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THE DESIGN AND ENGINEERING OF STARCH:POLYESTER
BIODEGRADABLE PLASTICS USING REACTIVE EXTRUSION

presented by

Dale Michael Smith

has been accepted towards fulfillment
of the requirements for

M.S. degree in Chemical Engineering

Ramani Narayan
Major professor

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THE DESIGN AND ENGINEERING OF STARCH:POLYESTER BIODEGRADABLE PLASTICS USING REACTIVE EXTRUSION

by

Dale Michael Smith

A THESIS

Submitted to
Michigan State University
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ABSTRACT

THE DESIGN AND ENGINEERING OF STARCH:POLYESTER BIODEGRADABLE PLASTICS USING REACTIVE EXTRUSION

By

Dale Michael Smith

Environmental and life cycle considerations have excited recent interest in biodegradable polymeric materials. Properties of many of the commercially available biodegradable materials are not competitive with traditional non-biodegradable materials. In this study reactive extrusion was used to compatibilize a commercially available biodegradable polyester. This polyester was then blended with thermoplastic starch. The properties of these blends were examined and a plant design and cost analysis was performed to determine the feasibility of producing such blends on a large scale.

To my parents who made this all possible, and
To Tammy who never let me lose sight of this dream.

ACKNOWLEDGEMENTS

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-Jose Sanchez , thank you for providing me inspiration and wisdom in so many ways-

Finally, I thank my Lord who has guided my down this path of life bringing me only true happiness when I follow him willingly!

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CHAPTER 1

INTRODUCTION

Goals and Objectives

The goal of this work are twofold:

1) the design and engineering of biodegradable starch:copolyester blend. The copolyester used in this blend is Eastar Bio Copolyester (EBC), a biodegradable copolyester containing Adipic acid, Terepthalic acid, and 1,4-Butanediol.

2) the evaluation of maleated soybean oil (MSO) as a compatibilizing agent.

Specifically the objectives are as follows:

1) Design of a compatibilizing agent
    a) Maleation of soybean oil
    b) Grafting of maleated soybean oil onto the Eastar Bio Copolyester
    c) Characterization of the maleated soybean oil and the grafted copolyester products
2) Preparation of Materials
    a) Preparation of Thermoplastic Starch
    a) Reactive blending of thermoplastic starch with the grafted copolyester

3) Determination of properties of the biodegradable EBC-g-MSO: TPS blends

    a) Examination of morphology by Environmental Scanning Electron microscopy.

    b) Tensile testing of materials

    c) Biodegradability testing of the EBC-g-MSO: TPS blends

4) Engineering of a large scale process

    a) description of a 5 million pound per year plant

    b) calculation of material and energy balances

    c) sizing of process equipment

5) Analysis of process economics

    a) Determination of the Discounted Cash Flow selling price

    b) Analysis of sensitivity of selling price to cost fluctuation

Chapter 2 provides the literature background for this work. Objective 1 is discussed in Chapter 3. Objective 2 is described in Chapter 4. Objective 3 is outlined in Chapter 5. The process engineering and economics are described in Chapters 6 and 7. Conclusions and further work are finally discussed in Chapter 8. An outline of this work is shown in Figure 1.1.

