)	
130	23.23	0.60	63,400	14
130	23.23	0.41	94,550	14
130	40.75	1.22	54,800	14
150	23.23	0.60	63,400	14
150	23.23	0.41	94,550	14
150	40.75	1.22	54,800	14
170	23.23	0.60	63,400	14
170	23.23	0.41	54,800	14

## of Optimal Conditions.

a) Monomer Mass Rate

b) Initiator Solution Mass Rate

In contrast to strong strands of PCL, PPDX strands are very low viscosity and liquid like. These values can be related to the low values of torque as observed and explained in Table 2-6. PDX monomer was co-polymerized with three different mole fractions of CL monomer to produce reactively extruded PCL-co-PPDX polymers. The feed set up was very similar to the case of homo polymerization of PDX monomer with the CL monomer being pumped to the feed port of the extruder. The Degree of Polymerization of the copolymer can be obtained using equation (2.37) as follows.

$$DP_{CL-co-PDX} = \frac{[M]_{0,molCL} + [M]_{0,molPDX}}{[I]_{0,mol}}$$
(2.37)

The theoretical desired molecular weight of the co-polymer can be calculated knowing the relative rates of the PDX monomer, CL monomer and the initiator solutions. The extrusion processing conditions are shown in Table 2-7.

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Table 2-7: PCL-co-PDX by reactive extrusion at 130°C: Effect of the addition of

PM R <sup>a)</sup>	ISR <sup>b)</sup>	C M R <sup>c)</sup>	Theoretical	Imposed	Torque
(g/min)	(g/min)	(g/min)	M <sub>n</sub> PPDX	F <sub>CL</sub>	(%)
			(each arm,		
			g/mol)		
23.23	0.62	-	94,550	-	14
23.23	0.407	2.369	104,200	0.08	9
40.7	1.21	3.294	107,950	0.11	16
23.23	0.60	5.12	77,550	0.16	19

## limited amounts of CL monomer

a) PDX Mass Rate

b) Initiator Solution Mass Rate

c) CL Mass rate

## 2.2.5.1 Screw Configuration

The two types of elements that make up the screw in a twin-screw extruder are conveying and kneading elements as discussed earlier. Krishnan (40) has shown that use of a conveying + kneading screw configuration leads to extra hold up time in the kneading blocks, sufficient to increase the viscosity of the polymer in that section to a high level.

On account of this, the polymer-monomer mixture preceding that section cannot be conveyed forward against the backpressure generated by the "frozen" high molecular weight polymer melt. This could result in complete stoppage of flow of material through the extruder. However, when an entirely conveying screw configuration was employed. there were no problems associated with production of high molecular weight polymer. This study employed a completely conveying screw configuration. The screw configuration is shown in Figure 2-20. All polymerization experiments were carried out using the same screw configuration under different conditions of temperature, desired molecular weight, screw speed and throughput. Various extruder temperatures studied ranged from 130 to 180°C; the monomer to initiator feed ratios was adjusted to give the desired theoretical number-average molecular weight, M<sub>n</sub>; the monomer feed rate, which is the throughput of the extrudate was set at two values of 23.23 and 40.75 gm/min. A screw speed of 130 RPM was used for the study. The percent conversion of the monomer was obtained for each condition. RTD studies were also conducted using the same screw configuration.





#### **2.2.5.2 Residence Time Distribution Studies**

Residence time distribution studies were conducted for the polymerization of CL monomer in a BAKER PERKIN twin-screw extruder using an instantaneous charge of 50 mg of a fluorescent die, UV-XPBB, obtained from LDP NET. The die has a fluorescence emission and excitation at 453 nm and 365 nm respectively. RTD studies were conducted for the various operating conditions as shown in Table 2-8.  $M_n$  of the resulting PCL polymer was kept constant at 70,000 g/mol. Extrudate samples were collected every 30 seconds for the first three minutes and further on, every one minute up to 2 minutes. The samples were then dissolved in toluene and the concentration of the dye obtained using UV-Spectroscopy. The result was then plotted against time to give the distribution, E (t). The cumulative distribution, F ( $\theta$ ) was also plotted to determine the applicability of the Axial Dispersion model. Peclet no  $(Pe_r)$  values were fit to a model deemed appropriate, using STATEASE 'Design of Experiment' 6.0 modeling software. Conversion of the monomer to polymer was determined for all of the above cases (Section 2.2.2). Experimentally observed conversion values were compared to conversion values obtained from the model shown in equation (2.22).

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Desired Throughput (ml/min)	Extrusion Temperature ( <sup>0</sup> C)	Screw Speed (RPM)
14	130	125
22	130	125
14	130	225
22	130	225
14	170	125
22	170	125
. 14	170	225
22	170	225

Table 2-8: Experimental Scheme to synthesize REX-PCL for RTD studies.

### 2.2.6 Intrinsic Viscosity

Intrinsic viscosity  $[\eta]$  reflects the contribution of the polymeric solute to the difference between the viscosity of the mixture and that of the solvent. Intrinsic viscosity is determined using an Ubbelohde viscometer. The viscometers are available in different sizes, and the type and size to be used depends on the range of viscosity of a particular polymer/solvent combination. In this study, size 0C was used. Firstly, the dilute polymer solution of known concentration was made by dissolving pre-weighed polymer (between 0.1 to 1.5 g depending on the type of polymer) into a known volume of solvent, usually between 50 to 100 ml. For the case of PCL polymer, toluene was used as the solvent while a 3:2 v/v mixture of tetrachloroethane/phenol solvent used for the PPDX polymer. Typically efflux times (to be discussed later) are between 5-10 minutes for the particular concentration of the polymer. Both the viscometer and the solution to be tested were made particle-free to prevent clogging of the capillary tube inside the viscometer.

The viscometer was cleaned by flushing solvent through all the three tubes, followed by dry air to remove final traces of solvent. The polymer solution to be tested was then introduced through the largest tube (tube A) till the level of the solution was between the two lines at the bottom of the tube. The viscometer was then placed in a constant-temperature water bath (temperature maintained at  $24^{\circ}$ C) such that the water level was above the bulb on tube B. The viscometer was then left for at least 20 minutes to bring the water and the solution temperature to be at equilibrium. The Ubbelohde was vertically aligned inside the water bath, a finger was placed over the third tube (tube C) and suction applied to tube B, until the solution reached to the bulb on the tube B. Suction was then removed from tube B, followed by removing the finger from tube C and the solution was allowed to flow freely. The efflux time was determined by measuring the time required for the level of solution in tube B to drop from one marking to the other. The above procedure was repeated at least three times for each solution and the average efflux time was determined.

Either the Huggins equation or the Kraemer equation can be used to determine intrinsic viscosity. These equations are explained in (2.38) [Huggins] and (2.39) [Kraemer] below.

$$c^{-1}(\eta/\eta_0 - 1) = [\eta] + k_H [\eta]^2 c$$
 (2.38)

$$c^{-1} \ln(\eta / \eta_0) = [\eta] - k_1 [\eta]^2 c$$
 (2.39)

where c is the concentration of the polymer solution tested,  $\eta$  is the solution viscosity,  $\eta_0$  is the solvent viscosity,  $[\eta]$  is the intrinsic viscosity and  $k_H$  and  $k_1$  are the proportional constants associated with each equation. Both constants depend on the type of polymers being tested. For dilute solutions, it can be said that:

$$\eta / \eta_0 = t / t_0$$
 (2.40)

where t is the efflux time of dilute polymer solution and  $t_o$  is the efflux time of solvent alone. The intrinsic viscosity was determined as the y-intercept obtained by plotting the left-hand-side of either the Huggins or the Kraemer equation against concentration.

Mark-Houwink-Sakurada (MHS) equation relates intrinsic viscosity ( $[\eta]$ ) of a polymer to the viscosity average molecular weight ( $M_{\nu}$ ) with the equation (2.41)

$$[\eta] = KM_{\nu}^{a} \tag{2.41}$$

MHS constants, 'K' and 'a' depend on the polymer, type of solvent used and the solution temperature used for testing. Since MHS constants, representing a wide range of polymers with different types of solvents and testing temperatures, have been published in various literatures,  $M_v$  can be determined if the intrinsic viscosity of a polymer is determined at the condition in which MHS constants are known. If MHS constants are unknown for a particular combination of polymer, solvent, and testing temperature, they can be calibrated by determining  $[\eta]$  and plotting  $\ln[\eta]$  versus  $\ln(M_w)$  or  $\ln(M_n)$ . 'K' and 'a' are determined as the slope and intercept of the above plot. This method, however, is merely an estimate and determination of exact  $M_{\nu}$  involves fractionation of the whole polymer sample into subspecies of relatively narrow molecular weight distributions and then averaging the measured  $M_n$  and  $M_w$  to calculate  $M_{\nu}$ .

In general, MHS equation can be applied to estimate  $M_w$  or  $M_n$  of unknown samples, only if a fraction of a molecular weight distribution is very similar to the sample used for the calibration. However, this restriction does not apply to the polymers with random molecular weight distribution, such as linear polyamides and polyesters polymerized under equilibrium conditions. For these types of polymers,  $M_w = 2M_n$  and the relation  $[\eta] = KM_v^a$  can be applied.

#### 2.2.7 Thermal Analysis

Standard DSC measurements were carried out with a 2920 CE Modulated DSC from TA Instruments. Samples, after extraction of the aluminum alkoxide functions by liquid/liquid extraction, were heated from  $-110^{\circ}$ C to  $140^{\circ}$ C at the rate of  $10^{\circ}$ C per minute under nitrogen flow. Glass transition temperature (T<sub>g</sub>) and Melting temperature (T<sub>m</sub>) were determined from the plot.

TGA measurements were performed, by using a Hi-Res TGA 2950 of TA Instruments under helium flow. Samples were heated from room temperature to  $180^{\circ}$ C at the rate of  $20^{\circ}$ C per minute and held at  $180^{\circ}$ C for 70 minutes. The thermal stability of the various homo and copolymers were determined from the plot.

#### 2.2.8 UV-Spectroscopy

UV/Vis Spectroscophotometer 'Lambda 25' from Perkin Elmer was used to determine the concentration of the fluorescent dye in the extruded PCL sample. This concentration data was further used to determine the RTD at a given temperature, screw speed and overall throughput. PCL sample, containing the dye, was dissolved in toluene. Concentrations of the solution were in the range of  $10^{-3}$  to  $10^{-5}$  M. Samples were put into glass cuvettes (plastic cuvettes dissolved in toluene). A reference containing the same concentration of the PCL sample in toluene (without the dye) was used. A spectrum of Absorbance vs. Wavelength was obtained. Only absorbance values in the range of 0.15to 1.5 are valid. A peak was obtained corresponding to 370 nm, which is the fluorescence excitation of UV-XPBB.  $\Lambda_{max}$ , the wavelength at which the molecule absorbs the most light was obtained as the maximum value of the peak. A calibration curve of  $\Lambda_{max}$  vs. Concentration was obtained by dissolving known amounts of the dye in the PCL solution. (The concentration of PCL in toluene was kept constant). Using Beer's law, which states that the number of photons absorbed is proportional to the concentration of the substance in solution, the actual concentration values were interpolated from the calibration data. Care must be taken that the solution does not absorb any light in the same range as that of the solute. Figure 2-21 shows a block diagram of UV-Spectroscopy.



Figure 2-21: UV Set Up Block Diagram

## 2.3 RESULTS AND DISCUSSION

The results of batch polymerization studies of CL and PDX monomer using ATSB initiator will be explained. The results of the effects of different temperatures, screw speeds and throughput on monomer conversion and molecular weight in the extrusion of PPDX polymer will be discussed in this section. Moreover, the effect of addition of different mole percentages of CL monomer on monomer conversion during the bulk extrusion polymerization of PDX will be discussed. Thermal analysis results of PPDX and PCL-co-PPDX polymers will be presented and discussed. The results of RTD studies on the polymerization of CL monomer will also be presented. The suitability of the Axial Dispersed PFR model on RTD and CL conversion in the extrusion polymerization of CL monomer will be evaluated.

### **2.3.1 Batch Polymerization Studies**

The conversion results of the batch polymerization experiments of CL and PDX monomers are shown in Table 2-9. It can be observed that the conversion of CL monomer is greater than 95% as opposed to a 71% conversion of the PDX monomer. As known, since the PDX polymerization is characterized by monomer-polymer equilibrium above the melting temperature of the polymer, conversion values of around 71% is permissible. These experiments further lead us to test the polymerizability in a twinscrew extruder.

### Table 2-9: Conversions of PDX and CL monomers in experimental conditions close

Experiment	Lactone	T <sub>poly</sub>	Conversion
		( <sup>0</sup> C)	
1	PDX	140	71
2	CL	160	96

to Reactive Extrusion (Polymerization time = 2 minutes)

## 2.3.2 Effect of extrusion process parameters on CL and PDX monomer conversion

For the various extrusion process conditions shown in Table 2-5, the conversion of CL monomer was 99%. Torque values remained constant (60%) even as the molecular weight increased from 44,400 g/mol to 193,780 g/mol. Thus, it is clear that at a temperature of 150°C, for different overall throughputs, using a completely conveying screw configuration, near complete conversion is observed (99). PCL polymer strands were of high viscosity and could be easily pelletized by quenching in a water bath.

The conversion results of PDX homopolymerization (Processing conditions shown in Table 2-6) by reactive extrusion are shown in Table 2-10.

## **Table 2-10: Polymerization of PDX monomer by Reactive Extrusion: Determination**

T <sub>poly</sub>	M M R <sup>a)</sup>	ISR <sup>b)</sup>	Theoretical	Torque	Conversion <sup>c)</sup>
(°C)	(g/min)	(g/min)	M <sub>n</sub> PPDX	(%)	(%)
			(each arm,		
			g/mol)		
130	23.23	0.60	63,400	14	68
130	23.23	0.41	94,550	14	78
130	40.75	1.22	54,800	14	68
150	23.23	0.60	63,400	14	62
150	23.23	0.41	94,550	14	68
150	40.75	1.22	54,800	14	60
170	23.23	0.60	63,400	14	61
170	23.23	0.41	54,800	14	60

## of optimal Conditions.

a) Monomer Mass Rate

b) Initiator Solution Mass Rate

c) Determined by gravimetry

In contrast to strong strands of PCL, the strands of PPDX are low viscosity. From Table 2-10, based on the conversion values; it is evident that the homo polymerization of PDX proceeds similarly to that of a system using a standard vacuum technique. For example, the monomer conversion at 130<sup>o</sup>C is 68% and 66% for the polymerization of PDX by reactive extrusion and standard vacuum technique respectively. In the case of the homo polymerization of PDX monomer to PPDX polymer, irrespective of the monomer flow

rate used, the maximum conversion obtainable was limited to about 78% which is close to the thermodynamic equilibrium monomer conversion value. It is also observed that for quite identical theoretical molecular weights (54, 800 g/mol and 63,400 g/mol), conversions are identical even as monomer flow rate increases from 23.23 to 40.75 gm/min. It is evident that as temperature increases, monomer conversion decreases due to the dynamic chemical equilibrium between the monomer and the polymer. It is also evident from Table 2-10 that as the monomer flow rate increases from 23 to 40 gm/min, the conversion drops. This is in agreement with batch polymerization studies done by various researchers (24,37,38 and 39) who report that the conversion of PDX monomer passes through maximum and then levels off at the equilibrium monomer conversion value.

### 2.3.3 Effect of CL addition on PDX Polymerization

The conversion results of PDX monomer on addition of a few-mol% CL during the PDX extrusion polymerization are shown in Table 2-11.

Table 2-11: Polymerization of PDX by reactive extrusion: Effect of the addition of

P M R <sup>a)</sup>	ISR <sup>b)</sup>	C M R <sup>c)</sup>	Theoretical	Imposed	Torque	Conv. <sup>d)</sup>
(g/min)	(g/min)	(g/min)	M <sub>n</sub> PPDX	f <sub>CL</sub> <sup>d)</sup>	(%)	(%)
			(each arm,			
			(g/mol)			
23.23	0.60	-	94,550	-	14	65
22.22	0.41	2.27	104.200	0.09	10	00
23.23	0.41	2.37	104,200	0.08	19	99
40.75	1.22	3.29	107,950	0.11	16	99
23.23	0.60	5.18	77,550	0.16	19	100

## limited amounts of CL monomer

a) PDX Mass Rate

b) Initiator Solution Mass Rate

c) CL Mass rate

d) Determined by gravimetry

It is clear from Table 2-11 that with incorporation of 8%, 11% and 16% CL monomer, the conversion is almost complete (~ 100%). This makes the process economical leading to the formation of a melt-stable blocky copolymer structure.

## 2.3.4 Intrinsic Viscosity Results

The results of the intrinsic viscosity experiments conducted on PPDX and PCL-co-PPDX polymers are shown in Table 2-12. It can be noted from the Table 2-12 that there is a sharp decrease in the  $[\eta]$  values on incorporation of CL units into the PPDX chain. However, the molecular weight of the polymers remains constant (first three entries). Thus, the decrease in  $[\eta]$  values could be attributed to a change in the conformation of the copolymers in solution. Unfortunately, it was not possible to determine the actual molecular weight of the copolymers by Size Exclusion Chromatography (SEC) or osmometry due to the poor solubility of the obtained copolymers in conventional organic solvents.