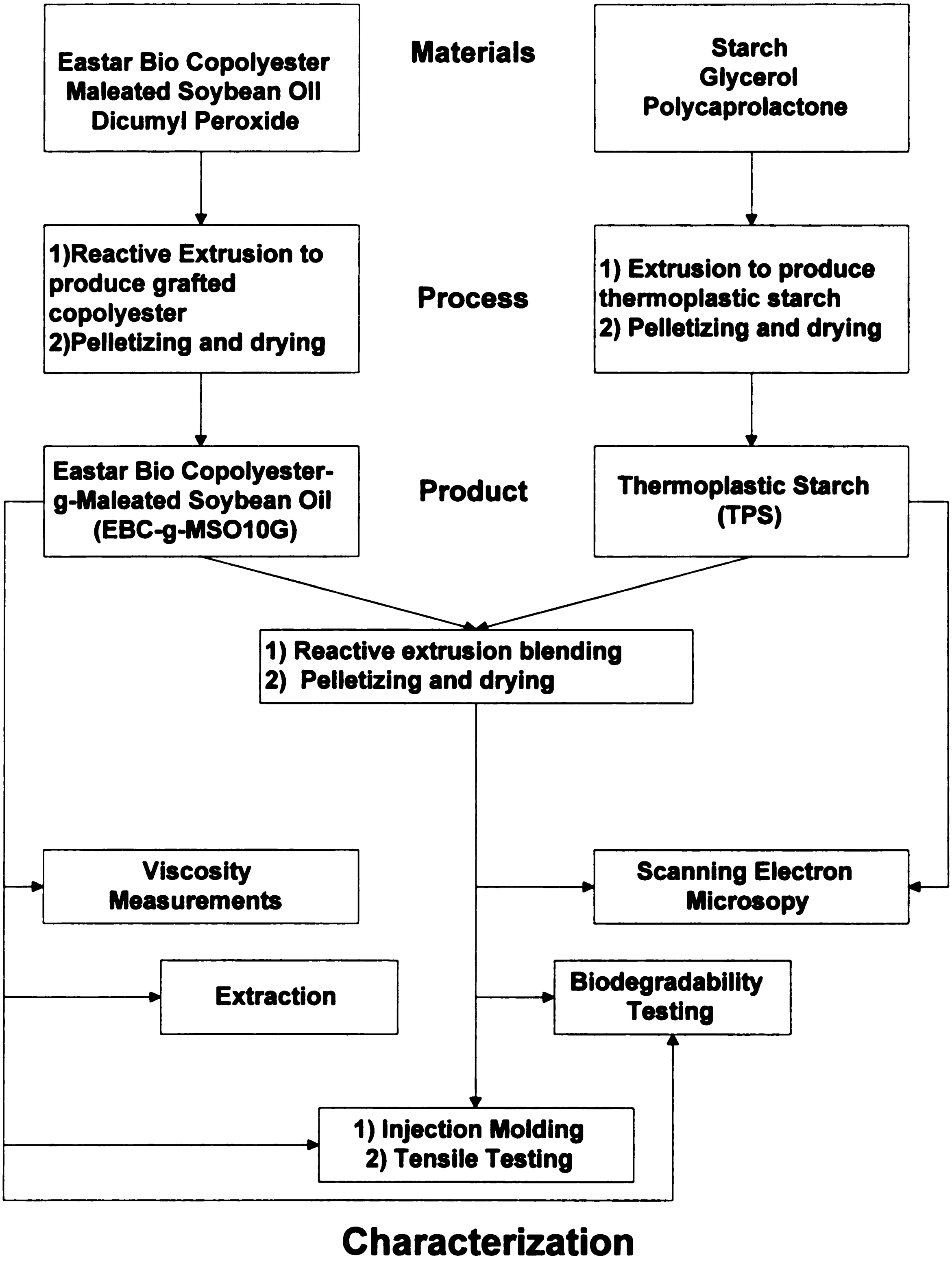


Figure 1.1 Experimental Protocol

Rationale for Biodegradable Plastics

New environmental regulations, societal concerns, and a growing environmental awareness throughout the world have triggered the search for new products and processes that are compatible with the environment. Thus, new products have to be designed and engineered from cradle to grave incorporating a holistic "life cycle thinking" approach. The impact of raw material resources used in the manufacture of a product and the ultimate fate (disposal) of the product when it enters the waste stream have to be factored into the design of the product. The use of annually renewable resources and the biodegradability or recyclability of the product are becoming important design criteria. This has opened up new market opportunities for developing biodegradable products.(Narayan, 1998).

Currently, most products are designed with limited consideration of their ultimate disposability. Of particular concern are plastics used in single-use disposable packaging. Designing these materials to be biodegradable and ensuring that they end up in an appropriate disposal system is environmentally and ecologically sound. For example, by composting our biodegradable plastic and paper waste along with other "organic" compostable materials like yard, food, and agricultural wastes, we can generate much-needed carbon-rich compost (humic material). Compost amended soil has beneficial effects by increasing soil organic carbon, increasing water and nutrient retention, reducing chemical inputs, and suppressing plant disease. Composting infrastructures, so important for the use and disposal of biodegradable plastics, are growing in the U.S. and are in part being regulatory driven on the state level.

Polymers have been designed in the past to resist degradation. The challenge is to design polymers that have the necessary functionality during use, but destruct under the stimulus of an environmental trigger after use. The trigger could be microbial, hydrolytic or oxidation susceptible linkages built into the backbone of the polymer, or additives that catalyze breakdown of the polymer chains in specific environments. More importantly, the breakdown products should not be toxic or persist in the environment, and should be completely utilized by soil microorganisms. In order to ensure market acceptance of biodegradable products, the ultimate biodegradability of these materials in the appropriate waste management infrastructures needs to be demonstrated beyond doubt.

The U.S generates 207 million tons of municipal solid waste each year. (Franklin and Associates, 1994) Plastics account for 9.3 % of this waste stream as seen in Figure 1.2. The traditional waste disposal alternatives-recycling, incineration, and landfilling account for 22%, 16% and 62% of the total Municipal solid waste disposed of today.

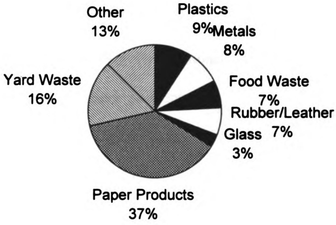


Figure 1.2: Composition of municipal solid waste in the USA, 1993

Mounting societal concerns about our environment have led to an increased interest in making polymeric materials from renewable resources. The primary reasons for this interest are (Narayan 1991):

- Environmental concerns
- Providing alternate feedstocks to non-renewable imported petroleum feedstocks
- The need to utilize the nation's abundant agricultural feedstocks
- Legislation and public opinion

The incorporation of renewable resources into polymeric systems can often result in polymers that are partially or fully biodegradable. Bags for collection of yard trimmings, food residuals, and other organics, cutlery, plates, and agricultural film are among the items made from such polymer systems that are commercially available.(Riggle, 1998) These biodegradable products in a composting infrastructure will can be converted into CO_2 and water by microbial activity thus helping reduce the solid waste problem in this country.

Biodegradable Polymer Systems

ASTM, European (CEN), and ISO (International Standards Organization) Standards have been developed or are under development to evaluate biodegradability under different environmental/disposal conditions like composting, soil, marine, wastewater treatment facility, and anaerobic digestors. Armed with an understanding of the rationale for biodegradable plastics, and with standards in place to evaluate biodegradability, technologies are under development that meet biodegradability and/or compostability criteria.

The technologies can be classified in the following manner:

1. Aliphatic polyester
    - petrochemical feedstock
    - agricultural feedstock
    - microbial synthesis
2. Natural polymer
    - starch & starch derivatives (starch esters)
    - cellulose and cellulose esters
    - proteins, polysaccharides and amino acids
3. Blends, alloys and graft copolymers of natural polymers and polyesters

Aliphatic polyesters are excellent candidates for biodegradable plastic products. The basic composition involves a polyester prepared by using diols like ethylene glycol, 1,4-butanediol, 1,6-hexanediol, 1,4-cyclohexanedimethanol and dicarboxylic acids like succinic, sebacic, and adipic acid. In some cases, a few mole percent terephthalic acid has been used along with adipic acid to generate copolyesters to obtain suitable properties for plastics applications. Polyesteramide copolyesters have also been introduced into the marketplace as fully biodegradable resins for plastic applications.