## Table 2-12: Intrinsic viscosity of PPDX and PCL-co-PPDX polymers produced by

P M R <sup>a)</sup>	ISR <sup>b)</sup>	C M R <sup>c)</sup>	Imp. F <sub>CL</sub>	Conv <sup>d)</sup>	[η] <sup>e)</sup>
(g/min)	(g/min)	(g/min)		(%)	(dL/g)
23.23	0.60	-	-	65	0.77
23.23	0.41	2.37	0.08	99	0.65
40.75	1.22	3.29	0.11	99	0.55
23.23	0.60	5.18	0.16	100	0.37

# reactive extrusion (T=130<sup>o</sup>C and Screw Speed = 130 RPM)

a) PDX mass flow rate

b) Initiator solution mass flow rate

c) CL mass flow rate

d) As determined by gravimetry after solubilization of crude product in 1, 1, 2, 2tetrachloroethane, precipitation in 7 volumes of heptane, filtration and drying up to constant weight.

e) As determined by solution viscometry in 1, 1, 2, 2-tetrachloroethane/phenol (3:2 v/v) at 25°C.

## 2.3.5 Thermal Analysis Results

DSC thermograms of PPDX and PCL-co-PPDX polymers produced by reactive extrusion are shown in Figure 2-22. The effect of CL addition on the thermal transitions is explained in Table 2-13.



Figure 2-22: DSC thermogram of PPDX homopolymer and PCL-co-PPDX copolymers obtained by reactive extrusion with different final molar fractions in CL:  $F_{CL}$ = 0.00 (a), 0.11 (b), 0.16 (c) and 0.20 (d) (heating rate = 10°C/min, under N<sub>2</sub>, only the second run is considered)

As expected, the incorporation of around 11-mol% CL into PPDX chains does not significantly modify the thermal properties. The co-polymer is characterized by a melting temperature around 94°C, close to the homopolymer melting temperature value of 106°C.
Moreover, there is an interesting internal plasticizing effect as the glass transition temperature of the co-polymer decreases from  $-11^{\circ}$ C (homo PPDX) to  $-22^{\circ}$ C. The melting temperature of the co-polymers further reduces to  $85^{\circ}$ C and  $68^{\circ}$ C with incorporation of 16-mol% and 24-mol% CL respectively. The glass transition temperatures also decrease with increasing amount of CL. As the molar fraction in CL in the copolymers increases from 0 to 20- mol%, the melting enthalpy and melting temperature decrease smoothly. For  $F_{CL} = 0.20$ , the melting dip centered at  $68^{\circ}$ C is very broad and the ability of the copolymer to crystallize is highly limited as evidenced by the low value of crystallization enthalpy. This low melting temperature of the copolymer limits the available service temperature range.

Table 2-13: DSC data of PPDX and PCL-co-PPDX polymers as obtained by reactive extrusion (under nitrogen flow, from  $-100^{\circ}$ C to  $140^{\circ}$ C at a heating rate of  $10^{\circ}$ C/min,  $2^{nd}$  scan)

Entry	Imposed	Tg	∆H <sub>c</sub>	T <sub>c</sub>	$\Delta H_m$	T <sub>m</sub>
	F <sub>CL</sub>	(°C)	(J/g)	(°C)	(J/g)	(°C)
1	0	-11	38	22	69	106
2	0.11	-22	33	13	56	94
3	0.16	-23	36	19	48	85
4	0.20	-29	27	29	32	68



Figure 2-23: Time-dependence of weight loss at  $180^{\circ}$ C for PPDX and PCL-co-PPDX polymers obtained by reactive extrusion with different final molar fractions in CL:  $F_{CL}$ = 0.00 (a), 0.11 (b), 0.16 (c) and 0.20 (d) (T = 180°C under a He flow)

Figure 2-23 shows the isothermal thermogravimetric analyses of the polymers obtained by reactive extrusion. As previously mentioned for DSC measurements, aluminum residues were extracted by liquid-liquid extraction. It can be seen from Figure 2-23 that the thermal stability of the copolymers is substantially improved by the incorporation of CL into PPDX chains. The rate of weight loss of the PPDX homopolymer and the PCLco-PPDX polymers are shown in Figure 2-24. This is in perfect agreement with our previous observations and the formation of a blocky-like copolymer structure. Moreover, this enhancement of the thermal stability is much higher than the one achieved by a simple end-capping process (Shell Process)



Figure 2-24: Rate of weight loss for PPDX and PCL-co-PPDX polymers obtained by reactive extrusion with different final molar fractions in CL:  $F_{CL}$ = 0.00 (a), 0.11 (b), 0.16 (c) and 0.20 (d) (T = 180°C under a He flow)

#### 2.3.6 Residence Time Distribution Studies

RTD studies were conducted for the reactive extrusion polymerization of CL monomer using the conditions mentioned in Table 2-8. A completely conveying screw configuration was employed for the polymerization process. Figure 2-25 and Figure 2-26 show the RTD data. It can be observed that at both 130<sup>o</sup>C and 170<sup>o</sup>C, for a constant monomer feed rate, increasing the screw speed from 125 to 225 RPM slightly decreases the peak value of residence time. However, the major reduction in the peak residence time value is obtained when the monomer feed rate is increased from 14 to 22 ml/min at a constant screw speed and temperature. In all the cases, a broad distribution of residence times was observed, with a fair amount of tailing, despite the excellent self-wiping characteristic of a co-rotating twin-screw extruder. This can be attributed to the presence of liquid films of monomer which would be present in the screw elements and will be eluted only after very long times. The RTD data at 170°C is very similar to the RTD data at 130°C for the same screw speed and monomer feed rate. This is expected since the only influence of the higher temperature was to accelerate the polymerization kinetics.



Figure 2-25: RTD curves at 130<sup>o</sup>C



Figure 2-26: RTD curves at 170°C

#### 2.3.6.1 Reactive Extrusion Modeling

The above RTD data for polymerization of CL monomer in a co-rotating twin-screw extruder was analyzed to determine if it fit the Axial Dispersed Plug Flow Reactor Model discussed earlier. Figure 2-27 through Figure 2-34 represent the prediction of RTD by the Axial Dispersed Plug Flow model [Refer equations (2.16),(2.17) and (2.18)]. From the figures, it can be seen that the Axial Dispersed PFR model is a suitable choice to predict flow in a co-rotating extruder for the case of CL polymerization. A plot of  $F_{model}$  vs.  $F_{experimental}$  yielded fit coefficients 'b' ( $F_{model}/F_{experimental}$ ) in the range of 0.92 to 0.98.

Table 2-14 presents the fit coefficients for the various conditions.

## Table 2-14: Fit coefficients 'b' predicting goodness of fit of the Axial Dispersed PFR

Desired Throughput (ml/min)	Extrusion Temperature ( <sup>0</sup> C)	Screw Speed (RPM)	В
14	130	125	0.94
22	130	125	0.90
14	130	225	0.94
22	130	225	0.98
14	170	125	0.96
22	170	125	0.96
14	170	225	0.96
22	170	225	0.97

## model to experimental data in the case of CL polymerization



Figure 2-27: Axial Dispersed PFR model applied to RTD data for CL

polymerization at 130°C (Screw speed of 125 RPM and monomer feed rate of 14

ml/min)



Figure 2-28: Axial Dispersed PFR model applied to RTD data for CL polymerization at 130<sup>o</sup>C (Screw speed of 125 RPM and monomer feed rate of 22

ml/min)



Figure 2-29: Axial Dispersed PFR model applied to RTD data for CL

polymerization at 130°C (Screw speed of 225 RPM and monomer feed rate of 14

ml/min)



Figure 2-30: Axial Dispersed PFR model applied to RTD data for CL polymerization at 130°C (Screw speed of 225 RPM and monomer feed rate of 22

ml/min)



Figure 2-31: Axial Dispersed PFR model applied to RTD data for CL polymerization at 170°C (Screw speed of 125 RPM and monomer feed rate of 14

ml/min)



Figure 2-32: Axial Dispersed PFR model applied to RTD data for CL polymerization at 170°C (Screw speed of 125 RPM and monomer feed rate of 22

ml/min)



Figure 2-33: Axial Dispersed PFR model applied to RTD data for CL polymerization at 170°C (Screw speed of 225 RPM and monomer feed rate of 14

ml/min)



Figure 2-34: Axial Dispersed PFR model applied to RTD data for CL polymerization at 170°C (Screw speed of 225 RPM and monomer feed rate of 22

ml/min)

Peclet number ( $Pe_r$ ) was calculated for the various experimental conditions shown in Table 2-8 using equation (2.16). The Peclet number values for the various experimental conditions are shown in Table 2-15.

Table 2-15: Peclet Number values under different experimental processing
conditions (Table 2-8) in the synthesis of three-arm PCL polymer

Desired Throughput	Extrusion Temperature	Screw Speed	Peclet
(ml/min)	( <sup>0</sup> C)	(RPM)	No
14	130	125	6.41
22	130	125	6.8
14	130	225	3.03
22	130	225	9.98
14	170	125	11.56
22	170	125	5.26
14	170	225	9.31
22	170	225	7.49

It is observed from Table 2-15 that maximum dispersion is obtained under conditions of 130°C, 225 RPM and 14-ml/min monomer feed rate. Least dispersion is obtained at 170°C, 125 RPM and 14-ml/min monomer feed rate. At 130°C, due to the presence of low molecular weight pre-polymers along-with the polymer melt, dispersion effects become pronounced. Moreover, dispersion effects increase as overall throughput increases (increase of monomer feed rate).

A 2Fl model was fit using STATEASE 'Design of Experiment' 6.0 modeling software with  $Pe_r$  as the response data and Screw Speed, temperature and thruput as the factors. From the model, the significant terms were determined to be temperature, interaction of screw speed, and thruput and interaction of temperature and thruput. The final model equation in terms of the actual factors is shown in equation (2.42).

$$Pe_{r} = -42.41 - 0.12 * Screwspeed + 0.48 * Temperature + 2.39 * Thruput$$

$$+ 0.007 * Screwspeed * Temperature - 0.02 * Temperature * Thruput$$
(2.42)

The experimentally determined conversions were compared to the ones obtained from the model. The fit is shown in Figure 2-35. It can be observed from Figure 2-35 that the model provides sort of a good fit to experimental data.



Figure 2-35: Model vs. Experimental conversions in the polymerization of CL monomer to form three-arm PCL polymer (Table 2-8).

Chapter 3

#### **REACTIVE EXTRUSION CROSSLINKING OF BIODEGRADABLE**

## POLYESTER AND BLENDING WITH INORGANIC FILLERS.

#### **3.1 INTRODUCTION**

#### 3.1.1 Cross-linking Chemistry

Cross-linking is typically carried out to increase molecular weights of polymers to make them suitable for practical use. Ostromislenski first reported the initial use of organic peroxide as a cross-linking agent in 1915 for the vulcanization of natural rubber. Since around 1950, the interest in the industrial use of peroxides as cross-linking agents has been increasing, partly as a result of the introduction of saturated rubbers such as ethylene-propylene monomer and silicone rubber which cannot be vulcanized with the usual sulfur systems (100,101). On the other hand, many researchers have tried to introduce cross-links into aliphatic polyesters to improve properties such as mechanical strength and elasticity. Han et al. (102) prepared biomedical materials by the thermal cross-linking of unsaturated polyesters using free radical initiators. Pramanick and Ray synthesized cross-linked polyesters from a mixture of glycerol, citric acid and aspartic acid (103,104). A schematic showing a cross-linked polymer network as opposed to uncross- linked one is shown in the Figure 3-1 below.



Figure 3-1: Schematic showing cross-linked and uncross-linked networks

Depending on the type and the amount of initiator used, polyesters can be highly crosslinked to form a thermoset or lightly cross-linked to provide more elastomeric properties. There are numerous patents in the area of cross-linking biodegradable polyesters to use as binders in toner applications. U.S. Patent 3, 681,106 provide a method to modify a polyester resin by mixing a trivalent or more polyol or polyacid with the monomer to generate branching during polycondensation. In U.S. Patent 3, 941,898, a cross-linked vinyl type polymer was prepared by conventional cross-linking. The patents also describe that the initiator, whether solid or liquid, is mixed with the polyester resin, for example in a rotary tumble blender or a batch mixer. U.S. Patent Application 20020086944 provides a method to cross-link rubber particles using metal peroxides in extruders. U.S. Patent 6,359,105 provides a method to form cross-linked polyester resins using a liquid chemical initiator such as 1, 1-bis (t-butyl peroxy)-3, 3, 5-trimethylcyclohexane. The method includes spraying the initiator onto the unsaturated polyester resin prior to, during or subsequent to melting of the unsaturated polyester resin to form a polymer melt and subsequently cross-linking the polymer melt under high shear. In all of the above cases, cross-linking is carried out to improve the xerographic performance of the toner.

#### 3.1.2 Cross-linking Principles

Chemical cross-linking is one of the most severe mechanisms for decreasing molecular freedom. It links the polymer chains together through covalent or ionic bonds to form a network. Cross-linking can be achieved in two broad ways: 1) cross-linking during polymerization by use of polyfunctional instead of difunctional monomers, 2) cross-linking using external initiators such as peroxides. The cross-links may contain the same structural features as the main chains, which are usually the case with the former, or they may have an entirely different structure, which is more characteristic of the latter.

A number of changes occur due to cross-linking. If previously soluble in a particular solvent, the cross-linked polymer will be partially or totally insoluble in the

same solvent. When the cross-linked polymer is dissolved in a good solvent, the polymer absorbs a portion of the solvent and subsequently swells. The extent of swelling is a competition between two forces. The free energy of mixing will cause the solvent to penetrate and try to dilute the polymer solution. Increasing the temperature may enhance this entropic increase. As the polymer chains in the cross-linked polymer network begin to elongate under the swelling action of the solvent, they generate an elastic retractive force in opposition to this deformation. The volumetric swelling reaches steady state when the two forces balance each other. Given that the steady state swelling ratio is a direct function of the extent of cross-linking in the sample, swelling experiments are an effective and low-cost technique to characterize cross-linked networks. At the simplest level of analysis, swelling measurements can be used for quality control and serve as an indexing tool for polymer systems with different levels of cross-linking. At a higher level of analysis, molecular weight between cross-links and the number of cross-links per chain can be computed, if one knows the Flory interaction parameter for the polymersolvent system (105). With network polymers, it is common to speak of cross-link density, which is the number of cross-linked monomer units per main chain. Cross-link density is defined mathematically as shown in equation (3.1).

$$v_{x} = -\frac{\ln(1-v_{2}) + v_{2} + \chi_{1}v_{2}^{2}}{\Phi_{1}(v_{2}^{\sqrt{3}} - v_{2}/2)}$$
(3.1)

In equation (3.1),  $v_x$  is the cross-link density;  $v_2 = \frac{V_0}{V}$  where  $V_0$  is the volume of the uncross-linked network and V, volume of the cross-linked network;  $\chi_1$  is the Flory Interaction parameter and  $\Phi_1$  is the molar volume of the solvent. The higher the cross-link density, the more rigid the polymer behaves. Elastomers are characterized by having

a very low cross-link density; about one cross-link per 100 monomer units-together, with highly flexible main chains to allow large deformations. If the gel particles are very small, in the range of 300-1000 microns, they are called as microgels. Microgels behave as tightly packed spheres that can be suspended in solvents. They have attracted considerable interest in recent years with the development of solid phase synthesis and techniques for immobilizing catalysts.

Covalent cross-linking has certain disadvantages. Once cross-linked, a polymer cannot be dissolved or molded. Scrap cross-linked polymer cannot be recycled. One approach to circumvent this problem is to introduce thermally labile cross-links, that is, chemical cross-links that break apart on heating and reform on cooling. The other approach has been to introduce strong secondary bonding attraction between polymer chains, such that the polymer exhibits properties of a thermosetting material while remaining thermoplastic. In recent years, the technology of block co-polymers has been applied to the area of physical cross-linking. The aggregations impart a significant degree of elastic behavior, yet the copolymers still exhibit the flow properties of thermoplastics.

In this work, biodegradable polyesters are cross-linked using free radical initiating systems to yield gel particles, termed as "microgels", which reinforce the main polyester matrix improving the properties. When the polyesters are cross-linked in batch reactors as opposed to extruders, gel particles obtained are large in size and are termed as "macrogels". These "macrogel" particles lead to problems during blown film processing.

#### 3.1.3 Filled Composites

Fillers are added to polymers for a variety of reasons. Reinforcing fillers improve tensile strength or tear strength. Carbon black and silica are typical examples of reinforcing fillers. Axisymmetric particles such as fibers and flakes are used to increase the modulus and heat deflection temperatures and they also come under the category of reinforcing fillers. The highest reinforcement effect is, apparently, obtained from carbon fibers. It is interesting to mention that carbon fibers themselves are not at all stronger than glass fibers. However, their modulus of elasticity is 3-5 times higher. The higher Young's modulus of composites filled with carbon fibers, compared with those filled with glass fibers (at the same concentration), leads to a situation where the fraction of load transmitted to the fiber is higher, whereas that received by the matrix is lower (106). The elasticity modulus of asbestos fibers is about 1.5 times higher than that of glass fibers. However, these fibers have a very uneven length distribution, which reduces the reinforcement effect. Compared to glass fibers, standard organic polymer fibers have a lower Young's modulus and provide a correspondingly lower reinforcement effect. Natural organic fibers, including cellulose, wood flour etc. provides almost zero reinforcement effect due to their small size, moisture holding capability, poor interfacial adhesion and great flexibility.

Composites may also be reinforced with lamellar fillers. For these fillers, the aspect ratio is defined as the ratio of linear dimension to thickness. Lamellar composite fillers exhibit reinforcing effect in two directions, rather than in one as in the case of fibers. Therefore, randomly distributed lamellar fillers are expected to produce better

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reinforcement effect than fibers, for the same filling ratio. Common fillers such as talc and kaolin also have a lamellar structure, but do not exhibit a reinforcing effect due to their low aspect ratios.

The behavior of inert filler is illustrated by the measurements of Han on calcium carbonate-filled polypropylene (107). The viscosity increases considerably as the filler concentration increases. Vinogradov and co-workers (108) studied the influence of carbon black on the rheology of polyisobutylene. It was established that the addition of carbon black reduced die swell, improving processability. In a study of the injection molding of highly filled phenolic compounds, Beck (109) found that the mold filled by 'jetting'; at the mold entrance, the jet emerging from the gate traveled through the mold until it hit the opposite wall; mold filling occurred by the buckling and spreading of the solid like jet. Hall and co-workers (110) studied the injection molding process of a 40percent glass fiber filled polycarbonate blend. It was observed that the ultimate tensile strength varied from 22,000 psi for a small tensile bar to 11,000 psi in the square plate perpendicular to the flow direction. Various researchers (111,112) have shown that the volume fraction of the filler as well as the filler size affects the flow of the filled composite in a mold. Inert fillers and pigments do not change the final properties in a desirable direction, but make the polymer easier to mold or extrude and lower the cost of the final composite. However, the most important issue to be addressed is the compatibility between the filler and the matrix, which can be improved by modifying either the filler or the matrix using chemical treatments. Clay, talc and calcium carbonate are some examples of inert fillers. Brittle fillers of little strength, such as perlite, will fail in a loaded specimen. This will initiate cracks and an early specimen failure. Organic

fillers may be divided into two groups, elastic and pseudo-plastic ones. The first group has been extensively used for improving the impact strength of materials. In all cases, the added elastomer reduces the tensile strength of the composite. The second group includes fillers prepared from plastic wastes, nutshells, wood flour etc. Typical examples of plastic wastes are powdered thermoset plastics and powdered polymer mixtures. Their effect on the strength of the composites depends on the composition of the plastic wastes and on the strength of the polymer matrix. As usual, the strength of the composites is reduced compared to the pure polymers, although this negative effect may be offset by an improvement of other properties (113).

Petroleum-based oils, fatty acids, and esters are also used as plasticizers and lubricants. Antioxidants act as free-radical sinks and stop chain reactions in oxidation. Curatives are essential to form network of cross-links that guarantee elasticity rather than flow. Sulfur for unsaturated and peroxides for saturated polymers are used with auxiliaries to control reaction rate (114).

The primary objective of this work was to create lightly cross-linked (low crosslink density) biodegradable polyester systems containing microgels, using 2, 5-Bis (tertbutylperoxy)-2, 5-dimethylhexane (Luperox 101), a free-radical initiator, in a twin-screw co-rotating extruder. The biodegradable polyesters studied were Polycaprolactone (PCL), aliphatic polyester, and Ecoflex, aliphatic-aromatic co-polyester. Another important goal of this work was to blend Ecoflex and cross-linked Ecoflex (LEcoflex) with talc in a twin-screw co-rotating extruder to form blends suitable to be blown into films with improved mechanical properties.

#### **3.2 EXPERIMENTAL DETAILS**

The process requirements needed to develop an extrusion process to continuously crosslink PCL and Ecoflex are as follows:

- Accurate metering of the biodegradable polyester and initiator.
- Adequate length of the extrusion zone to meet residence time requirements needed to cross-link the polyesters.
- Suitable screw configuration in order to meet residence time requirements, melt pumping needs and mixing requirements.
- Good melt temperature control.
- Reasonable product throughputs of the polymer.

Based on these requirements, extrusion process was developed to continuously cross-link PCL and Ecoflex in a CENTURY twin-screw co-rotating extruder. Further, Ecoflex and cross-linked Ecoflex were extrusion processed with talc to form blends suitable for blown film applications. The details of the extrusion cross-linking and blending process will be outlined in the pages that follow. The characterization of the cross-linked polyesters and the blends will be discussed.

#### **3.2.1 Materials and Equipment**

A twin-screw co-rotating CENTURY extruder having a length: diameter ratio (L/D) of 40 and a screw diameter of 30 mm was used for cross-linking chemistries. The extruder was electrically heated and cooled using circulating water. The screw elements needed for the screw configuration were also obtained from CENTURY. The same extruder was also used for the blending of Ecoflex and LEcoflex with talc. The auxiliary equipment included a water bath to cool the extrudate and a pelletizer to cut the strand into small pellets.

PCL, marketed under the trade name TONE polymers, was obtained from Dow Chemicals. TONE polymers are homopolymers of ε-caprolactone, a seven-member ring compound. The chemical structure of the PCL polyester is shown in Figure 3-2.



Figure 3-2: Chemical structure of PCL polyester

The TONE polymer product family consists of: 1) TONE P-767 and P-787 polymers of Number average molecular weight ( $M_n$ ) of 50,000 g/mol and 80,000 g/mol respectively, and 2) TONE P-737 and P-757 polymers of  $M_n$  32,000 g/mol and 43,000 g/mol respectively. The polymer used in this study was *TONE P-787*. Unlike most commercial polymers, PCL polymers, as aliphatic polyesters, offer the unique property of being truly biodegradable without the requirement of prior photo degradation. In compost environments, TONE polymers will undergo assimilation by microorganisms. Microorganisms of the type found in compost are essential for degradation, since no microbial degradation of TONE polymers, either in water or in air alone, has been observed for periods of at least a year. Thus, most applications of TONE polymers (e.g., adhesive, polymer additive, orthopedic) will not encounter problems with microbial degradation. TONE polymers are assimilated by microorganisms and used as an energy source in their growth, with the result that carbon dioxide (CO<sub>2</sub>), water, and biomass are produced. Intermediate metabolism products would not be expected to be harmful to plant or animal life. This biodegradability is useful in applications such as films for food or yard waste compost bags, tree planting containers, and matrix systems for controlled or slow release of pesticides, herbicides and fertilizers. TONE P-787 is miscible with a wide variety of polymers like Poly (vinyl chloride), Polycarbonate, cellulose propionate etc. It offers excellent melt formability and rigidity in the solid state. TONE P-787 will run on most Linear Low Density Polyethylene (LLDPE) film lines at temperatures of around 200-250°F. 1 mil P-787 blown film exhibits a tensile strength of around 7900 psi and an elongation to break % value of around 400% (115).

Aliphatic-aromatic co-polyesters represent an innovative group of biodegradable polyesters made by BASF & Eastman Chemical under the trade names Ecoflex and Eastar Bio respectively, which degrade with the aid of naturally occurring enzymes. Ecoflex is aliphatic-aromatic co-polyester based on the monomers adipic acid, terephthalic acid and 1, 4-butane diol. The generic structure of Ecoflex is shown in Figure 3-3.

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Figure 3-3: Chemical structure of aliphatic-aromatic copolyester

Ecoflex is completely biodegradable to EN13432 as more than 90-percent of the organic carbon in the material gets converted to carbon dioxide during a test period not exceeding 180 days. The degradation curve below (Figure 3-4) shows that Ecoflex liberates more than 90-percent carbon dioxide in after only 80 days.



Figure 3-4: Theoretical percent Carbon dioxide evolution of Ecoflex under EN

#### 13432 test protocol.

Ecoflex is very compatible with natural materials such as starch, cellulose etc. Blown film extrusion is a particular area where Ecoflex shows balance in processing properties.

The cross-linking reactions were carried out using a free radical initiator. The initiator was 2, 5-Bis (tert-butylperoxy)-2, 5-dimethylhexane (Luperox 101) obtained from Aldrich Chemicals [78-63-7]. It was used as obtained.

Talc was obtained from Luzenac, Canada. The median diameter was 2.2 microns with a specific gravity value of 2.8. Talc was dried in an oven at 100<sup>o</sup>C overnight prior to extrusion.

#### 3.2.2 Extrusion Cross-linking Studies

PCL and Ecoflex were pre-blended with Luperox 101 in a kitchen blender for 15 minutes. Luperox 101 concentrations of 0.1-wt%, 0.5-wt% and 1-wt% were used in the cross-linking of Ecoflex, while 0.1-wt% Luperox 101 concentration was used in the case of PCL cross-linking. The mixture was fed to the feed port of the extruder using a CENTURY feeder. Samples were removed from the die and in some cases from the vent port (cross-linking of PCL and Ecoflex using 0.1-wt% Luperox 101). The screw configuration used for the cross-linking consisted of conveying and kneading elements and is shown in Figure 3-5. The extrusion processing conditions are shown in Table 3-1.

ZONE	SET	ACTUAL	°C
ZONE1	15	24	°C
ZONE2	85	85	°C
ZONE3	125	124	°C
ZONE4	145	145	°C
ZONE5	160	160	°C
ZONE6	165	177	°C
ZONE7	165	173	°C
ZONE8	165	171	°C
ZONE9	150	170	°C
DIE	145	150	°C
MELT TEMP.	154	°C	
MOTOR SPEED	74	RPM	
TORQUE	55-60	%	
PRESSURE	90	Psi	
FEEDER SPEED, CENTURY	150 (Rate = 10 lbs/hr)	%	
FEEDER SPEED, MiNi	-	%	
FEEDER SPEED, EXT	-	%	

 Table 3-1: Processing Conditions for Cross-linking PCL and Ecoflex



Figure 3-5: Screw Configuration used for Cross-linking studies

The extruded strand was cooled using a water-bath and pelletized in line. The pellets were dried in an oven at 75<sup>o</sup>C overnight to remove absorbed moisture before further processing.

#### 3.2.3 Determination of gel fraction

Cross-linked PCL (LPCL) and cross-linked Ecoflex (LEcoflex) were analyzed for their gel fraction by Soxhlet Extraction Studies conducted in TetraHydroFuran (THF) solvent. Around 2-3 grams of the sample was accurately weighed into a cellulose extraction thimble (33 mm x 94 mm) and placed into the thimble holder. The evaporated solvent condensed into the thimble, containing the sample. The extraction was run for 24 hours. After extraction, the thimble along-with the sample was removed and dried to constant weight. The final weight of the thimble with the sample was measured from which the gel fraction was calculated using equation (3.2), where  $w_{f and} w_i$  are the final and initial weights of sample and thimble respectively.

$$Gelfraction = \frac{w_f}{w_i}$$
(3.2)

#### 3.2.4 Extrusion blending of Ecoflex with talc

The pellets of Ecoflex were dried in an oven overnight at 75<sup>o</sup>C before further downstream processing. Ecoflex was mixed with talc in a kitchen blender for 15 minutes. The ratio of Ecoflex: talc was 70: 30. The mixture was fed to the feed port of a twin-screw co-rotating CENTURY extruder (L/D of 40 and screw diameter of 30 mm) extruder. The extrusion processing conditions are shown in Table 3-2 below. The screw configuration was exactly same as the one used for the cross-linking studies as shown in Figure 3-5. The resulting strand was cooled using a water bath and pelletized. The pellets were stored in an oven at 75<sup>o</sup>C to remove surface moisture. The process schematic is shown in Figure 3-6.



Figure 3-6: Process Schematic of extrusion processing of Ecoflex with talc

# Table 3-2: Extrusion Processing Conditions for Ecoflex blending with talc

ZONE	SET	ACTUAL	°C
ZONE1	15	23	°C
ZONE2	85	85	°C
ZONE3	125	125	°C
ZONE4	145	144	°C
ZONE5	160	162	°C
ZONE6	165	174	°C
ZONE7	165	169	°C
ZONE8	165	167	°C
ZONE9	150	163	°C
DIE	145	147	°C
MELT TEMP.	150	°C	
MOTOR SPEED	177	RPM	
TORQUE	50-55	%	
PRESSURE	91	Psi	
FEEDER SPEED, CENTURY	150 (~12 lbs/hr)	%	
FEEDER SPEED, MINI		%	
FEEDER SPEED, EXT		%	

#### 3.2.5 Thermal Analysis

A high resolution Differential Scanning Calorimeter (DSC) 2920 from TA Instruments was used to determine the melting temperature  $(T_m)$  of the cross-linked polyesters and their blends with talc. Nitrogen was used as the purge gas at 50 ml/min. The sample was heated from 0<sup>o</sup>C to 200<sup>o</sup>C at the rate of 10<sup>o</sup>C per minute, cooled and re-heated again.2<sup>nd</sup> scan data was plotted.

A high resolution Thermal Gravimetric Analyzer (TGA) 2950 from TA Instruments was used to determine the degradation temperature of the cross-linked gels along-with their blends with talc. Nitrogen was used as the purge gas with the sample purge being 60 ml/min and the balance purge being 40 ml/min. The sample was heated to 550°C at the rate of 20°C per minute.

#### 3.2.6 Environmental Scanning Electron Microscopy (ESEM) Studies

Films of Ecoflex, LEcoflex and all the blends with talc were examined under an ESEM, Electro Scan 2020 outfitted with a LaB<sub>6</sub> filament. Sample was introduced into the specimen chamber and vacuum (1 Torr) was applied. All measurements were taken using a bullet detector with a working distance of 6-9 mm and a take off angle of  $30^{\circ}$ . Accelerating voltage of 20kV was used. Various magnifications ranging from 50X to 2000X were studied.

## 3.2.7 Blown Film Processing

Films of the samples were made using a Killion single-screw blown film unit. The screw diameter was 25.4 mm with L: D ratio of 25:1. The die inner diameter was 50.8 mm with a die gap size of 1.5 mm. The blow up ratio of the films was 2-2.5, comparable to Polyethylene films. The blown film processing conditions are shown in Table 3-3.

Table 3-3: Blown Film Processing Conditions for talc filled polyester blends

	Die 3	Die 2	Die 1	Adaptor	Clamp Ring	Zone 3	Zone 2	Zone 1
	70	250	255	2(0	2(0	205	205	200
Set (F)	/0	350	355	360	360	395	395	300
1.000		-0.50	0.5.6	0.50	0(0	0.50		200
Actual (°F)	73	350	356	359	360	370	395	300

Melt ( <sup>0</sup> F)	355
Screw Speed (RPM)	14.6
FPM (ft/min)	5-6
Pressure (psi)	1500-3000

The schematic of a blown film process is shown in Figure 3-7.



**Figure 3-7: Blown Film Processing Schematic** 

### 3.2.8 Mechanical Property Determination

Tensile properties of the films were determined using INSTRON Mechanical Testing Equipment fitted with a 100 lbs load cell. The crosshead speed was 1 inch per minute. Rectangular film samples, 5'x1' dimension were conditioned at  $25^{\circ}$ C and 60% Relative Humidity for 40 hours before being tested according to ASTM D-882 testing protocols.

#### 3.3 RESULTS AND DISCUSSION

The cross-linking chemistry by free radical reaction is postulated in this section. The effect of residence times and initiator concentrations on the gel fraction of cross-linked PCL and Ecoflex (with increased molecular weight) will be discussed in this section. The effect of various kneading elements used in the screw configuration on dispersion of the talc particles in the Ecoflex polyester matrix will be schematically presented and discussed. Thermal Analysis results elucidating the effect of cross-linking and blending on percent crystallinity, melting and degradation profiles of the cross-linked polyesters and the blends will be presented. ESEM results depicting the particle sizes of the gel phase in the cross-linked polyester matrix and talc in polyester/talc blends will be evaluated. Finally, film properties (tensile, tear and puncture) of the blends will be presented.

#### **3.3.1 Cross-linking Studies**

#### 3.3.1.1 Cross-linking Chemistry

Figure 3-8 shows the cross-linking chemistry occurring by free radical reaction using Luperox 101. From Figure 3-8, it can be observed that branching can occur either by intermolecular or intramolecular reaction (116). Other side reactions such as backbiting and hydrolysis may be occurring too. However, from the tensile properties of crosslinked polyester films, we can postulate that branching is the dominant reaction. Further, as the polyester was dried in an oven before extrusion, hydrolysis reactions can be treated as not dominant.



Figure 3-8: Cross-linking chemistry by free radical reaction
# 3.3.1.2 Effect of Residence Time on gel fraction of cross-linked polyesters

Gel fraction results of LPCL and LEcoflex samples removed from the vent port (distance of 34 D from the feed port) and the die are shown in Table 3-4.

# Table 3-4: Gel fraction results of LPCL and LEcoflex samples obtained from the vent and the die.

Polyester	Gel fraction-Sample from vent	Gel fraction-Sample from die
PCL	0.516	0.631
Ecoflex	0.282	0.401

It is clearly observed from data in Table 3-4 that cross-linking reaction is dependent on the residence time in the extruder. Samples removed from the vent exhibited lower values of gel content as compared to the ones removed from the die. Moreover, LEcoflex exhibited lower values of gel fraction than LPCL. This is attributed to the presence of bulky aromatic rings in the Ecoflex structure, which make them less prone to free radical chemistries.

# 3.3.1.3 Effect of Initiator Concentration on the gel fraction of cross-linked polyesters

The effect of increasing Luperox 101 content on the gel fraction of LEcoflex samples obtained from the die is shown in Table 3-5.

# Table 3-5: Gel fraction results of LEcoflex containing varying amounts of Luperox

Luperox 101 content	Gel fraction		
(Wt-%)			
0.1	0.401		
0.5	0.482		
1	0.527		

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It can be seen that as the initiator concentration increases, gel fraction increases. However, the rate of increase reduces as the initiator concentration increases suggesting that the gel fraction would level off at a particular initiator concentration. These results are in accordance with previously published reports (100,101). Takashima and Nakayama reported that the gel content of PE cross-linked using dicumyl peroxide at 140-180<sup>o</sup>C and then extracted using xylene exhibited higher values of gel fraction as compared to PCL or Ecoflex. This could be due to the fact that PCL and Ecoflex have a lower amount of methylene group content in the main chain as compared to PE. This makes the number of cross-linking sites fewer. Moreover, the polymer-solvent solubility difference could also be involved.