Poly(lactic acid) polymers (PLA) are derived from agricultural feedstocks. There is considerable commercial and R&D activity in this area. The basic chemistry involves step polymerization (condensation polymerization) of lactic acid (α-hydroxy acid). High molecular weight poly(lactic acid) polymer has been prepared by the direct condensation route. This has been achieved by carrying out the reaction in a high boiling solvent using Sn compounds or protoic acids as catalysts. The conventional route to high molecular weight PLA is through the dilactone of lactic acid by ring opening polymerization.

Polyhydroxyalkanoates (PHBV, poly(3-hydroxybutyrate-co-3-hydroxyvalerate)) are novel thermoplastic polyesters that are prepared by microbial synthesis using a variety of feed stocks including glucose and acetic acid .

Starch formulated with addditives & plasticizers has found application as loose-fill packaging material. They offer a biodegradable, water soluble, anti-static, environmentally friendly alternative to expanded polystyrene (peanut packaging). Water functions as a plasticizer and blowing agent. Starch based foams have captured 15-20% of this market. However, because of starch's extreme water sensitivity, it cannot be used in the majority of plastics applications. Starch esters and blends of starch esters with biodegradable aliphatic polyesters provide better water resistance and processability, and are being evaluated for various molded products and film applications. Cellulose esters with a degree of substitution of around 2 are also potential biodegradable resins.

Blends of starch and poly(caprolactone) (PCL) have been successfully used as compost bags. However, because PCL has a low melting point it is unsuitable for many other film applications.

Polymers based on renewable resources such as starch, tend to be more expensive and have inferior properties compared to petroleum based polymers. To offset these problems these polymers are often blended with other synthetic biodgradable polymers.(Karnani, 1996). Blending of polymers offers several advantages (Utracki, 1989):

- Extending engineering resin performance by diluting it with a low cost polymer
- Developing materials with a full set of desired properties
- Forming a high performance blend from synergistically interacting polymers
- Adjusting the composition of the blend to customer specifications
- Recycling industrial and/or municipal plastics scrap

Polymer Blend Terminology

In the study of polymer blends, some terminology must be introduced. The relationship between the various terms used in the polymer blending field can be visualized as shown in Figure 1.2. The terminology described below (Utracki, 1989) will be used throughout this thesis:

a) Polymer Blend: a mixture of at least two polymers or copolymers.

b) Miscible Polymer Blend: a polymer blend homogenous down to the molecular level, associated with the negative value of the free energy of mixing

(1) $$\Delta G_m \cong \Delta H_m \leq 0$$

c) Immiscible Polymer Blend: any polymer blend whose $G_m \cong \Delta H_m > 0$

d) Compatible polymer blend: a utilitarian term indicating a commercially attractive polymer mixture, normally homogenous to the eye, frequently with enhanced physical properties over the constituent polymers

e) Polymer Alloy: an immiscible PB having a modified interface and/or morphology

f) Compatibilization: a process of modification of interfacial properties of an immiscible polymer blend, leading the creation of a polymer alloy.

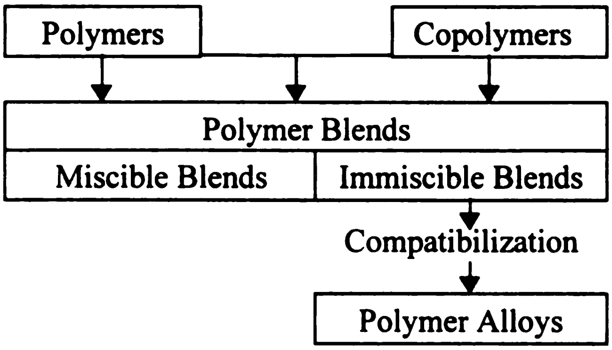


Figure 1.3 Polymer blend classification scheme

Polymer Blend Compatibility

Most polymer blends are not miscible, (Paul, 1978) but miscibility is neither required nor desired in all polymer blends. Immiscible but compatibilized blends-polymer alloys, often exhibit synergistic properties that are characteristic of both components in the blend. For this synergism to occur however there must be some adhesion between the two phases in the system.

Mixing natural polymers with synthetic ones results often in two-phase morphologies with high interfacial tension and poor adhesion between the phases. An incompatible blend with poor properties is the result. Two ways to improve adhesion between the phases are by using a compatibilizing agent or by modification of the blend components. (Xanthos, 1988) Block and graft A-B copolymers located at the interface between the two phases can reduce the surface tension between the A-rich and B-rich phases thereby serving well as compatibilizers.

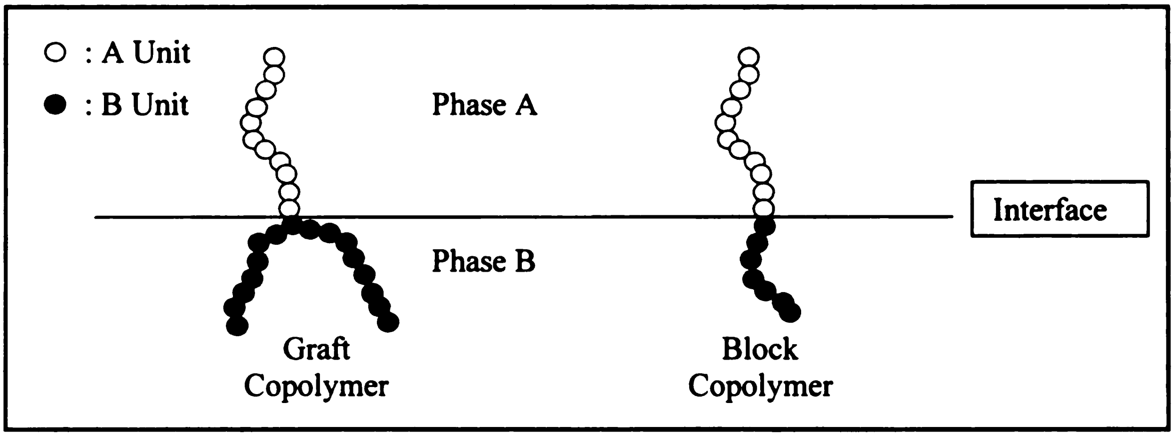


Figure 1.4: Location of block or graft copolymers at the interface in blend systems