## **3.3.1.4 Thermal Analysis**

Figure 3-9 show the DSC results of Ecoflex and LEcoflex (cross-linked with 0.1-wt% Luperox 101).



Figure 3-9: DSC results of Ecoflex and cross-linked Ecoflex (0.1-wt% Luperox 101)

As seen from Figure 3-9 shown above, crystallinity was present in both cross-linked Ecoflex and regular Ecoflex. The area under the melting peak of the Ecoflex polyester was 13.11 J/g while that of LEcoflex was 6.865 J/g. It is well known that the crystallinity of a polymer reduces with the introduction of cross-linking. However, in the case of

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cross-linking Ecoflex polyester using peroxide initiators, the level of cross-linking are low such that the polymer chains have mobility to crystallize. However, as cross-linked domains cannot crystallize and reduce crystallinity, the area under the melting peak of LEcoflex was lower than Ecoflex. Moreover, the melting temperature of LEcoflex (114.58°C) was lower than Ecoflex (123.56°C). This can be explained by the fact that the size and perfectness of LEcoflex crystals are relatively low because cross-links restrict chain motions. Further, peak crystallization temperature of LEcoflex was 26°C lower than that of Ecoflex. This could be attributed to the presence of some substances acting as nucleating agents. Hurnki (117) attributed the process of so-called spontaneous nucleation to foreign substances such as catalyst residues, oxidatively degraded polymer, or other processing determined impurities. The nucleating agent should be wetted or absorbed by the polymer and considering this instance; a by-product of the cross-linking reaction could act as impurity that can initiate crystallization. Similar results were observed when PCL was cross-linked using Luperox 101. Figure 3-10 represents the TGA results of Ecoflex and LEcoflex.



Figure 3-10: TGA Results of Ecoflex and LEcoflex (cross-linked using 0.1-wt% Luperox 101)

It is evident from Figure 3-10 that LEcoflex degrades faster as compared to Ecoflex. This is confirmed by the fact that at  $450^{\circ}$ C, 56.86% of the Ecoflex polymer is degraded while 73.67% of LEcoflex is degraded. Similar results are observed in the case of cross-linking of PCL. This could be attributed to thermal decomposition in the presence of a radical, as explained by Plage and Schulten (118).

#### 3.3.1.5 Environmental Scanning Electron Microscopy (ESEM) Results

ESEM images of Ecoflex and LEcoflex are shown in Figure 3-11 and Figure 3-12 respectively.



Figure 3-11: ESEM Results of Ecoflex



Figure 3-12: ESEM Results of LEcoflex

It can be observed from Figure 3-11 and Figure 3-12 that the size of the cross-linked gels is of the order of 1-5 microns and hence they are termed as 'micro gels'. The gel particles are uniformly distributed in the polyester matrix. Thus, in this system, the cross-linked polyester microgels reinforce the polyester matrix and provide for increased strength. The use of an extruder (discussed in the next section <u>3.3.2.1</u>) with its high shearing action results in 'microgel' formation as opposed to macrogels.

# 3.3.2 Polyester-talc blending studies

# 3.3.2.1 Effect of screw configuration on extrusion processing of Ecoflex with talc

The screw configuration used for the extrusion processing of Ecoflex with talc consisted of conveying and kneading elements as shown in Figure 3-5. The main function of the kneading blocks is to break and disperse the talc particles in the polyester matrix. The process of dispersion is illustrated in Figure 3-13. In the figure below, (a), (b), (c) and (d) have the same notations as represented in Figure 3-5.



Figure 3-13: Schematic of mixing provided by kneading blocks used for the extrusion processing of Ecoflex with talc

Let 'A' and 'B' represent two particles present inside the extruder. KB 40/5/42 represents a wide kneading block effective for dispersive mixing. Hence, it can be observed that the individual particles A and B break down into many smaller particles respectively in zone 1. Zone 2 is merely a conveying zone and the respective particles are conveyed down the length of the extruder. Zone 3 has KB 45/5/14 elements, which are small kneading blocks effective in distributive mixing. Hence, it can be observed that particles A and B are distributed amongst each other in zone 3. Zone 4 has a neutral kneading block represented as KB 90/5/28. A neutral kneading block effectively accomplishes both dispersive and distributive mixing functions. Hence, it can be observed that particles 'A' and 'B' are even further broken down and distributed in zone 4. In zones 5, 6 and 7, the particles are further conveyed and kneaded and finally exit from the die.

### **3.3.2.2 Thermal Analysis Results**

Figure 3-14 and Figure 3-15 represent the DSC scans of Ecoflex/talc (70/30; w/w) and LEcoflex/talc (70/30; w/w) respectively.



Figure 3-14: DSC Results of Ecoflex/talc (70/30; w/w)



Figure 3-15: DSC Results of LEcoflex/talc (70/30; w/w) [LEcoflex made with 0.1wt% Luperox 101]

It is observed from Figure 3-14 and Figure 3-15 that blending with talc reduces the crystallinity of both Ecoflex and LEcoflex. Thus the area under the melting peak of Ecoflex reduces from 13.52 J/g to 3.126 J/g for the Ecoflex/talc blend. Similarly, the crystallinity of LEcoflex reduces from 7.5 J/g to 3.727 J/g for the LEcoflex/talc blend. This effect is similar to the one observed during the cross-linking of Ecoflex. This is explained by the fact that addition of talc particles disrupts the orderliness and hence brings down the crystallinity. Moreover, this crystallization process is enhanced in the presence of talc particles, which act as nucleating agents. This is the reason for the peak

crystallization temperature of the Ecoflex/talc blend being  $78.94^{\circ}$ C while that of pure Ecoflex being  $40.88^{\circ}$ C. It can also be observed that the melting temperature slightly reduces on blending with talc. Thus, while the T<sub>m</sub> reduces by  $8^{\circ}$ C for the Ecoflex/talc blend as compared to pure Ecoflex, it reduces by about  $1^{\circ}$ C for the LEcoflex/talc blend. This is again due to the fact that the size and perfectness of the crystalline domains in the blends are low. Thus, while presence of talc increases the crystallization rates, it brings down the overall crystallinity of the Ecoflex or LEcoflex. Figure 3-16 and Figure 3-17 represent the TGA scans of Ecoflex/talc (70/30; w/w) and LEcoflex/talc (70/30; w/w) respectively.



Figure 3-16: TGA Results of Ecoflex/talc (70/30; w/w)



# Figure 3-17: TGA Results of LEcoflex/talc (70/30; w/w) [LEcoflex made with 0.1wt% Luperox 101]

From Figure 3-16, it can be observed that the degradation profile of Ecoflex is very similar to Ecoflex/talc. This is evident by the fact that 56.86% Ecoflex has degraded while 57.12% of Ecoflex/talc has degraded. From Figure 3-17, it can be observed that the degradation profile of LEcoflex is also nearly similar to LEcoflex/talc. At a temperature of 450°C, while 73.67% of LEcoflex was degraded, only 81% of LEcoflex/talc was degraded. This slight difference in data can be ignored due to processing and instrument errors.

#### 3.3.2.3 Environmental Scanning Electron Microscopy (ESEM) Results

ESEM results of Ecoflex/talc (70/30; w/w) and LEcoflex/talc (70/30; w/w) are shown in Figure 3-18 and Figure 3-19.





Figure 3-18: ESEM Results of Ecoflex/talc (70/30; w/w)



Figure 3-19: ESEM Results of LEcoflex/talc (70/30; w/w)

It can be observed from Figure 3-18 and Figure 3-19 that the talc particles are uniformly distributed in the polyester matrix. The size of the talc particles is less than 10 microns, which makes the visual appearance of films made with these blends devoid of particles. Moreover film processing is very stable and no necking issues are observed.

#### 3.3.2.4 Mechanical Property Results

The tensile test results of films made from Ecoflex/talc blends are shown in Figure 3-20, Figure 3-21 and Figure 3-22.



Figure 3-20: Tensile strength of Ecoflex and LEcoflex blends with talc

From Figure 3-20, it can be clearly seen that the tensile strength values of LEcoflex and Ecoflex are comparable. However, LEcoflex/talc blend exhibits improved tensile strength as compared to Ecoflex/talc blend in the Machine Direction. This is attributed to the presence of "microgel" reinforcing particles, having the same chemical nature as the polyester matrix, thereby leading to a two-phase system with improved properties. Further, in the Transverse direction, the values are comparable. Tensile strength of Ecoflex/talc is lower than pure Ecoflex. This is due to the fact that talc acts as inert filler, lowering the properties. Finally, it must be noted that the tensile strength of LEcoflex/talc is comparable to LEcoflex.



Figure 3-21: Modulus of Elasticity of Ecoflex and LEcoflex blends with talc

From Figure 3-21, it can be noted that modulus increases on addition of filler. Thus, modulus of both Ecoflex/talc and LEcoflex/talc are at least twice higher than plain Ecoflex and LEcoflex respectively. Typically, modulus values are higher in the transverse direction as observed in Ecoflex/talc blend.



Figure 3-22: Break Elongation of Ecoflex and LEcoflex blends with talc

From Figure 3-22, it can be observed that in the machine direction, the break elongation is relatively unaffected on addition of talc. However, in the transverse direction, Ecoflex/talc and LEcoflex/talc show lower values of break elongation as compared to plain Ecoflex and LEcoflex respectively. This is due to the good dispersion and orientation of the fillers in the machine direction. Moreover, LEcoflex and LEcoflex/talc show lower values of break elongation as compared to show lower values of break elongation as compared to Ecoflex and LEcoflex/talc show lower values of break elongation as compared to Ecoflex and LEcoflex/talc show lower values of break elongation as compared to Ecoflex and Ecoflex/talc show lower values of break elongation as compared to Ecoflex and Ecoflex/talc show lower values of break elongation as compared to Ecoflex and Ecoflex/talc show lower values of break elongation as compared to Ecoflex and Ecoflex/talc show lower values of break elongation as compared to Ecoflex and Ecoflex/talc show lower values of break elongation as compared to Ecoflex and Ecoflex/talc show lower values of break elongation as compared to Ecoflex and Ecoflex/talc show lower values of break elongation as compared to Ecoflex and Ecoflex/talc respectively.

The tear and puncture properties of Ecoflex/talc (70/30) blend are explained in Table 3-6 and compared with PE values.

Material	Thickness	Tear (g)	Tear (g)	Puncture	Puncture
	(in)	MD	CMD	Max. (lb <sub>f</sub> )	Ext. (in)
		ASTM D	ASTM D	ASTM F	ASTM F
		1922	1922	1306	1306
LDPE	0.0010-	100-300	-	1.5-3.0	-
	0.0015				
Ecoflex/talc	0.0010-	314.6	485.8	1.47	0.59
(70/30)	0.0015				

Table 3-6: Tear and Puncture properties of Ecoflex/talc (70/30) blend

It can be observed from Table 3-6 that tear and puncture properties of Ecoflex/talc blend are comparable or better than LDPE. This makes these films a good replacement for LDPE in applications such as lawn and leaf compost bags, retail carryout bags etc.

Chapter 4

# POLYESTER-STARCH GRAFT COPOLYMERS BY REACTIVE EXTRUSION

# PROCESSING

# 4.1 BACKGROUND

This section of the work deals with the synthesis of Ecoflex-Starch graft copolymers by reactive extrusion polymerization. Such compositions were deemed suitable for fabricating biodegradable articles like moldings, sheets and films. Both starch and Ecoflex are biodegradable macromolecules and the use of starch can control biodegradation, provide renewable resource utilization and reduce cost. The following aspects will be discussed:

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- Ecoflex-Thermoplastic starch (TPS) graft copolymer
  - Synthesis of Ecoflex-TPS graft copolymer using maleic acid as a transesterification catalyst in a twin-screw extruder.
  - Characterization of the graft copolymer.
  - Mechanical properties of films.
- Ecoflex-Maleated Thermoplastic Starch (MTPS) graft copolymers.
  - Maleation of starch in a twin-screw extruder using maleic acid modifier in the presence of glycerol plasticizer to form starch maleates.
  - o Characterization of MTPS
  - o Synthesis of Ecoflex-MTPS graft copolymers by extrusion processing.
  - o Characterization of the reactive blends.
  - o Mechanical properties of films.

The study specifically addressed the development of Ecoflex-TPS graft copolymers with a focus on the issue of generating covalent linkages between the ester functionalities in Ecoflex and the hydroxyl functionalities in starch. These graft copolymers can be further used to produce viable compositions with useful performance properties. Further, the study focused on modification of starch using maleic anhydride/maleic acid to generate functional groups. Synthesis of Ecoflex-MTPS graft copolymers by extrusion processing was studied. Performance properties of such blends were determined

# 4.1.1 Starch Theory

Starch is the second most abundant carbohydrate in plants after cellulose. It is the main storage polysaccharide in plants and is similar in structure and function to glycogen, which is the main storage polysaccharide in animals. Main sources of commercial starch are maize, potato, wheat, cassava and waxy maize (123). Starch is an anhydroglucose polymer and consists of two distinct molecules, amylose and amylopectin, both containing  $\alpha$ -D-glucose units. Amylose is a linear or sparsely branched polymer of 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 4-1). The chains form a spiral-shaped single or double helix (124).



Figure 4-1: Structure of amylose

In contrast, amylopectin is highly multiple branched with a molecular mass of  $10^7$  to  $10^9$  g/mol. Amylopectin also contains  $\alpha 1 \rightarrow 4$  glucosidic linkages, but has in addition

 $\alpha 1 \rightarrow 6$  glucosidic branching points occurring every 25-30 glucose units. Figure 4-2 shows the structure of amylopectin.



Figure 4-2: Structure of amylopectin

The native starches differ in water content and the ratio of amylose to amylopectin. The amylose contents of most starches, such as wheat, maize and potato starch, are all in the range of 20-30%. However, in waxy starches, the amylose content is as low as 1% (125). Starch occurs naturally in granules. The granules vary in size and shape, depending upon species, and can range from approximately 1 micron to as large as 120 microns. The starch molecules are oriented radially in the granule to form roughly spherical shells. The radial nature of the organization gives rise to the granules' birefringence, resulting in the characteristic *Maltese cross* when observed under cross-polarized light. Wide –angle and small-angle X-ray scattering (WAXS and SAXS) have shown that starch is partially

crystalline. The overall crystallinity of the native starches is about 20-45% (126). The type of native, crystalline structure, labeled as A-, B- or C-type, depends on the starch source. Native A- and B-type crystal lattices consist of double helical, six-fold structures. The difference between the two types is the packing density of the double helices in the unit cell. The B-type structure is described as a more loosely packed hexagonal assembly of the helices with a column of water molecules present in the center of the hexagonal arrangement, whereas in the A-type structure, this column of water is replaced by a double helix. The C-type structure is thought of to be an intermediate between the A and B type structures (127).

As starch-water slurry is heated, a characteristic temperature is reached at which point the granules start to swell rapidly and take in water. This is known as the gelatinization temperature T (G). Below T (G), optical properties such as the birefringence and X-ray pattern of the starch granules are retained. Irreversible swelling of the starch granules occurs when an aqueous starch suspension is heated above T (G). Water penetrates the amorphous regions consisting of amylose and the branching points of amylopectin. During this process, amylose, the more soluble fraction of the starch granule, leaches into the surrounding water where it can eventually form a gel upon cooling (128). The disruption of the crystalline regions is followed by a further uncoiling of the double helices until the granular spherulite structure is partially or completely destroyed. Figure 4-3 represents diagrammatically the swelling process.

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Figure 4-3: Swelling of Starch granules

The gelatinization and melting process are dependent on the water content. A single peak, denoted as the gelatinization endotherm (G), is observed at water content above 66% (w/w). At water content below 66%, a shoulder appears at higher temperatures, denoted as a melting endotherm (M). At very low water contents, the G endotherm disappears and only the M endotherm is observed (129,130).

As the starch slurry is continually heated, the starch paste viscosity will begin to drop. Also, excessive shear of a starch paste will disrupt the swollen granules and eventually cause the viscosity to drop. This type of starch termed as "destructurized starch" (DSR) can be used for the production of several useful biomaterials. U.S. Patent No 5,095,054 to Lay et al., discloses the use of water as a plasticizer for starch in order to make the material processable in for example an extruder. The applicability of this starch is limited because of degradation due to water loss at elevated temperatures. At higher water content, the vapor pressure of water exceeds atmospheric pressure and water escapes leaving a brittle foamy material with a  $T_g$  above processing and decomposition temperatures with bad thermoplastic properties. The behavior of DSR is glassy and materials can only be processed by the addition of water or other plasticizers. Thermoplastic starch (TPS) is also described as 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 temperatures and pressure. Some of the common plasticizers used are glycerol, ethylene glycol, polyols etc. From the description above, it has to be concluded that the difference between DSR and TPS is still not well defined. DS is also entitled as TPS when it can be processed by any of the known thermoplastic processes such as extrusion, injection molding, blow molding and compression molding into shaped forms without the addition of extra plasticizers.

Plasticization of starch in an extruder using glycerol as the plasticizer breaks the hydrogen bonds, and disrupts the granular crystalline organization. It further releases the amorphous polymer chains with  $\alpha 1 \rightarrow 4$  and  $\alpha 1 \rightarrow 6$ linkages. Figure 4-4 and Figure 4-5 shows the ESEM pictures of starch and plasticized starch respectively.



Figure 4-4: ESEM image of starch



Figure 4-5: ESEM image of thermoplastic starch

X-ray diffractogram of regular corn starch and plasticized starch is shown in Figure 4-6.



Figure 4-6: X-Ray diffractogram results of starch and thermoplastic starch

As shown in Figure 4-6 (a), two single peaks at  $15^{\circ}$  and  $23^{\circ}$  and the double peak at  $17^{\circ}$  is characteristic of A type crystals in starch. On plasticization, the characteristic starch peaks disappeared resulting in new peaks at  $13^{\circ}$  and  $21^{\circ}$ . These new peaks obtained are evidence of crystalline domains formed by retrogradation of the amorphous chains (131).

# 4.1.2 Starch blends with polyesters

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 inert filler (132,133), typically in its native, unmodified state, which is generally water insoluble, granular material. Ramsay et al. (134) studied blends of granular starch with P (HB-co-HV). The inclusion of 25-wt% granular starch was reported to result in a composition with a tensile strength of about 60% 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 of the polymer granule interface. In such cases, the starch granules will normally behave as any other solid particulate filler and will contribute little, if any, in terms of improving 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 gelatinized dried, and then ground into a powder may also be added as particulate filler. Although starch may be added as filler, its more interesting and technologically challenging uses have been in the area of using starch as a binder, as a thermoplastically processable constituent within thermoplastic polymer blends, and as a thermoplastic material by itself. While native starch does not typically behave as a thermoplastic material by itself, it is thermoplastic in the presence of a plasticizer when heated and sheared. 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 to Stepto et al. and U.S. Patent 5,405,564 to Stepto et al. Lately, there have been considerable publications in the use of thermoplastic starch (TPS) as a component in multi phase blends (135-139). Still others have manufactured thermoplastic starch blends in which native starch is initially blended with a small quantity of water and a less volatile plasticizer such as glycerin in order to form starch melts that are subjected to a degassing procedure prior to cooling and solidification in order to remove substantially all of the water therefrom. Examples of such patents include U.S. Patents 5,412,005, 5,280,055, 5,288,765, 5,262,458, 5,462,980 and 5,512,378 to Bastioli et al. Although many have attempted for years to discover the "perfect" starch/polymer blend that would yield an environmentally sound polymer while, at the same time, fulfilling desired mechanical and cost criteria, such a combination has been difficult to achieve. The reason for this is that the emphasis has been on finding the optimal polymer or mixture of polymers and other admixtures in order to thereby "optimize" the properties of the starch/polymer blend. One drawback is that most of the polymers and other admixtures are themselves significantly more expensive than starch, which tends to increase the cost of such polymer blends compared to starch melts. Another drawback is that such additives will only be able to marginally alter the mechanical properties of the starch/polymer blends when viewed from a materials science perspective. Hence the thermodynamic incompatibility between the starch and the polyester at the molecular level leads to the poor performance properties of such materials. The theory underlining incompatible blends is discussed in more detail in

the next section. There is also considerable discussion related to processes and methods needed to achieve efficient compatibilization.

### 4.1.2.1 Incompatible Blends

Polymer blends have become an important subject of scientific investigation in recent years because of their growing commercial importance (140). Broadly classified, the two types of polymer blends are homogeneous (i.e., miscible or compatible) blends and heterogeneous (i.e., immiscible or incompatible) blends. In the case of homogeneous 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 (141) is explained in equation (4.1) as follows:

$$\frac{1}{T_g} = \frac{\Phi_1}{T_{g_1}} + \frac{\Phi_2}{T_{g_2}}$$
(4.1)

Here  $T_{g_1}$  and  $T_{g_2}$  are the glass transition temperatures of the components 1 and 2 respectively, and  $\Phi_1$  and  $\Phi_2$  are the volume fractions of components 1 and 2 in the blend respectively.

Heterogeneous polymer blends, on the other hand, have many interrelated variables that affect their rheological behavior, processability, and the mechanical/physical properties of the finished product. For instance, the method of blend preparation controls the morphology of the blend (e.g., the state of dispersion, the size of the dispersed phase, and the dispersed phase size distribution), which in turn controls the rheological properties of the blend. On the other hand, the rheological properties strongly dictate the choice of processing conditions, which in turn strongly influence the morphology.

Most of the polymer pairs are not thermodynamically miscible and so exist in two different phases in the polymer blend. This breakdown into two phases creates an interface, which might lead to poor performance of the blend system. Poor adhesion also produces very low mechanical properties due to poor stress transfer between phases and hinders the formation of highly structured morphologies. 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 equation (4.2).

$$N_c = (Experimental Probe size)/(Domain sizes of phases)$$
 (4.2)

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; when  $N_c \rightarrow 1$ , and when  $N_c \rightarrow 0$ , the system is incompatible. (142, 143, 144).

Incompatible polymer blends can be organized into a variety of morphologies. Many properties, and subsequently uses, of a blend depend critically on the nature of this arrangement of the two phases. One phase may be dispersed in a matrix of the other, and in this case the matrix phase dominates the properties. A parallel arrangement allows both phases to contribute to many properties in direct proportion to their composition in the blend, but this is a nonisotropic structure since perpendicular to this direction the system may represent a series arrangement with properties that disproportionately favor one phase. Most incompatible blends investigated to date 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 4-7 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 (145).



Figure 4-7: Effect of composition and viscosity on phase morphology

# 4.1.2.2 Compatibilization Theory

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. This leads to the following conditions:

- Poor interfacial adhesion
- Difficulty of attaining the desired degree of dispersion
- Poor mechanical properties.

In general, two component polymer mixtures can be described by the following equation (4.3)

$$P = P_1 w_1 + P_2 w_2 + \Delta P^E (w)$$
 (4.3)

In equation (4.3), P is the property of the blend, P<sub>1</sub> and P<sub>2</sub> are the property values of the components,  $w_1$  and  $w_2$  are the mass fractions of components 1 and 2 and  $\Delta P^E(w)$  is an excess term, which is dependent on the composition under consideration. If  $\Delta P^E(w)$  equals zero, there is an additive result, and the property of the blend is the weighted arithmetic average of the constituents' properties. For polymer alloys, however, the compatibilization achieved results in positive values of  $\Delta P^E(w)$ , which means that the modulus of the polymer combination is better than the weighted arithmetic average of the constituents of the transfer that the modulus of the polymer combination is better than the weighted arithmetic average of the constituents of the transfer that the modulus of the polymer combination is better than the weighted arithmetic average of the constituents' properties for obtaining this effect of compatibilization.

The primary way to improve interfacial adhesion is to use a compatibilizing agent such as a block or graft copolymer. The compatibilizer added stabilizes the morphology by lowering the interfacial tension between the two phases and thus improves the properties of the blend. These graft or block copolymers can be formed in situ during the blend preparation by using polymers containing reactive functional groups. The blending is performed under the conditions that promote the reaction. This method is commonly known as 'reactive blending'. The reactivity of the functional groups is an important parameter in reactive blending. Most of the blends are commercially prepared in an extruder. The functional groups should react to form the required concentration of graft or block copolymer in the short residence times typical of extrusion processes. From this point of view, a cyclic anhydride group may react more quickly than the carboxylic group because of its higher reactivity. Anhydride functionality can be incorporated into a polymer chain by copolymerization or grafting of anhydrides like maleic anhydride. If a reaction occurs between the compatibilizer and the blend components, it will improve adhesion tremendously. The adhesive strength resulting from chemical bonding is about 35 times greater than that resulting from Van Der Waals attraction. In order for a reaction to occur, the components of the blend need to be functionalized, i.e. specific segments need to be incorporated on the polymer chain that can react with the copolymer. When the adhesion between two polymers is due to the reaction between one of the polymers and a functional group contained in the other, then the adhesive strength is given by the expression as shown in equation (4.4).

$$f = aC^{b} \tag{4.4}$$

where f is the adhesive strength, C is the concentration of the functional group, and a and b are positive constants. There are also examples in literature where the compatibilizer added does not undergo reaction with the blend components (147,148). In this study, two
methods were employed to achieve this compatibilization as explained above. The first method was to reactively graft a hydrophilic polymer such as starch onto Ecoflex polyester backbone using trans-esterification chemistry. The second method was to maleate starch to form maleated thermoplastic starch and then use the new maleated starch to form graft copolymers with Ecoflex. Prior work in the areas of reactive blending and starch derivatization is explained in sections 4.1.3 and 4.1.4 respectively.

#### 4.1.3 Starch-Polyester Reactive Blends

As explained in the previous sections, the thermodynamic incompatibility between the starch and the polyester often leads to poor performance of these blends. In order to improve this drawback, graft copolymerization of vinyl monomer on the starch backbone was used to modify starch. Fanta and Bagley have reviewed the synthesis and discussed some applications of starch graft copolymers (149,150). Otey et al. (151,152,153) blended starch with poly (ethylene-co-acrylic acid) (EAA). In these papers, the authors suggested the formation of hydrogen bonds between the carboxylic group in EAA and the hydroxyl group in starch. Increasing the level of starch decreased the percentage elongation of the film and increased the diffusion rate of water. Similar complexes like EAA can also be formed with the hydroxyl groups of the polyethylene-vinyl alcohol (EVOH) copolymer. They report a reaction between the anhydride group in the synthetic polymer with the –OH groups of starch. Bloembergen et al. (144) have reported on blends and alloys containing lignocelluloses like starch, cellulose acetate etc. U.S. Patent 5,314,934 to Tomka et al. provides a process to produce a polymer mixture essentially

consisting of thermoplastically processable starch (up to 70-wt %). During this mixing process, an esterification reaction takes place between the maleic anhydride groups in the terpolymer with free hydroxyl groups in the starch. These reactive blends can be blown into film with properties comparable to LDPE. U.S. Patent 5,234,977 to Bastioli et al. discloses a material used for the production of biodegradable articles in film, sheet or fiber form, which can be produced by extrusion from a molten mass that includes a synthetic thermoplastic polymer and a destructured starch to which a boron containing compound such as boric acid has been added. Narayan et al. (154) have grafted starch onto aliphatic polyesters. They report on the fact that when starch is not plasticized, only surface grafting is possible. However, when starch is plasticized, the hydroxyl groups are freely available for reaction, thus enhancing the reactivity.

#### 4.1.4 Starch Derivatives

The term "starch derivative" includes those modifications, which change the chemical structure of some of the D-glucopyranosyl units in the molecule. Derivatization of starch is generally conducted to modify the gelatinization and cooking characteristics of granular starch, to decrease the retrogradation and gelling tendencies of amylose-containing starches and to enhance hydrophilic or hydrophobic characteristics. Starch can also be derivatized to increase its reactive capability in further downstream blending operations with other biodegradable polyesters. A starch derivative is fully defined by a number of factors: plant source (corn, waxy maize, potato); amylose to amylopectin ratio; Degree of Polymerization; type of derivative (ester, ether etc.); nature of the substituent

group (acetate etc.); Degree of Substitution (DS) or molar substitution (MS) and physical form (granular, pregelatinized).

Most commercially produced derivatives have a DS, generally less than 0.2. The DS is a measure of the average number of hydroxyl on each D-glucopyranosyl unit, which is derivatized by substituent groups. DS is expressed as moles of substituent per D-glucopyranosyl unit. Since the majority of the glucose units in starch have three hydroxyl groups available for substitution, the maximum possible DS is three. DS can be expressed using the equation (4.5) as shown below; where W is the weight-% of the substituent (based on the total weight) and M is the molecular weight of the substituent.

$$D.S. = \frac{162 * W}{100 * M - (M - 1) * W}$$
(4.5)

Modified starch products have low DS levels. They were primarily designed to alter their solution properties for food applications or adhesion to paper. Acetylated starches, for example, have been known for more than 100 years. Starch triacetates were prepared earlier by carrying out the acetylation in acetic-anhydride-pyridine solution. This procedure was impractical to scale up due to the high costs involved with pretreatment and recovery of pyridine (155). More recently (156), cornstarch was fully acetylated by reacting with fourfold quantities of acetic anhydride at 123°C for 5 hours. The reaction was carried out in an alkaline medium of sodium hydroxide. The solubility of these starch acetates is dependent upon the acetyl value, the degree of degradation, polymerization of the ester, the type of starch and the nature of the solvent. Undegraded starch acetates are soluble in relatively few solvents, although many reagents cause the formation of gels. Acetyl derivatives of starch give molded products, which are brittle, clear and

transparent. Dispersions of triacetates in dichloromethane gave clear and flexible films with tensile strengths in the range of 3500 psi (157).

Highly acetylated starches, historically, were of some interest because of their organic solvent solubility and their thermoplasticity for film and fiber applications analogous to thermoplastic cellulose esters. In spite of this development, high DS starch esters have not been developed commercially because they could not compete with similar cellulose derivatives in terms of strength and cost. Such high DS starch esters are characterized by their crystalline properties exhibiting clear melt transitions (144).

Cyclic dibasic acid anhydrides such as succinic anhydride yield starch esters containing a free carboxylate group that increases the waterholding capacity of the product (158). The same chemistry could be carried out with maleic anhydride to yield the maleate half ester. The reaction schemes are depicted below in Figure 4-8. Treatment of a starch suspension with a cyclic dicarboxylic acid anhydride containing a hydrophobic substituent group yields products with emulsion stabilizing properties (159).



Figure 4-8: Starch Reaction with half-esters of dicarboxylic acids

Most of the modifications of starch using cyclic anhydrides are disclosed in patents. This intermediate reaction product was further heated, after the addition of succinic anhydride, for 2 hours at the same temperature to give starch propionate succinate. These starch esters have value as dispersants in coatings replacing commercially available paint containing dispersants. U.S. Patent 3,732,207 discusses the production of starch esters by heating starch with maleic or succinic anhydride at 100-155 <sup>o</sup>C in the presence of 0.5-15% moisture to give a product with degree of substitution (DS) 0.02 to 0.04.

While all of the above work is related to the production of starch esters in batch, starches can be acylated on extrusion with cyclic anhydrides in the presence of carbonate buffers to yield the corresponding starch esters. Tomasik et al. (160) reacted corn starches in extruders containing varying amounts of moisture (18, 20 and 30%) with succinic, maleic and phthalic anhydrides. Carbonate buffer, either pH 8 or pH 9 was added as a medium during extrusion. It is demonstrated that extrusion of starch with cyclic anhydrides in alkaline medium presents a facile method of preparation of anionic starches of hydrophobic character based. However, based on up-to-date collected experiences, this method apart from some advantages seems to have several limitations. They result from the chemistry of the process as well as from construction of extruder. The fast, cheap, clean, waste less process together with a possibility of a large production of such kind starches is an advantage of this method. However, due to the high viscosity of the thermoplastic (TPS) melt, it is extremely difficult to extrude samples containing less than 25% moisture at temperatures of around 130°C. In all of the above studies, grafting of reactive moieties onto the starch backbone in the melt phase has not been conducted.

In this study, starch was maleated in the melt phase using maleic anhydride/maleic acid in a twin-screw co-rotating extruder in the presence of glycerol plasticizer. These starch maleates were further reactively blended with Ecoflex polyester in the melt phase to form Ecoflex-Maleated Thermoplastic Starch graft copolymers to be used in blown film applications.

#### 4.2 EXPERIMENTAL

Biodegradable graft copolymers of Ecoflex and starch were synthesized by reactive extrusion processing. The starch component in the copolymer was Thermoplastic Starch (TPS) in one case and Maleated Thermoplastic Starch (MTPS) in another. Both TPS and MTPS were synthesized in a twin-screw co-rotating extruder using glycerol plasticizer. The details of the experimental protocols to make TPS, MTPS and the graft copolymers will be elucidated. Further, characterization of the products along with the mechanical properties of films made from the graft copolymers will be discussed.

#### 4.2.1 Materials and Equipment

Granular starch was obtained from Cargill-grade SMP 1100, un-modified corn-starch with equilibrium moisture content of about 12 percent (w/w). Ecoflex polyester [poly butylene (adipate-co-terephthalate)] was obtained from BASF. Anhydrous glycerol [2136-03], 99.9% assay was obtained from J.T. Baker. Maleic anhydride or 2, 5

Furandione [108-31-6] was obtained from Sigma. Maleic acid was obtained from J.T. Baker. Luperox 101 [78-63-7] was obtained from Aldrich Chemicals. All the above materials were used as obtained.

A twin-screw co-rotating CENTURY extruder having a length: diameter ratio (L/D) of 40 and a screw diameter of 30 mm was used for the plasticization as well as the reactive blending chemistries. The extruder was electrically heated and cooled using circulating water. The screw elements needed for the screw configuration were also obtained from CENTURY. The auxiliary equipment included a water bath to cool the extrudate and a pelletizer to cut the strand into small pellets.

#### 4.2.2 Ecoflex-Thermoplastic Starch graft copolymers

In this section, experimental details on reactive extrusion processing of Ecoflex-TPS graft copolymers along-with the characterization by Soxhlet extraction are outlined.