Compatibilization of Polymer Blends by Reactive Extrusion

Extruders can melt, mix, pump compound, and devolatilize high viscosity polymers. These characteristics are essential characteristics for a chemical reactor. Reactive extrusion is a process by which polymers undergo a chemical modification during the extrusion process. The advantages to performing a reaction in an extruder as opposed to in a solvent or diluent include (Xanthos, 1992):

- eliminate the energy of recovery of the diluent
- if no solvent or diluent is used, there will be no emissions from it.
- most of the plant equipment and the space it occupies can be saved
- controlled residence time and temperatures
- improved surface/volume ratio

Reactive extrusion is beneficial in production of polymer blends because the blending and compatibilization of the two components can be performed in one step. This in-line compounding can reduce the machinery investment and energy cost for processors by more than 50%. (Kreisher, 1990)

CHAPTER 2

Background

Polymer Blends

Over the last several decades the realization that new molecules are not necessary for the development of new materials has driven the commercial and scientific progress of the field of polymer blends. Blending can usually be implemented more rapidly and economically than the development of new materials. It is estimated that successful commercialization of a new polymer requires 15-20 years while development of an alloy or blend based on existing polymers may take half as long. (Kienzle, 1988) Blending already consumes 30 wt% of all polymers, and is growing at a rate of around 9%/year. Successful polymer blending requires a sound scientific basis.

Two component polymer mixtures can be described often by the following equation: (Kienzle, 1988)

$$P = P_1C_1+P_2C_2+IP_1P_2 \qquad (1)$$

P is a property value of the blend. P_1 and P_2 are the property values of the components. C_1 and C_2 are the concentrations of the components, and I is an interaction coefficient. The property relationship of polymer blends is illustrated below in figure 2.1. The polymer properties of the blend are a weighted arithmetic average of the constituents properties if I equals zero. If the blend is incompatible, usually because of poor interfacial adhesion, I has a negative value. Polymer compatibilization results in polymer alloys that possess positive values of I, i.e. the properties of the polymer combination are better than the weighted arithmetic average of the constituents properties.

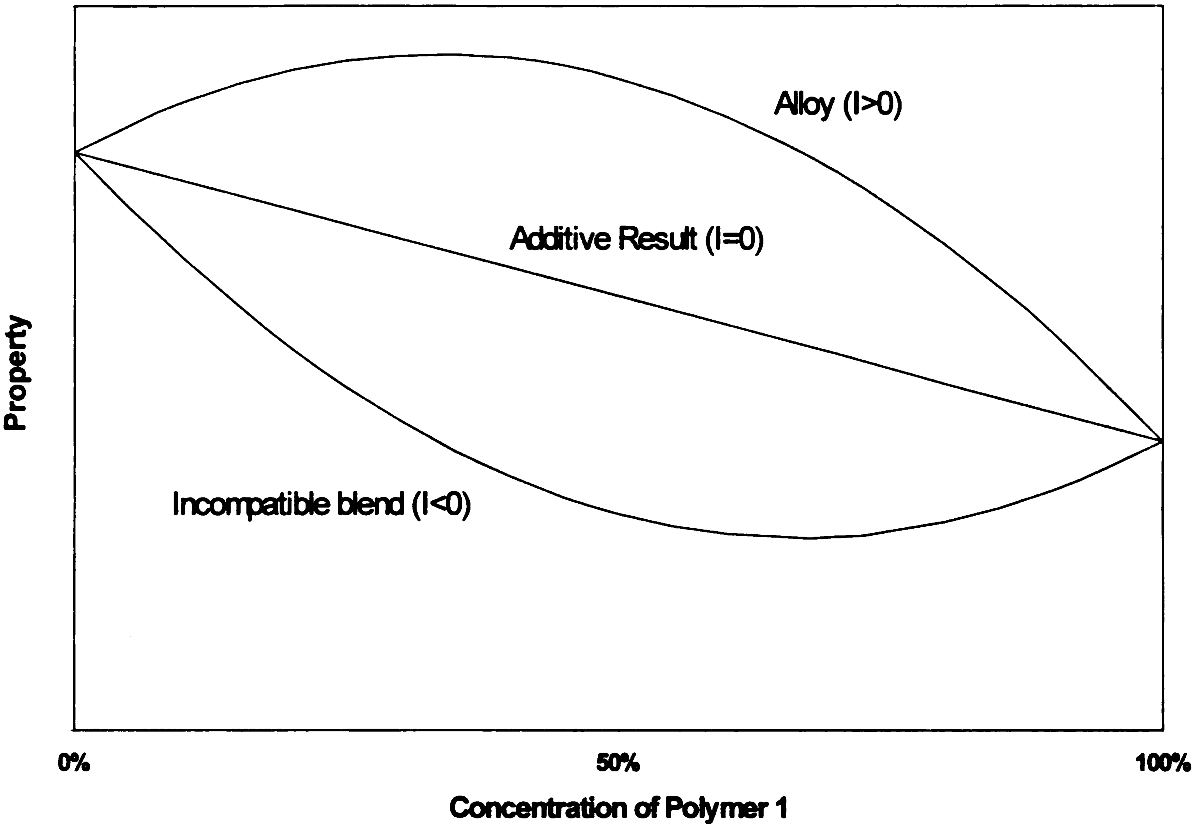


Figure 2.1: Property relationship in polymer blends

Basic Thermodynamics

The free energy of mixing governs the equilibrium phase behavior of mixtures as illustrated by the expression:

$$\Delta G_{mix} = \Delta H_{mix} - T\Delta S_{mix} \qquad (2)$$

where ΔG_{mix} is the free energy of mixing, ΔH_{mix} the enthalpy of mixing, T the temperature, and ΔS the entropy of mixing. The Flory-Huggins equation can be used to calculate the entropy of mixing.

$$\Delta S_{mix} = -k\ (N_1 \ln\phi_1 + N_2 \ln\phi_2) \qquad (3)$$

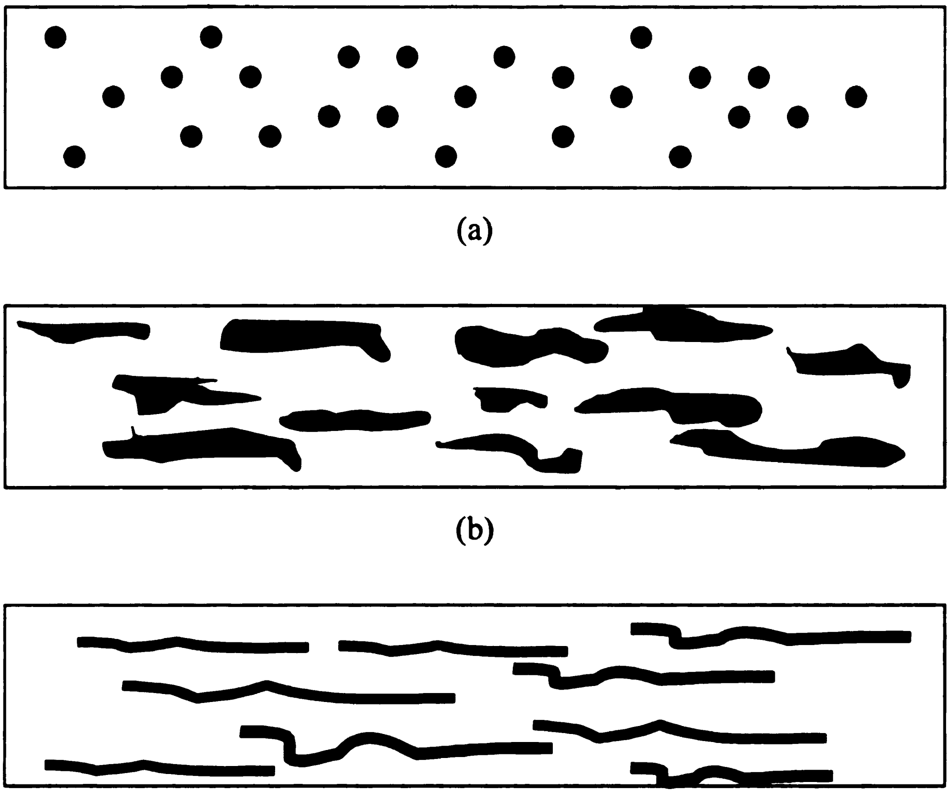
where k is Boltzman's constant, ϕ_i is the volume fraction of component I, and N_I is the number of moles of component i. As a result of the large molecular weight of each polymer in a typical blend, the number of moles of each polymer and hence the ΔS_{mix} is very small. It therefore does not contribute substantially to the free energy of mixing. The enthalpy of mixing then becomes key to determining the miscibility of a polymer blend. The enthalpy of mixing expressed as a function of solubility parameters δ, volume fractions ϕ, and total volume V is always positive.

$$\Delta H_{mix} = V\phi_1\phi_2(\delta_1 - \delta_2)^2 \qquad (4)$$

This results in a positive ΔG_{mix} since ΔS_{mix} is very small. The entropy of mixing can at best approach zero. The enthalpy of mixing can be negative however if specific interactions such as hydrogen bonding or dipole-dipole interactions occur. This negative enthalpy of mixing in turn can result in a negative free energy of mixing and the accompanying blend miscibility.

Blend Morphology

Most combinations of polymers are immiscible. Phase separated blends are often preferred for achieving useful properties. In principle such polymer-polymer composites yield materials whose stiffness could be adjusted to any value between those of the component polymers. To blend materials in such a fashion, control over the morphology of the phases must be exercised. The morphology generated during mixing of immiscible blends depends on three factors: interfacial tension between the phases, elasticity, and viscosity. (Han, 1981) Several general rules can be applied to determine which polymer is the continuous phase in the blend and which is the dispersed phase. Generally, three types of common morphology of immiscible blends include; the spherical droplet, the platelet, and the fibril. Fibrils are formed from droplets by uniaxial elongational flow, eg extrusion through a die. Bi-axial stretching of droplets forms platelets by processes such as blow molding. Examples of such morphologies can be seen in Figure 2.2



(a)

(b)

(c)

Figure 2.2: Dispersion of a polymer (dark regions in the matrix of an immiscible polymer: a) spherical droplets b) platelets c) fibrils

In these blends, the continuous phase is often the component occupying the most space. The lower viscosity component often will encapsulate the more viscous component reducing the rate of energy dissipation. These two factors can combine to yield a polymer that has a distinct continuous phase and dispersed phase or a blend with co-continuous phases of both polymers. What must be considered at all times is that morphology created during processing is a dynamic structure that is subject to change as a result of further processing.

Blend Preparation

Solution casting and melt mixing are the most common techniques used for preparing polymer blends. For immiscible pairs the details of the mixing process determine the composite morphology

The economics of melt mixing make it the most common method for preparing polymer blends. Disadvantages of melt mixing such as temperature induced degradation, difficulties in mixing materials with large differences in melt viscosity, and cleaning and the machinery, and equipment cost are often offset by the advantages of melt mixing. The primary advantages being speed, no solvents-environmentally friendly, and simplicity.