#### 4.2.2.1 Synthesis of Ecoflex-TPS graft copolymers by reactive extrusion processing

The synthesis of Ecoflex-TPS graft copolymers was accomplished in a twin-screw corotating CENTURY extruder using maleic acid as a trans-esterification catalyst. TPS was produced by plasticization of regular corn-starch using glycerol (20-wt %) as a plasticizer in the same extruder. Maleic acid was ground to a fine powder using a mortar and pestle and pre-blended with the Ecoflex polyester before being fed to the feed port of the extruder. The concentration of maleic acid used was 1-wt% with respect to the total concentration. Meanwhile, TPS, previously oven dried overnight at 75°C, was ground to a fine powder and fed using an external feeder to the feed port of the extruder. The feeder rates were adjusted accordingly to obtain a ratio of 70:30 (Ecoflex + Maleic acid): TPS. The temperature profile and the screw configuration used are shown in Table 4-1 and Figure 4-9 respectively. In Figure 4-9, the entire screw configuration 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 maleic acid and water. The extruded strand was cooled using a water bath and pelletized in line. The pellets were dried in an oven overnight at 75°C before being blown into a film.





copolymers

## Table 4-1: Extrusion Processing conditions for the synthesis of Ecoflex-TPS graft

## copolymers

ZONE	SET	ACTUAL	UNITS
ZONE1	15	70	°C
ZONE2	95	99	°C
ZONE3	125	122	°C
ZONE4	145	149	°C
ZONE5	160	170	°C
ZONE6	165	192	°C
ZONE7	165	196	°C
ZONE8	165	193	°C
ZONE9	150	185	°C
DIE	145	153	°C
MELT TEMP	153	°C	
MOTOR SPEE	254	RPM	
TORQUE	67	%	
PRESSURE	92	Psia	
FEEDER SPEED, CENTURY (E	135 (~8 lb/hr)	%	
FEEDER SPEED,		%	
FEEDER SPEED, EX	0.80 (3.4 lb/hr)	%	

#### 4.2.2.2 Soxhlet Extraction Studies

Ecoflex-TPS graft copolymer was extracted in Dichloromethane (DCM) solvent. Around 2-3 grams of the sample was accurately weighed into a cellulose extraction thimble (33 mm x 94 mm) and placed into the thimble holder. The evaporated solvent condensed into the thimble, containing the sample. The extraction was run for 24 hours. After extraction, the thimble along-with the sample was removed and dried to constant weight. FTIR and thermal analysis characterizations were conducted on the film sample obtained by solvent casting the extracted graft copolymer solution.

#### 4.2.3 Ecoflex-Maleated thermoplastic starch graft copolymers

In this section, experimental details on maleation of starch using maleic anhydride/ maleic acid in presence of glycerol plasticizer by reactive extrusion processing are outlined. Further, characterization techniques pertaining to analysis of MTPS are explained. Finally, experimental details pertaining to the synthesis and characterization of Ecoflex-MTPS graft copolymers are outlined.

#### 4.2.3.1 Maleation of starch by reactive extrusion processing

Regular silver medal pearl corn-starch, obtained from Cargill Inc. was reactively modified using maleic anhydride/maleic acid in a twin-screw co-rotating CENTURY extruder with a screw diameter of 30 mm and a L/D ratio of 40. Maleic anhydride/acid (MA) was ground to a fine powder using a mortar and pestle and mixed with the starch (800 gm starch + [20 or 40 or 80 gm] maleic anhydride/acid) using a kitchen blender for 15 minutes before being fed to the feed port of the extruder. Glycerol was mixed with 2,5-Bis (tert-butylperoxy)-2,5-dimethylhexane (Luperox 101) {200 gm glycerol + 1.6 gm Luperox 101} and pumped to the extruder using a peristaltic pump. The relative rates of the starch/MA mixture to the glycerol/Luperox 101 mixtures were maintained at 80:20. The calibration curve for the glycerol pump is shown in Figure 4-10. The screw configuration used for the maleation consisted of conveying and kneading elements as shown in Figure 4-9. Water vacuum was applied at the vent port to remove the unreacted maleic acid/water mixture. Due to the low viscosity of the extruded strand, MTPS was collected in aluminum pans and ground to a fine powder. Ground MTPS was stored in an oven at 50°C. The extrusion processing conditions for the reactive maleation is outlined in Table 4-2.



Figure 4-10: Calibration curve for Glycerol pump used in the reactive maleation of

starch

ZONE	SET	ACTUAL	UNITS
ZONE1	15	39	°C
ZONE2	95	103	°C
ZONE3	125	122	°C
ZONE4	145	146	°C
ZONE5	160	157	°C
ZONE6	165	161	°C
ZONE7	165	167	°C
ZONE8	165	164	°C
ZONE9	150	156	°C
DIE	145	147	°C
MELT TEMP.		148	°C
MOTOR SPEED		125	RPM
TORQUE		35	%
PRESSURE		92	Psia
FEEDER SPEED, CENTURY		155 (Rate = 12.3 lbs/hr)	%
GLYCEROL PUMP		0.1 (Rate = 3.07 lbs/hr)	%
FEEDER SPEED, EXT		-	%

 Table 4-2: Extrusion processing conditions for the reactive maleation of starch using

 maleic anhydride/maleic acid modifier in the presence of glycerol plasticizer

## 4.2.3.2 Synthesis of Ecoflex-MTPS graft copolymers by reactive extrusion processing

The synthesis of Ecoflex-MTPS graft copolymers was accomplished in a twin-screw corotating CENTURY extruder. MTPS was produced by reactive plasticization of regular corn-starch using MA modifier and glycerol (20-wt%) plasticizer as explained above. MTPS, previously oven dried overnight at  $75^{0}$ C, was ground to a fine powder and fed using an external feeder to the feed port of the extruder. The feeder rates were adjusted accordingly to obtain a ratio of 70:30 (Ecoflex: MTPS). The temperature profile and the screw configuration used are shown in Table 4-3 and Figure 4-9 respectively. In Figure 4-9, the entire screw configuration 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 maleic acid and water. The extruded strand was cooled using a water bath and pelletized in line. The pellets were dried in an oven overnight at  $75^{0}$ C before being blown into a film.

## Table 4-3: Extrusion processing conditions in the synthesis of Ecoflex-MTPS graft

## copolymers

ZONE	SET	ACTUAL	UNITS
ZONE1	15	37	°C
ZONE2	95	96	°C
ZONE3	125	132	°C
ZONE4	150	150	°C
ZONE5	160	164	°C
ZONE6	165	176	°C
ZONE7	170	173	°C
ZONE8	170	169	°C
ZONE9	170	169	°C
DIE	150	152	°C
MELT TEMP.		155	°C
MOTOR SPEED		150	RPM
TORQUE		75	%
PRESSURE		95	Psia
FEEDER SPEED, CENTURY (Ecoflex)		145 (Rate = 5.5 lbs/hr)	%
FEEDER SPEED, MINI			%
FEEDER SPEED, EX	T (MTPS)	92 (Rate = 2.4 lbs/hr)	%

#### 4.2.3.3 Soxhlet Extraction Studies

Ecoflex-MTPS graft copolymer was extracted in Dichloromethane (DCM) solvent. Around 2-3 grams of the sample was accurately weighed into a cellulose extraction thimble (33 mm x 94 mm) and placed into the thimble holder. The evaporated solvent condensed into the thimble, containing the sample. The extraction was run for 24 hours. After extraction, the thimble along-with the sample was removed and dried to constant weight. FTIR and thermal analysis characterizations were conducted on the film sample obtained by solvent casting the extracted graft copolymer solution.

#### 4.2.3.4 Fourier Transformed Infrared Spectroscopy (FTIR) Studies

FTIR analysis was conducted on samples of MTPS and the graft copolymers using Perkin Elmer. MTPS was extracted using THF in a Soxhlet extraction unit, dried and ground to a fine powder. 1% MTPS 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 FTIR to obtain the spectrum. A background scan was also conducted with just the KBr pellet, which was subtracted from the total spectrum to obtain just the sample spectrum. Films obtained by solvent casting the graft copolymer solution were directly introduced into the sample chamber to obtain the FTIR spectrum of the graft copolymer.

#### 4.2.3.5 Thermal Analysis Studies

A high resolution Differential Scanning Calorimeter (DSC) 2920 from TA Instruments was used to determine the melting temperature  $(T_m)$  of the MTPS and the graft copolymer samples. Nitrogen was used as the purge gas at 50 ml/min. MTPS samples were heated to 200  $^{0}$ C at the rate of 10  $^{0}$ C per minute, cooled to -50  $^{0}$ C and then reheated to 200  $^{0}$ C. 2<sup>nd</sup> scan data was taken for analysis. The graft copolymer samples were heated from 0 $^{0}$ C to 200  $^{0}$ C at the rate of 10  $^{0}$ C per minute, cooled and re-heated again.2<sup>nd</sup> scan data was plotted.

A high resolution Thermal Gravimetric Analyzer (TGA) 2950 from TA Instruments was used to determine the degradation temperature of the MTPS and the graft copolymer samples. Nitrogen was used as the purge gas with the sample purge being 60 ml/min and the balance purge being 40 ml/min. The samples were heated to 550°C at the rate of 20°C per minute.

#### 4.2.3.6 Intrinsic Viscosity Studies

The intrinsic viscosity of starch, TPS and the MTPS samples were determined using a Cannon Ubbelohde viscometer (size 0B) in DMSO solvent at 25<sup>o</sup>C. Details on the process are explained clearly in Chapter 2, section 2.2.6.

#### 4.2.3.7 Blown Film Studies

Films of the graft copolymers made from both TPS and MTPS were made using a Killion single-screw blown film unit. The screw diameter was 25.4 mm with 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 4-4.

Table 4-4: Blown Film Processing Conditions for Polyester-Starch graft copolymers

	Die 3	Die 2	Die 1	Adaptor	Clamp Ring	Zone 3	Zone 2	Zone 1
Set ( <sup>0</sup> F)	70	350	355	360	360	395	395	300
Actual ( <sup>0</sup> F)	73	351	358	357	360	380	395	300

Melt ( <sup>0</sup> F)	364
Screw Speed (RPM)	12.4
FPM (ft/min)	5-6
Pressure (psi)	500-1000

#### 4.2.3.8 Mechanical Property Determination

Tensile properties of the films were determined using INSTRON Mechanical Testing Equipment fitted with a 100 lbs load cell. The crosshead speed was 1 inch per minute. Rectangular film samples, 4'x1' dimension were conditioned at 23<sup>o</sup>C and 50% Relative Humidity for 40 hours before being tested according to ASTM D-882 testing.

#### 4.3 **RESULTS AND DISCUSSION**

The results of various aspects of Ecoflex-TPS and Ecoflex-MTPS graft copolymers discussed in previous sections will be presented. Trans-esterification reaction chemistry leading to the synthesis of a graft copolymer will be explained. Soxhlet extraction results of Ecoflex-TPS graft copolymers along with the FTIR analysis and TGA results confirming the existence of a graft copolymer will be discussed. Mechanical properties of films, produced by blown film processing will be presented and discussed. Processing and characterization results of MTPS will be evaluated. Finally, results pertaining to synthesis and characterization of Ecoflex-MTPS graft copolymers will be discussed. Note that Figure 4-12, Figure 4-18, Figure 4-19 and Figure 4-28 are presented in color.

#### 4.3.1 Ecoflex-TPS graft copolymers

# 4.3.1.1 Trans-esterification Reaction Chemistry in the Synthesis of Ecoflex-TPS graft copolymers

Acid-catalyzed trans-esterification reaction chemistry is shown in Figure 4-11. Acid catalyzed esterifications cause significant degradation of the starch. In this particular case, it would be expected to cause hydrolysis of the polyester in addition to the starch.



Figure 4-11: Acid-catalyzed trans-esterification chemistry in the synthesis of

**Ecoflex-TPS graft copolymers.** 

#### 4.3.1.2 **Proof of Grafting by Soxhlet Extraction**

The aim of the extraction was to selectively remove the unreacted Ecoflex from the Ecoflex-TPS graft copolymers. However, after 24 hours of extraction, the graft copolymer was completely extracted out and the solution in the round -bottomed flask was murky. When this solution was cast, a transparent film was obtained. This proves that Ecoflex and TPS are covalently linked. It is this covalent bonding which makes the graft copolymer extractable in Dichloromethane (solvent wherein Ecoflex is soluble, but TPS is not). However, due to the insolubility of TPS in the solvent, the graft copolymer forms a colloidal dispersion and not a clear transparent solution. The Soxhlet extraction results of Ecoflex-TPS graft copolymers are shown in Table 4-5. From Table 4-5, it is clear that when maleic acid is not used as a catalyst, no reaction occurs, which is confirmed by the fact that the amount of polyester (Ecoflex or LEcoflex) extracted is close to the amount of polyester initially present in the blend. This proves that the TPS component in the blend is not attached covalently and only acts as particulate filler. However, for an Ecoflex/TPS/Maleic acid system, 97% of the material taken is extracted out, suggesting complete reaction and formation of covalent linkages between the ester functionalities in the Ecoflex backbone and hydroxyl groups in TPS.

System	Polyester	Starch component	Amount	Percent
	(Ecoflex or	(Granular starch or	extracted	extracted
	LEcoflex)	thermoplastic	(gm)	(%)
	initially	starch) initially		
	present	present		
	(gm)	(gm)		
Ecoflex/TPS (70/30;	1.2075	0.5175	1.2595	73
w/w)				
Ecoflex/TPS/Maleic	1.3812	0.5722	1.9074	97
acid (70/29/1)				

Table 4-5: Soxhlet Extraction results of Ecoflex-TPS graft copolymers

### 4.3.1.3 Proof of Grafting by FTIR Analysis

The extracted Ecoflex-TPS graft copolymer solution was cast into a film and the FTIR spectrum is shown in Figure 4-12.



Figure 4-12: FTIR Spectrum of Ecoflex-TPS graft co-polymers

From Figure 4-12, it can be observed that the graft copolymer exhibits the carbonyl stretch peak at 1720 cm<sup>-1</sup>, similar to pure Ecoflex and the extracted Ecoflex/TPS blend. Further, the ester C-O stretch at 1270 cm<sup>-1</sup> is observed in the graft copolymer but not in TPS. The graft copolymer also exhibits a peak between 3200-3400 cm<sup>-1</sup> corresponding to –OH stretch. This peak is also observed in TPS, but not in the other two. Moreover, primary alcohols peak (1025-1060 cm<sup>-1</sup>) is seen in TPS and the Ecoflex-TPS graft copolymer, but not in the other two. All of the above data confirm the true existence of a graft copolymer. Finally,  $\delta$  (O-H) bend of water at 1640 cm<sup>-1</sup> is observed in TPS and not in any of the other materials.

#### 4.3.1.4 Proof of grafting by Thermal Gravimetric (TGA) Analysis

The TGA results of solvent cast films of extracted Ecoflex-TPS graft copolymers are shown in Figure 4-13 as shown below.



Figure 4-13: TGA Results of Ecoflex-TPS graft copolymers

From Figure 4-13, it is worthwhile to note that without the addition of maleic acid as a trans-esterification catalyst, i.e. for the Ecoflex/TPS blend, no degradation corresponding to starch is observed from the extracted portion, confirming the fact that only the

unreactedpolyester is extracted out. However, for the Ecoflex-TPS graft copolymer, starch degradation along-with the polyester (Ecoflex) is evident. This confirms the existence of a graft copolymer wherein the Ecoflex polyester is covalently bonded to TPS.

#### 4.3.1.5 Mechanical Properties Results

The tensile property results of Ecoflex-TPS graft copolymers are schematically shown in Figure 4-14, Figure 4-15 and Figure 4-16.



Figure 4-14: Tensile strength results of Ecoflex-TPS graft copolymers



Figure 4-15: Modulus of elasticity results of Ecoflex-TPS graft copolymers



Figure 4-16: Break elongation results of Ecoflex-TPS graft copolymers

It is observed from Figure 4-14 that the tensile strength values of Ecoflex-TPS graft copolymer, containing around 30% TPS, exhibit almost a six fold decrease as compared to pure Ecoflex polyester values. This reduction in tensile strength could be attributed to two reasons:

- Addition of TPS, which possesses poor properties
- Reduction in the molecular weight of Ecoflex due to acid hydrolysis, catalyzed by maleic acid.

The tensile strength values of the graft copolymer are lower than even LDPE values as seen from Figure 4-14.

Modulus of elasticity results, as seen from Figure 4-15, also follow the same trend as the tensile results. It is observed from Figure 4-15 that the modulus values of the graft copolymer are lower than both LDPE and pure Ecoflex. Break elongation values of the graft copolymer (Figure 4-16) are higher than Ecoflex and LDPE. This is due to the chemical covalent linkages, which enable stretching.

#### 4.3.2 Maleated Thermoplastic Starch (MTPS)

This section presents the chemistry and results on reactive extrusion processing of MTPS followed by the subsequent characterization. Characterization techniques include FTIR, Thermal Analysis and Intrinsic viscosity measurements.

#### 4.3.2.1 Starch Maleation chemistry

The maleation of starch using maleic anhydride is shown in Figure 4-17. Alternatively, maleic anhydride could react with water to form maleic acid, which could further react with starch to form the starch maleate. During the process of maleation, there is a reduction in the molecular weight of starch due to the hydrolysis of the starch backbone in the presence of maleic acid.



Figure 4-17: Maleation of starch using maleic anhydride

#### 4.3.2.2 Results on reactive extrusion processing of MTPS

The reactive modification of regular corn- starch using maleic anhydride and maleic acid was accomplished in a twin-screw co rotating CENTURY extruder using glycerol as the plasticizer (18-wt%) and optional Luperox 101 as a free radical initiator. When compared to regular TPS production, the value of torque in the synthesis of MTPS was very low (reduction in molecular weight) due to the acid hydrolysis of starch in the presence of maleic acid. This reduction in molecular weight leads to decrease in melt viscosity values

of MTPS. Due to this, reactive maleation processing can be done at much higher throughputs as compared to the regular thermoplastic processing of starch. Moreover, difficulties in regular corn- starch plasticization, such as, foaming at high throughputs or clogging near the die are prevented during the synthesis of MTPS. However, MTPS is difficult to pelletize due to its reduced viscosity and hence use of rollers to convey the strand is recommended. This strand could then be taken to a grinder to form MTPS powder.