Solution casting is often used for small quantities of for polymers that do not process well by melt mixing methods. Care must be exercised when preparing a solution cast material if the true miscibility is to be determined. For example two immiscible polymers form a single phase solution when diluted enough in solvent. Rapid solvent removal can trap the polymer in a non-equilibrium homogenous state. (Schultz, 1976, 1980). In any processing situation, if miscibility is to be determined care must be exercised to determine if in fact physical equilibrium has been achieved.

Miscibility Determination

Visual inspection of an immiscible blend reveals a material of limited transparency that is caused by the light scattering due to phase separation. Domain sizes that are small relative to the wavelength of light or are of similar refractive indices limit light scattering, making visual inspection unreliable. Another problem associated with polymer visual inspection occurs if a blend with a miscible amorphous phase also contains a crystalline phase. This phase will scatter light as described and reduce transparency (Paul, 1988).

Examination of the glass transition is a simple and often reliable method for determining the miscibility of a blend. Miscible blends exhibit a single transition, while two-phase blends exhibit two T_g's, characteristic of the separate components. Several relationships have been proposed to describe the composition dependence of the glass transition. One of the simplest of these is the Fox relationship, (Fox, 1956):

$$\frac{1}{T_g} = \frac{\phi_1}{T_{g_1}} + \frac{\phi_2}{T_{g_2}} \qquad (5)$$

For accurate results however, the glass transitions must be separated by approximately 20 °C, and the concentration of the lesser material should be greater that 10%. Dynamic mechanical analysis is more sensitive than DSC. Less than 1% of the non-miscible component can be detected. However it requires relatively more complex equipment.

A third analytical technique that is extensively used for determining miscibility is electron microscopy.(Shaw, 1985) Appearance of two phases in electron microscopy would show that the components are not miscible. Poor phase contrast and expensive equipment, though disadvantages of this technique have not outweighed the advantages associated with it.(Folkes, 1993)

Compatibilization

Most polymers are thermodynamically immiscible and do not result in homogenous blends upon mixing. Typically, high interfacial tension and poor adhesion is seen at the interface. The high viscosity and inherent difficulty of imparting the desired degree of dispersion to random mixtures caused by the interfacial tension leads to lack of stability of the blend upon further processing (Paul, 1978b). The brittle mechanical behavior observed in dispersed blends is caused by the poor adhesion. (Paul, 1978b)

The two general routes for achieving compatibility are by a) adding a third component capable of interactions with the blend constituents, block or graft copolymer are examples of this or b) blending functionalized polymers capable of enhanced specific interactions, and/or chemical reactions.(Xanthos, 1988)

Systems compatibilized by graft or block copolymers include polystyrene-polyethylene blends (Barentsen et al, 1974) and cellulose acetate-polyacrylonitrile blends.(Paul, 1978b) Functionalized polymers can be prepared via reactive extrusion. (Tucker, 1987). Examples of such functionalized polymers include anhydride-modified polypropylene used in nylon 6/polypropylene blends. Styrene-glycidyl methacyrlate-reacts with poly ethylene terephthalate- to form an in situ compatibilizer in PET/PS blends (MAA, 1993). In natural fiber systems, biomass fibers have been compatibilized with hydrophobic materials (Narayan, 1991)

The addition of compatibilizer can in principle affect the blend system in three ways:

1. Reduce interfacial tension leading to finer dispersions during mixing
2. Increase adhesion at the phase boundaries thereby facilitating stress transfer.
3. Stabilize the dispersed phase against growth.

These factors usually lead to an increase in mechanical properties such as impact strength, and tensile strength. Consequently, these macroscopic properties can be used as an indirect means of measuring compatibilization.

Viscosity of Dilute Polymer Systems

The viscosity of dilute polymer solutions is considerably higher than that of pure solvent. This increase in viscosity depends on temperature, the nature of the solvent and polymer, the polymer concentration, and the sizes of the polymer molecules. Since viscosity is dependent on sizes of molecules, an average molecular weight can be determined from the solution viscosity of such a system.

If no slip boundary conditions at the tube wall are imposed on a fluid flowing through a tube, the resulting velocity profile can be visualized as in Figure 2.3.A. A particle suspended in such a flowing fluid would rotate since it impinges on fluid particles flowing at different rates as shown in Figure 2.3.B.

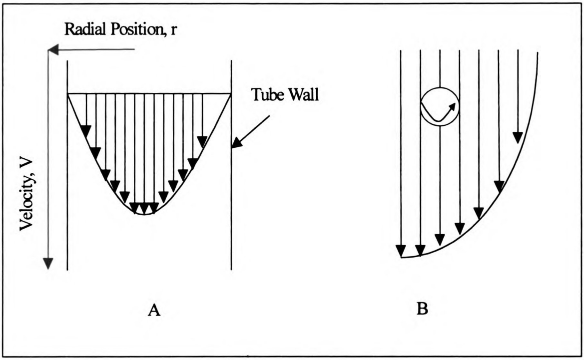


Figure 2.3: Fluid flow behavior A) Variation of laminar flow with respect to the distance r from the center of a tube. B) Sphere suspended in a flowing fluid

Rotation of this suspended particle, since it is wetted by the liquid, brings adhering liquid from a region with one velocity into a volume element which is flowing at a different speed. The readjustments of momenta because of this wetting cause an expenditure of energy, which is greater than that which, would be required to keep the same volume of fluid moving with a particular velocity gradient. Consequently, the suspension has a higher viscosity than the suspending medium.