## 4.3.2.3 Proof of reaction of maleic anhydride and maleic acid onto starch by FTIR Analysis

MTPS samples made using maleic anhydride and maleic acid were extracted in THF solvent. Samples from the thimble and solvent (after evaporation of THF) were analyzed. FTIR results of MTPS samples are shown in Figure 4-18 and Figure 4-19.



Figure 4-18: FTIR results of MTPS samples using maleic acid modifier



Figure 4-19: FTIR results of MTPS samples using maleic anhydride modifier

From Figure 4-18 and Figure 4-19, it can be observed that samples from the thimble and the solvent exhibit the carbonyl stretch peak at 1720 cm<sup>-1</sup>. This was not observed in either the pure granular starch or TPS. This proves that the maleic acid and maleic anhydride are covalently linked to the starch backbone. Moreover, from Figure 4-19, since the MTPS samples show no peaks at 1780 cm<sup>-1</sup> corresponding to ring anhydride, it is suggested that the maleic anhydride ring is open. This is expected due to the presence of moisture during extrusion. Further, -OH stretch peak between 3200-3400 cm<sup>-1</sup> is observed in all the four samples.

#### 4.3.2.4 Thermal Analysis Results

DSC results of MTPS are shown in Figure 4-20.



Figure 4-20: DSC Results of MTPS samples

From Figure 4-20, it can be observed that no melting for starch is observed. This is evident as starch degrades before it melts. However, plasticizers in the presence of heat and shear break the hydrogen bonds in starch and destroy the crystalline nature. Thus, a broad melting endotherm is observed in TPS, while two sharp melting endotherms are observed in MTPS. This is attributed to the maleation of starch leading to segments having slightly different melting characteristics. The melting temperatures of MTPS are around 153°C MTPS and are around 10°C higher than TPS. TGA results are shown in Figure 4-21 and Figure 4-22.



Figure 4-21: TGA Results of MTPS samples



Figure 4-22: TGA Results of MTPS samples modified with 2.5%, 5% and 10% maleic acid

From Figure 4-21, it can be observed that MTPS is more stable than either starch or TPS. At a temperature of 350.38<sup>o</sup>C, while 75% and 63% of starch and TPS have degraded respectively, only 58% of MTPS has degraded. Further, TPS and MTPS show additional degradation due to glycerol.

From Figure 4-22, it can be observed that all the MTPS samples show the derivative peak for the degradation of glycerol. Further, MTPS samples modified with 5 and 10% maleic acid show two peaks in the derivative curve for the degradation of starch as opposed to one peak shown by MTPS modified with 2.5% maleic acid. This is due to

the fact that increased maleation leads to the development of fractions having varied degradation characteristics.

#### 4.3.2.5 Intrinsic viscosity Results

The intrinsic viscosity of starch, TPS, MTPS (2.5% maleic anhydride and 0.1% Luperox 101) and MTPS (no Luperox 101) were determined in DMSO solvent and are shown in Figure 4-23 through Figure 4-26. The intrinsic viscosity of starch (Figure 4-23) was around 1.5 dl/g while that of TPS (Figure 4-24) reduced to 1.2 dl/g. However, on maleation without addition of Luperox 101, the intrinsic viscosity of MTPS (Figure 4-25) drastically dropped to 0.27 dl/g. This reduction is attributed to a decrease in molecular weight due to the hydrolysis of starch in the presence of maleic acid. However, on addition of Luperox 101, the intrinsic viscosity (Figure 4-26) increased back to 0.32 dl/g. This increase can be attributed to cross-linking reactions taking place, increasing the molecular weight slightly. Further, k'-k'' for the various plots were found to be close to 0.5.


Figure 4-23: Intrinsic viscosity of regular corn starch



Figure 4-24: Intrinsic viscosity of TPS



Figure 4-25: Intrinsic viscosity of MTPS (2.5% Maleic anhydride)



Figure 4-26: Intrinsic viscosity of MTPS (2.5% Maleic anhydride and 0.1%

Luperox 101)

#### 4.3.3 Ecoflex-MTPS graft copolymers

Trans-esterification reaction chemistry leading to the synthesis of Ecoflex-MTPS graft copolymers will be discussed. The extraction results of Ecoflex-MTPS graft copolymers will be presented. FTIR analysis of films, produced by solvent casting the extracted graft copolymer solution will be evaluated to confirm reactivity. Other characterization techniques such as Differential Scanning Calorimetry (DSC) and Thermal Gravimetric Analysis (TGA) will be presented. Synthesis of blown films of Ecoflex-MTPS graft copolymers, and the effect of varying blown film pressures for different materials will be discussed. Further, mechanical properties of films made with the graft copolymers will be discussed in this section.

# 4.3.3.1 Trans-esterification Reaction Chemistry in the synthesis of Ecoflex-MTPS graft copolymers

Chemistry in the synthesis of Ecoflex-MTPS graft co-polymers is exactly similar to the one showed in Figure 4-11. However, a further trans-esterification reaction between MTPS and the hydroxy terminated polymer formed is possible and is shown in Figure 4-27.



Figure 4-27: Trans-esterification reaction chemistry in the synthesis of Ecoflex-MTPS graft copolymers.

#### 4.3.3.2 **Proof of grafting by Soxhlet Extraction**

As explained in section 4.3.1.1, the aim of the extraction was to selectively remove the unreacted Ecoflex from the Ecoflex-MTPS graft copolymers. The Soxhlet extraction results of Ecoflex-MTPS graft copolymers are shown in Table 4-6. As seen from Table 4-6, almost complete extraction is achieved for Ecoflex/MTPS (70/30 and 60/40) graft copolymers. When this solution was cast, a transparent film was obtained. This proves that Ecoflex and MTPS are covalently linked making the graft copolymer extractable in

Dichloromethane (solvent wherein Ecoflex is soluble, but TPS is not). However, due to the insolubility of TPS in the solvent, the graft copolymer forms a colloidal dispersion and not a clear transparent solution. This result is applicable even to blends containing MTPS made with no peroxide (see row 6 in Table 4-6). However, for the 50/50 and 40/60 blends, only 47% and 38% respectively (close to the respective Ecoflex amount) were extracted out. This confirms the fact that Ecoflex has not reacted with MTPS. Thus, the reaction is also dependent on the relative amounts of the polyester and MTPS phases present. Also, from Table 4-6 (rows 7 and 9), it is clearly seen that when TPS is used instead of MTPS, there is very minimal or no reaction taking place. This suggests that the reaction between the hydroxyl groups in starch and the ester functionalities in Ecoflex occurs only in the presence of a trans-esterification catalyst such as maleic acid. When Ecoflex polyester was extracted out. This could be due to the fact that certain gel (network) portions of the cross-linked polyester are impermeable to chemical reaction.

System	Polyester	Starch	Material	%
	(Ecoflex or	component	extracted	Extracted
	LEcoflex)	(TPS or MTPS)	(gm)	
	initially	initially present		
	present (gm)	(gm)		
Ecoflex/MTPS	1.3510	0.579	1.8878	98
(70/30;w/w)				
Ecoflex/MTPS	1.0682	0.7122	1.7010	96
(60/40;w/w)				
Ecoflex/MTPS	0.7998	0.7998	0.7503	47
(50/50;w/w)				
Ecoflex/MTPS	0.8639	0.5759	0.5513	38.2
(40/60;w/w)				
Ecoflex/MTPS	1.9018	0.8150	2.6530	98
(70/30;w/w) No				
Luperox 101				
Ecoflex/TPS	1.2075	0.5175	1.2595	71
(70/30;w/w)				
LEcoflex/MTPS	3.25	1.748	4.1272	83
(65/35;w/w)				
LEcoflex/TPS	1.0225	0.4382	1.0602	73
(70/30;w/w)				

### Table 4-6: Soxhlet Extraction results of Ecoflex-MTPS graft copolymers

#### 4.3.3.3 Proof of grafting by FTIR Analysis

The extracted Ecoflex-MTPS graft copolymer solution was cast into a film and the FTIR spectrum is shown in Figure 4-28.



Figure 4-28: FTIR Results of Ecoflex-MTPS graft copolymers

From Figure 4-28, it can be observed that the Ecoflex-MTPS graft copolymer exhibits the carbonyl stretch peak at 1720 cm<sup>-1</sup>, similar to pure Ecoflex. Further, the ester C-O stretch at 1270 cm<sup>-1</sup> is observed in the graft copolymer but not in granular corn starch. The graft copolymer also exhibits a peak between 3200-3400 cm<sup>-1</sup> corresponding to –OH stretch.

This peak is also observed in corn starch, but not in the other two. Moreover, primary alcohols peak (1025-1060 cm<sup>-1</sup>) is seen in corn starch but not in the other three materials. All of the above data confirm the true existence of a graft copolymer. Finally,  $\delta$  (O-H) bend of water at 1640 cm<sup>-1</sup> is observed in starch and not in any of the other materials.

#### 4.3.3.4 Proof of grafting by Thermal Analysis

DSC and TGA experiments were carried out on solvent cast film samples of the extracted Ecoflex-MTPS graft copolymer. The results are shown in Figure 4-29 and Figure 4-30.



Figure 4-29: DSC Results of Ecoflex-MTPS graft copolymer



Figure 4-30: TGA Results of Ecoflex-TPS graft copolymer

From Figure 4-29, it can be observed that the melting temperature of the Ecoflex-MTPS graft copolymer is very similar to pure Ecoflex. However, crystallinity of the graft copolymer reduces as evinced by the area under the melting peak. Thus, the area under the melting peak for pure Ecoflex is 15.67 J/g while that of Ecoflex-MTPS graft copolymer is 5.89 J/g. This is expected as the incorporation of starch into the Ecoflex matrix breaks the orderliness of Ecoflex bringing down the crystallinity. Moreover, peak crystallization temperature of the graft copolymer (78.69<sup>o</sup>C) is higher than that of pure Ecoflex (40.88<sup>o</sup>C). This is due to the presence of impurities such as catalyst residues, which act as nucleating agents that fasten the crystallization process.

From Figure 4-30, it is seen that Ecoflex-MTPS graft copolymer exhibits two degradations; one corresponding to the starch and the other corresponding to Ecoflex. This further confirms that MTPS is chemically grafted onto Ecoflex. Further, at a temperature of 330<sup>o</sup>C, while 78% of the graft copolymer is un-degraded, only 63% of starch is left behind. This is evident as MTPS is more stable than pure granular starch. However at 450<sup>o</sup>C, while 45% of Ecoflex is left behind, only 7% of the graft copolymer is left behind.

#### 4.3.3.5 Blown Film Processing Results of Ecoflex-MTPS graft copolymers

Blown films of the graft copolymers were made using a Killion single screw blown film unit. Temperature profile in the blown film unit, melt pressure, draw rates and blow up ratio are some of the important processing parameters that need to be considered. Melt temperatures greater than 420<sup>o</sup>C made the bubble raise process difficult. Hence melt temperatures below 370<sup>o</sup>C were used. At very low (less than 5 ft/min) and very high (greater than 6.5 ft/min) draw rates; the films were either too thick or too thin respectively. This made the bubble instable, causing it to collapse. Hence, draw rates around 5-6 ft/min were used. Blow up ratio was calculated to be around 2.5-3, similar to LDPE film processing. Blow up ratios higher than 3 led to necking issues during blown film processing, causing the bubble to break and collapse. The melt pressures observed for the various graft copolymers are shown in Figure 4-31.



Figure 4-31: Blown film pressures of Ecoflex-MTPS graft copolymers

From Figure 4-31, it is observed that the melt pressure decreases on increasing the MTPS weight fraction in copolymer. This is attributed to a reduction in the molecular weight (maleic acid catalyzed acid hydrolysis) of Ecoflex on reaction with MTPS. However, for the same weight fraction of MTPS, melt pressure increases on cross-linking. This was expected as cross-linking increases the molecular weight of the polyester. The melt pressure was least for the Ecoflex-TPS graft copolymer and was lower than Ecoflex-MTPS graft copolymer for the same TPS and MTPS weight fractions. This is attributed to the increased reactivity of MTPS with Ecoflex as compared to TPS, leading to stronger covalent linkages and increases melt pressures.

#### 4.3.3.6 Mechanical Property Results of Ecoflex-MTPS graft copolymers

The mechanical properties of Ecoflex-MTPS graft copolymers are shown in Figure 4-32, Figure 4-33 and Figure 4-34.



Figure 4-32: Tensile Strength Results of Ecoflex-MTPS graft copolymers



Figure 4-33: Modulus of Elasticity Results of Ecoflex-MTPS graft copolymers



Figure 4-34: Break Elongation Results of Ecoflex-MTPS graft copolymers

It is observed from Figure 4-32 that the tensile strength values of the graft copolymer reduce considerably as compared to Ecoflex. However, the values are only slightly less than LDPE values. Moreover, on cross-linking, due to the increased molecular weight, tensile strength values increase and are higher than LDPE values. The tensile strength of Ecoflex-TPS graft copolymer is the least. This is attributed to a reduction in the molecular weight by hydrolysis catalyzed by maleic acid.

The modulus of elasticity values (Figure 4-33) of the graft copolymers also follows the same trend as the tensile strength values. Thus, the modulus of elasticity of Ecoflex-MTPS graft copolymer is lower than pure Ecoflex. Further, modulus of elasticity increases on cross-linking.

Break elongation values (Figure 4-34) of Ecoflex-MTPS graft copolymer are higher than pure Ecoflex. This is attributed to chemical covalent linkages present in the graft copolymer, making it stretchable. However, LEcoflex-MTPS graft copolymers exhibit lower values of break elongation. This is due to a more rigid structure obtained on cross-linking. Finally, Ecoflex-TPS graft copolymers exhibit the highest break elongation values. All the values are comparable to LDPE.

The mechanical property results of Ecoflex-MTPS graft copolymers, containing varied weight percentages of maleic acid in the MTPS, are shown in Figure 4-35, Figure 4-36 and Figure 4-37.



Figure 4-35: Tensile Strength Results of Ecoflex-MTPS (70/30) graft copolymers

2.5-wt%, 5-wt% and 10-wt% maleic acid in MTPS



Figure 4-36: Modulus of Elasticity Results of Ecoflex-MTPS (70/30) graft copolymers 2.5-wt%, 5-wt% and 10-wt% maleic acid in MTPS



Figure 4-37: Break Elongation Results of Ecoflex-MTPS (70/30) graft copolymers 2.5-wt%, 5-wt% and 10-wt% maleic acid in MTPS

It is observed from Figure 4-35 that increase in the maleic acid content in MTPS leads to an increase in the tensile strength value. This is attributed to increased chemical reactivity between Ecoflex and MTPS. Increase in the maleic acid content leads to a greater probability of hydrolysis reactions. However, in this case, most of the unreacted maleic acid is removed in the vent port of the extruder, during the reactive maleation of starch, and does not get transferred to the next stage of processing. Thus, increase in the tensile strength is purely attributed to increased maleation and hence increased chemical reactivity. However, all the values are lower than LDPE.

The modulus of elasticity values (Figure 4-36) follows the same trend as the tensile strength values. They increase with increasing maleic acid content. All the values observed are lower than LDPE.

Break Elongation values (Figure 4-37) of the graft copolymers are higher than either pure Ecoflex or LDPE. Moreover, on increasing maleic acid content in MTPS, the break elongation values increase. This is again attributed to the enhanced chemical reactivity between Ecoflex and MTPS.

The tear and puncture properties of Ecoflex-MTPS (70/30) graft copolymer are explained in Table 4-7 and compared with PE values.

Material	Thickness	Tear (g)	Tear (g)	Puncture	Puncture
	(in)	MD	CMD	Max. (lb <sub>f</sub> )	Ext. (in)
		ASTM D	ASTM D	ASTM F	ASTM F
		1922	1922	1306	1306
LDPE	0.0010-	100-300	-	1.5-3.0	-
	0.0015				
Ecoflex-MTPS	0.0010-	767.7	802.7	1.52	0.62
(70/30) graft	0.0015				
copolymer					

Table 4-7: Tear and Puncture properties of Ecoflex-MTPS (70/30) graft copolymer

It can be observed from Table 4-7 that tear and puncture properties of Ecoflex-MTPS (70/30) graft copolymer are comparable or better than LDPE. Tear and puncture are 'energy related' properties and hence related to the crystallinity of the polymer. Hence, an improvement in the tear and puncture properties of the graft copolymers, as compared to LDPE, could be attributed to reduced crystallinity. This makes these films a good replacement for LDPE in applications such as lawn and leaf compost bags, retail carryout bags etc.

Chapter 5

#### SUMMARY AND CONCLUSIONS

#### 5.1 SUMMARY

The overall scope of this work was to study and evaluate three different chemistries; namely polymerization, cross-linking with blending, and grafting in a twin-screw corotating extruder. These biobased biodegradable polymeric materials and blends synthesized by reactive extrusion processing, have applications in the areas of biodegradable films, injection molded articles etc. Specifically, this work focused on the following:

- Extrusion polymerization of 1, 4-dioxan-2-one (PDX) monomer and copolymerization with ε-caprolactone (CL) monomer.
- Reactive extrusion cross-linking of biodegradable polyesters (Ecoflex and PCL) and blending with talc.
- Reactive extrusion processing in the synthesis of Ecoflex-Starch graft copolymers.