It can be shown that the intrinsic viscosity is related to Viscosity Average Molecular Weight by the Mark-Houwink-Sakurada (MHS) relation (Rudin, 1982).

$$[\eta] = K\overline{M}_V^a \qquad (6)$$

Given K, a, and $[\eta]$, the viscosity average molecular weight can be determined. K and a are constants that are characteristics of particular solute-solvent systems. Intrinsic Viscosity can be found by measuring the suspension viscosity at different polymer concentrations. An extrapolation method using the Kraemer equation (7):

$$[\eta] = \frac{1}{c}\ln\left(\frac{\eta}{\eta_0}\right) \qquad (7)$$

can be used to determine intrinsic viscosity. η and η_0 are the suspension and solute viscosities respectively while c is the concentration of the polymer in the solution. For dilute polymer solutions $\eta/\eta_0 = t/t_0$ where t and t_0 are the times require for viscometer flow times for the suspension and solvent respectively. By extrapolating equation (7) to zero concentration the intrinsic viscosity of a particular polymer can be obtained.

The other constants in the MHS relation can be found by can be found by first fractionating a polymer into nearly mono-disperse molecular weight fractions. For mono-disperse polymer fractions $\overline{M}_v = M_n =$ any average molecular weight of the sample. The intrinsic viscosities of a number of such mono-disperse fractions are then fit to the equation

$$\ln[\eta] = \ln K + a\ln(\overline{M}_v) \qquad (8)$$

to yield the MHS constants for a particular polymer/solvent system. With these parameters then the Viscosity average molecular weight of two samples of the same polymer can be compared by simple viscosity measurements using readily available equipment such as a Ubbelohde viscometer.

CHAPTER 3

Design of a Compatibilizing Agent

Synthesis of Maleated Soybean Oil

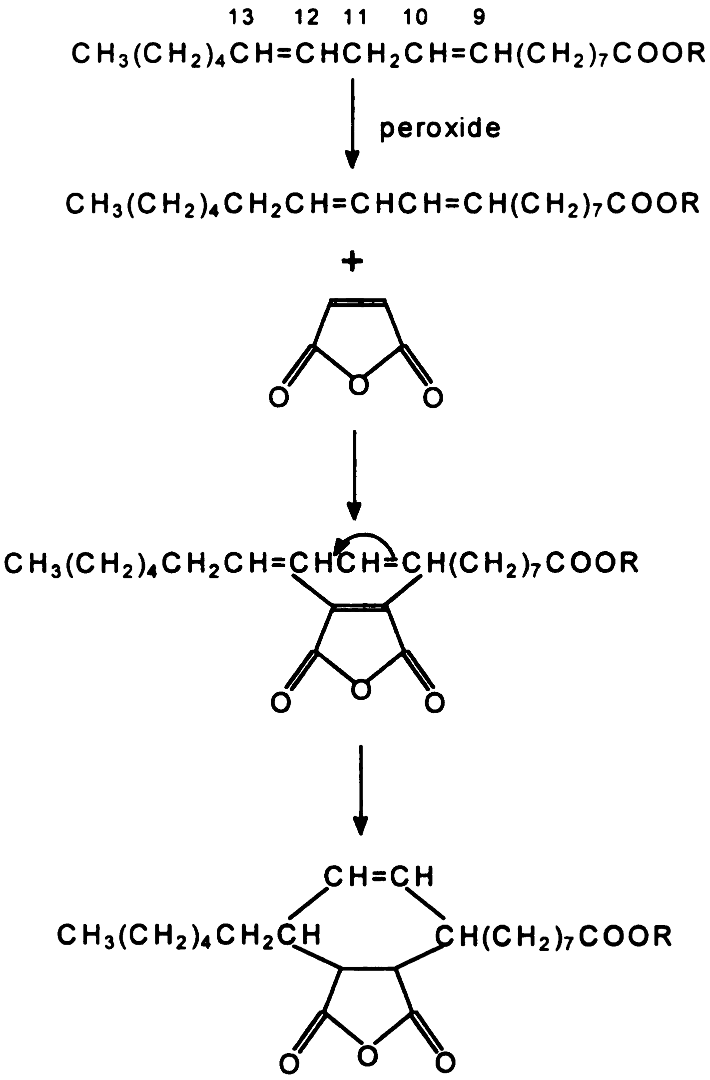
Soybean oil was purchased from Spectrum chemical. This oil had a molecular weight of approximately 872. The typical composition of soybean oil is shown in Table 3.1 (Kirk-Othmer, 1983).

Carboxylic acid	Chemical Acronym*	Wt% Soybean Oil[a]
Fatty Acid		
Saturated fatty acid		
Palmitic acid	16:0	10.7
Stearic acid	18:0	3.87
Unsaturated fatty acid		
Oleic acid	18:1	22.8
Linoleic acid	18:2	50.8
Linolenic acid	18:3	6.76

*Chain length, number of double bonds, and functional groups, if any

Table 3.1: Soybean Oil Composition

Maleation of soybean oil was performed using 99% pure reagent grade maleic anhydride, and Lupersol 101 as a catalyst. The reaction chemistry postulated by Root (Root, 1945) suggests that soybean oil in the presence of a catalyst like peroxide will form conjugated double bonds from non-conjugated double bonds. These double bonds can then undergo a 1-4 Diels-Alder type of a reaction, resulting in the addition of maleic anhydride to the soybean oil as shown below.



Synthesis of maleated soy oil was performed in a 2L Parr reactor. Approximately 975g of soybean oil were combined with 125g maleic anhydride and 10ml of Lupersol 101 in the reactor. Lupersol 101 a mixture of 2,5-Dimethyl-2,5-di-tert-butylperoxy-hexane, Di-tert-butyl peroxide, 3,3,6,6-tetramethyl-1,2-dioxacyclohexane, and 2,2,5,5-tetramethyl tetrahydrofuran, was obtained from Vanderbilt under the industrial name Varox BPDH. This organic peroxide used as a catalyst in the maleation of soy oil possesses a half-life of 1 minute at 180°C and 13 seconds at 200°C. Reaction time was 30 minutes. Reaction temperature was 150°C. The reaction times and temperatures and stoichiometries chosen were optimums based on previous work. (Seybold, 1997) The above reaction was performed under a nitrogen atmosphere. Vacuum was pulled on the reaction vessel at the end of the reaction time to remove any excess maleic anhydride and catalyst. A schematic of the reactor system used is shown in Figure 3.1.