The key studies of the above areas of this work will be summarized below:

### 5.1.1 Extrusion polymerization of 1, 4-dioxan-2-one (PDX) monomer and copolymerization with ε-caprolactone (CL) monomer.

The extrusion polymerization of PDX monomer in the synthesis of poly (1, 4-dioxan-2one) (PPDX) polyester, using aluminum tri-sec butoxide (ATSB) initiator in a BAKER PERKIN co-rotating twin-screw extruder was studied. The co-polymerization of PDX monomer with a few mole percent CL monomer in the synthesis of poly(caprolactone-co-1,4-dioxan-2-one) (PCL-co-PPDX), using aluminum tri-sec butoxide (ATSB) initiator in a BAKER PERKIN co-rotating twin-screw extruder was also studied. Finally, the extrusion polymerization process of CL monomer conducted in a BAKER PERKIN twinscrew extruder was modeled as an Axial Dispersed Plug Flow Reactor using Residence Time Distribution Analysis.

- A twin-screw extrusion process to polymerize PDX monomer to high molecular weight (up to 94,550 g/mol, each arm) PPDX polymer was designed.
- The extrusion process synthesis of PPDX with theoretical number average molecular weights ranging between 50,000 and 100,000 g/mol was targeted; extrusion temperatures ranging from 130 to 170°C were evaluated.
- A screw configuration comprising entirely of conveying elements was used for the synthesis of high molecular weight PPDX and PCL-co-PPDX polymers.
- PDX monomer conversions in the synthesis of PPDX polymer were determined by dissolution-precipitation method.
- A twin-screw extrusion process to co-polymerize PDX monomer with 11, 16 and 24-mol% CL monomer at a temperature of 130°C was designed.
- PDX monomer conversions in the synthesis of PCL-co-PPDX polymer were determined by dissolution-precipitation method.
- Glass transition, melting and crystallization were determined for the PPDX and PCL-co-PPDX polymers.

- Isothermal gravimetric analysis (TGA) experiments at 180<sup>o</sup>C under Helium flow were conducted for PPDX and PCL-co-PPDX polymers.
- Residence Time Distribution (RTD) studies were conducted during the polymerization of CL monomer to evaluate the applicability of the Axial Dispersed Plug Flow Reactor model to the observed RTD and conversion data.

## 5.1.2 Reactive extrusion cross-linking of biodegradable polyesters (Ecoflex and PCL) and blending with talc.

Micro-gelled cross-linking of Ecoflex (aliphatic-aromatic co-polyester) and PCL (aliphatic polyester) by reactive extrusion using peroxide initiator was evaluated. Blends of cross-linked polyesters with talc were prepared by extrusion processing. These blends were made into films useful for lawn and leaf disposal.

- Cross-linking of Ecoflex and PCL using 2, 5-Bis (tert-butylperoxy)-2, 5dimethylhexane (Luperox 101) was achieved in a CENTURY twin-screw corotating extruder at a temperature of around 160°C.
- Cross-linked Ecoflex (LEcoflex) and cross-linked PCL (LPCL) were characterized for the gel fraction by Soxhlet extraction studies.

- Melting, crystallization and degradation temperatures of LEcoflex and LPCL were evaluated.
- LEcoflex and LPCL were characterized by Environmental Scanning Electron Microscopy (ESEM) measurements.
- Ecoflex and LEcoflex were extrusion processed with talc in a CENTURY twinscrew extruder at a temperature of around 160°C.
- Melting, crystallization and degradation temperatures of talc filled polyesters were studied.
- The talc filled polyesters were characterized by Environmental Scanning Electron Microscopy (ESEM) measurements.
- The mechanical properties of Ecoflex and LEcoflex blends with talc were evaluated.

#### 5.1.3 Ecoflex-Starch graft copolymers by reactive extrusion processing

Graft copolymers of Ecoflex with thermoplastic starch (TPS) and maleated thermoplastic starch (MTPS) were evaluated. Films of these graft copolymers that were useful in making compostable bags were studied.

- Grafting of Ecoflex chains onto TPS by reactive extrusion processing, using maleic acid catalyst was conducted.
- Reactivity was confirmed by Fourier Transformed Infra Red Spectroscopy (FTIR) and Thermal Gravimetric Analysis (TGA).
- Mechanical properties of Ecoflex-TPS graft copolymers were evaluated.
- Maleation of starch in a twin-screw extruder using maleic anhydride or maleic acid modifiers and glycerol plasticizers with optional radical initiator was studied.
- Synthesis of starch maleates was confirmed by FTIR analysis.
- Intrinsic viscosity experiments were carried out to document the reduction in molecular weight and viscosity on maleation.
- Melting and degradation temperatures of MTPS samples were evaluated by Thermal Analysis experiments.
- Grafting of Ecoflex chains onto MTPS by reactive extrusion processing was conducted.

- Reactivity was confirmed by Fourier Transformed Infra Red Spectroscopy (FTIR) and Thermal Gravimetric Analysis (TGA).
- Ecoflex-MTPS graft copolymers were further characterized by Differential Scanning Calorimetry (DSC) measurements.
- Mechanical properties of films made from Ecoflex-MTPS graft copolymers were determined and compared to LDPE.

#### 5.2 CONCLUSIONS

This section outlines the specific conclusions derived from the work in each of the sections detailed above.

## 5.2.1 Extrusion polymerization of 1, 4-dioxan-2-one (PDX) monomer and copolymerization with ε-caprolactone (CL) monomer.

 A twin-screw extrusion process to polymerize PDX monomer into high molecular weight three-arm PPDX polymer was designed and engineered; three-arm PPDX polymers of theoretical number-average molecular weight ranging from 50,000 to 100,000 g/mol were made with good control over molecular weight.

- A polymerization temperature of 130<sup>o</sup>C was considered optimal on account of the monomer-polymer thermodynamic equilibrium leading to depolymerization above the melting temperature of the polymer.
- An extruder screw configuration comprising entirely of conveying elements was found to be suitable for the extrusion polymerization of PDX monomer.
- Maximum attainable monomer conversion in the case of PDX polymerization was limited to 78%, close to the equilibrium monomer conversion value.
- For molecular weights of 54,800 g/mol and 63,400 g/mol, conversion values are identical even as monomer flow rate increases from 23.23 to 40.75 g/min.
- At a screw speed of 130 RPM for a PPDX molecular weight of 63,400 g/mol, as temperature increases from 130 to 170°C, monomer conversion drops from 68% to 61%.
- Incorporation of 8, 11 and 16-mole % of CL monomer during the PDX polymerization process made the conversion of PDX monomer reach almost 100%.

- Lower intrinsic viscosity values of the PCL-co-PPDX copolymers as compared to PPDX polymers of the same molecular weight could be attributed to a change in conformation of the copolymers in solution.
- Copolymer with 11-mol% CL is characterized by a melting temperature of 94°C, close to the homopolymer melting temperature of 110°C. The melting temperature of the co-polymers further reduces to 85°C and 68°C with incorporation of 16-mol% and 24-mol% CL respectively. The glass transition temperature of the co-polymer (11-mol% CL) decreases from -11°C (homo PPDX) to -22°C.
- Thermal stability of the copolymers is substantially improved as compared to the homopolymer.
- Residence Time Distribution (RTD) studies indicated that the Axial Dispersed Plug Flow Reactor Model provided a good fit to the observed RTD and conversion data.
- Maximum dispersion (from Peclet number calculations) is obtained under conditions of 130°C, 125 RPM and 22-ml/min monomer feed rate while least dispersion is obtained at 170°C, 125 RPM and 14-ml/min monomer feed rate. At 130°C, due to the presence of low molecular weight pre-polymers along-with the polymer melt, dispersion effects become pronounced. Dispersion effects increase as overall throughput increases (increase of monomer feed rate).

- 5.2.2 Reactive extrusion cross-linking of biodegradable polyesters (Ecoflex and PCL) and blending with talc.
  - Reactive Extrusion of micro-gelled cross-linking of PCL and Ecoflex was accomplished in a twin-screw extruder using 2, 5-Bis (tert-butylperoxy)-2, 5-dimethylhexane (Luperox 101) free radical initiator.
  - Samples removed from the vent port in the extruder exhibited lower values of gel fraction as compared to those from the die proving that cross-linking chemistry is dependent on the residence time in the extruder.
  - Increase in Luperox 101 concentration leads to an increase in gel fraction. PCL polyester exhibits higher values of gel fraction as compared to Ecoflex for the same Luperox 101 concentration.
  - Percent crystallinity and melting temperature reduce on cross-linking, as the size and perfectness of cross-linked crystals are relatively low. Presence of impurities such as catalyst residues, which act as nucleating agents, enhance the crystallization process of cross-linked polyesters.
  - Rate of degradation of cross-linked polyesters is higher than regular polyester, which is attributed to backbiting reactions in the presence of radicals.

- Gel particles, as evinced by ESEM image, are of the order of 1-5 microns and are termed as "microgels". These microgels are uniformly distributed in the polyester matrix and provide reinforcement.
- Extrusion processing of Ecoflex with talc was accomplished in a twin-screw extruder at a temperature of around 170°C.
- Screw configuration comprising conveying and kneading elements was found to be effective in efficient breakdown and dispersion of talc particles in the polyester matrix.
- Percent crystallinity and melting temperature reduce on blending with talc, as the size and perfectness of the polyester crystals on blending are relatively low. Presence of impurities such as catalyst residues, which act as nucleating agents, enhance the crystallization process of polyesters in talc filled blends.
- Rate of degradation of Ecoflex/talc and LEcoflex/talc blends are very similar to pure Ecoflex and LEcoflex respectively.
- Size of the talc particles, as evinced from ESEM images, are of the order of 1-10 microns and are uniformly distributed within the polyester matrix.

- Tensile strength and break elongation values of talc filled polyesters are lower as compared to the unfilled ones. Modulus increases on filler addition.
- Cross-linking increases the tensile strength and modulus (increase in molecular weight), reducing the break elongation value.
- Tear and Puncture properties of Ecoflex/talc blends are better or comparable to LDPE.

#### 5.2.3 Ecoflex-Starch graft copolymers by reactive extrusion processing

- Ecoflex-TPS graft copolymers were produced by reactive extrusion processing using maleic anhydride or maleic acid as a trans-esterification catalyst.
- The graft copolymer was completely extractable in Dichloromethane using a Soxhlet extraction technique. On solvent casting the extracted polymer solution, a transparent film was obtained. In the absence of maleic acid, only the polyester was extracted out. These results confirm that Ecoflex and TPS are covalently linked, as opposed to a simple physical blend.
- FTIR results of Ecoflex-TPS graft copolymer, showing the carbonyl stretch at 1720 cm<sup>-1</sup>, ester C-O stretch at 1270 cm<sup>-1</sup> and the –OH polymer stretch at 3200-3400 cm<sup>-1</sup> confirm the true existence of a graft copolymer.

- Ecoflex-TPS graft copolymer exhibit degradation corresponding to both starch and Ecoflex as opposed to simple physical blends, which show degradation corresponding to only the polyester.
- Tensile strength and modulus of elasticity of the graft copolymer are lower as compared to LDPE. However, the graft copolymer exhibits break elongation values of around 500%, which is much higher than LDPE.
- Regular granular corn starch was maleated in a twin-screw co-rotating extruder using maleic anhydride or maleic acid modifiers in the presence of glycerol as the plasticizer and optional free-radical initiator such as Luperox 101.
- Due to the low viscosity of MTPS, reactive maleation can be done at much higher throughputs as compared to the regular thermoplastic starch (TPS) production.
- The reactive maleation process prevents problems during TPS production such as clogging of the thermoplastic starch melt and foaming at the die.
- Carbonyl stretch peak at 1720 cm<sup>-1</sup>, observed for the extracted MTPS sample (made using both maleic anhydride and maleic acid modifier), confirms reactivity.
- Differential Scanning Calorimetry (DSC) results of MTPS samples exhibit melting endotherms, not present in regular granular starch.

- Thermal Gravimetric Analysis (TGA) results show that MTPS is more stable as compared to either starch or TPS. At a temperature of 350.38<sup>o</sup>C, while 75% and 63% of starch and TPS have degraded respectively, only 58% of MTPS has degraded.
- Intrinsic viscosity of MTPS drops to 0.27 dl/g as compared to 1.6 dl/g and 1.2 dl/g for starch and TPS respectively. This reduction is attributed to a decrease in molecular weight due to the hydrolysis of starch in the presence of maleic acid. However, in the presence of Luperox 101, free-radical initiator, intrinsic viscosity increases to 0.45 dl/g, which is attributed to cross-linking reactions taking place.
- Ecoflex-MTPS graft copolymers were produced by the reactive extrusion processing of Ecoflex and MTPS.
- Ecoflex/MTPS (70/30 and 60/40; w/w) graft copolymers was completely extractable in Dichloromethane using a Soxhlet extraction technique. On solvent casting the extracted polymer solution, a transparent film was obtained. This reaction leading to the formation of a graft copolymer is dependent on the relative amounts of Ecoflex and MTPS present (Does not hold true for more than 50% MTPS). Cross-linked Ecoflex/MTPS (70/30;w/w) exhibits certain regions, which are impermeable to chemical reaction.

- FTIR results of Ecoflex/MTPS (70/30; w/w) graft copolymers (solvent cast films after extraction in Dichloromethane) made using both maleic anhydride and maleic acid, show the carbonyl stretch at 1720 cm<sup>-1</sup>, ester C-O stretch at 1270 cm<sup>-1</sup> and the –OH polymer stretch at 3200-3400 cm<sup>-1</sup> confirming the true existence of a graft copolymer.
- DSC Results shows that while the melting temperature of the Ecoflex/MTPS (70/30; w/w) graft copolymer is similar to pure Ecoflex, the crystallinity of the graft copolymer is reduced.
- TGA Results show that Ecoflex/MTPS (70/30; w/w) graft copolymer exhibits two degradations, one corresponding to Ecoflex and the other corresponding to MTPS. This confirms the true existence of a graft copolymer.
- Melt Pressures, during blown film processing, decrease with increasing MTPS fraction in the graft copolymer. However, for the same starch content in the graft copolymer, Ecoflex/MTPS graft copolymer exhibits higher pressures as compared to the Ecoflex/TPS graft copolymer. Moreover, for the same MTPS fraction, melt pressures increase with the use of cross-linked Ecoflex.
- Tensile strength and modulus of elasticity values of Ecoflex/MTPS graft copolymers are comparable to LDPE and higher than Ecoflex/TPS graft copolymer. The values increase and are better than LDPE for cross-linked

Ecoflex-MTPS graft copolymers (LEcoflex/MTPS). Break elongation values for Ecoflex/MTPS graft copolymers are higher than pure Ecoflex and LEcoflex/MTPS graft copolymer.

• Tear and Puncture properties of Ecoflex/MTPS (70/30; w/w) graft copolymer are comparable to LDPE.
Chapter 6

### RECOMMENDATIONS

### 6.1 **RECOMMENDATIONS**

The recommendations with respect to the future work are explained in the following sections.

# 6.1.1 Bulk Extrusion Polymerization of 1, 4-dioxan-2-one monomer

 Detailed molecular weight analysis of Poly (1, 4-dioxan-2-one) (PPDX) and Poly (ε-caprolactone)-co-Poly (1, 4-dioxan-2-one) (PCL-co-PPDX) polymers produced by reactive extrusion polymerization.

- Mechanical properties of films made from PPDX and PCL-co-PPDX polymers.
- Dart, tear and puncture properties of films made from PPDX and PCL-co-PPDX polymers.
- Economics of extrusion polymerization of PDX monomer and co-polymerization of PDX monomer with CL monomer.
- Extension of Axial Dispersed PFR model to polymerization of PDX monomer and co-polymerization of PDX monomer with CL monomer.

# 6.1.2 Reactive Extrusion Cross-linking of Biodegradable Polyester and Blending with Inorganic Fillers.

- Further investigation into cross-linking of PCL and Ecoflex using varying amounts of Luperox 101 initiator.
- Rheological studies on cross-linked Ecoflex (LEcoflex) and cross-linked PCL (LPCL).
- Mechanical Properties of Blends of Ecoflex and talc containing varying amounts of talc (greater than 30-wt %).
- Use of compatibilizers such as maleated Ecoflex (added externally or generated insitu during extrusion processing) in Ecoflex/talc blends to improve mechanical properties.
- Water vapor and oxygen permeability studies on blends of Ecoflex/talc.

# 6.1.3 Polyester-Starch graft copolymers by Reactive Extrusion Processing

- Incorporation of varying amounts of TPS content in the graft copolymers and study the effect on mechanical properties.
- Further investigation into using other catalyst systems such as FASCAT and Stannous Octoate instead of maleic anhydride and maleic acid in the formation of Ecoflex/TPS graft copolymers.
- Study effect of changing catalyst concentration on processing, thermal and mechanical properties of graft copolymers.
- Develop a method to quantify the exact amount of maleic anhydride and maleic acid grafted onto the starch backbone.
- Rheological Studies on Maleated Thermoplastic Starch samples using various amounts of modifiers.
- Particle size distribution studies on starch, TPS and MTPS samples.
- Mechanical, dart, tear and puncture properties on Ecoflex/MTPS graft copolymers containing varying amounts of MTPS.
- Detailed analysis on phase reversal of graft copolymers containing greater than 50% MTPS by conducting FTIR analysis.
- Develop a single-step procedure for the production of Ecoflex/MTPS or LEcoflex/MTPS graft copolymers. Compare mechanical properties with graft copolymers formed by a two-step process.
- Economics of Polyester-Starch graft copolymer production.

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