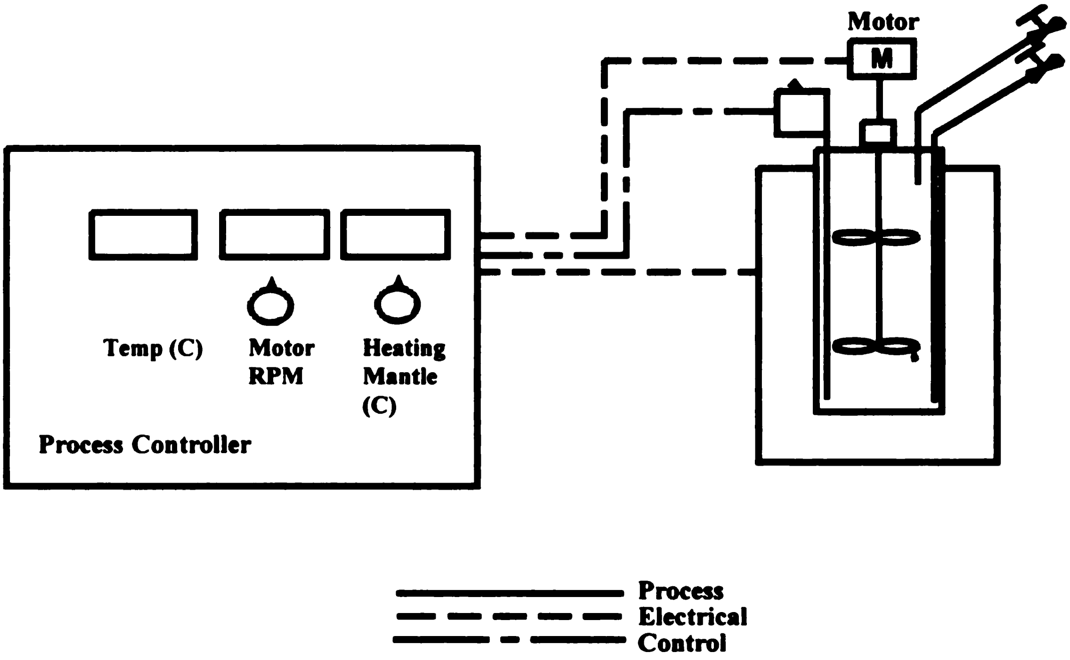


Figure 3.1: Experimental apparatus for the maleation of soybean oil

Grafting of Maleated Soybean Oil onto Eastar Bio Copolyester

Maleated Soybean Oil was reactively grafted to Eastar Bio Copolyester using the ZSK 30 twin screw extruder, and Dicumyl Peroxide as a catalyst. (DCP) Dicumyl Peroxide is a dialkyl peroxide that is often used as an initiator in polymerization and crosslinking reactions. (Kirk Othmer, 1983b) The material used in the grafting reactions was obtained from Aldrich. The melting point of this material is 78°C and the 10hr half-life temperature is 115°C. The structure of Dicumyl peroxide is shown below.

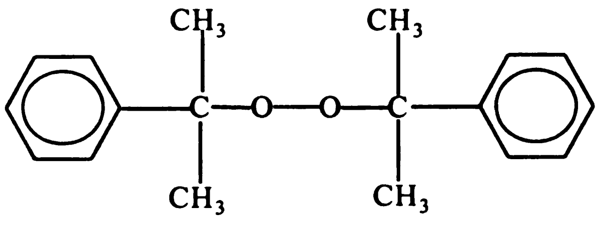


Figure 3.2: Molecular Structure of Dicumyl Peroxide

Eastar Bio Copolyester (EBC) is a random copolymer of Adipic acid, Terepthalic acid, and 1,4-butanediol. (Buchanan et al, 1995) The repeat structure of EBC is shown below.

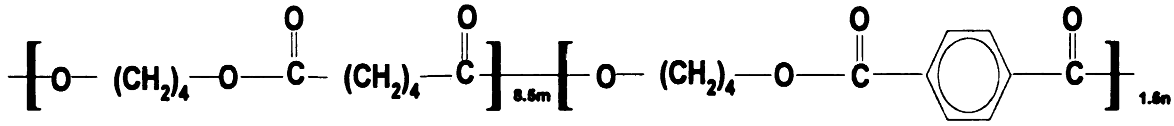


Figure 3.3: Structure of Eastar Bio Copolyester

In the structure, m and n are dependent on degree of polymerization. Weight average is 67,000, while number average molecular weight is 20,000. (Wright, 1998) Melt temperature at peak melt is approximately 110°C. Properties of Eastar are listed in Table

3.2. Biodegradability testing of Eastar as measured by ASTM D-5338 standards indicates the polymer reaches full degradation within 60-90 days.

Properties	**ASTM Method**	**Value**	**Units**
Film Thickness	D 374	1.0	mils
Density		1.27	g/cm^3
Crystalline T_m		110	°C
T_g	D 3418	-33	°C
Melt Index	D 1238		
at 190°C		25-31	g/10 min
at 125°C		0.7-2.6	g/10min
Tensile Strength at Break	D 882	18.9	MPa
Elongation at Break	D 882	425	%
Tensile Modulus of Elasticity	D 882	86	MPa
Dart Impact	D 1709	100	g

Table 3.2: Selected Properties of Eastar Bio Copolyester

The reaction proceeds via a peroxide catalyzed attack at the carbon nearest the ester bond in the copolyester. This attack creates a radical that can then attack at double bond in the MSO. The result of this reaction is the grafted copolyester structure shown in Figure 3.4.

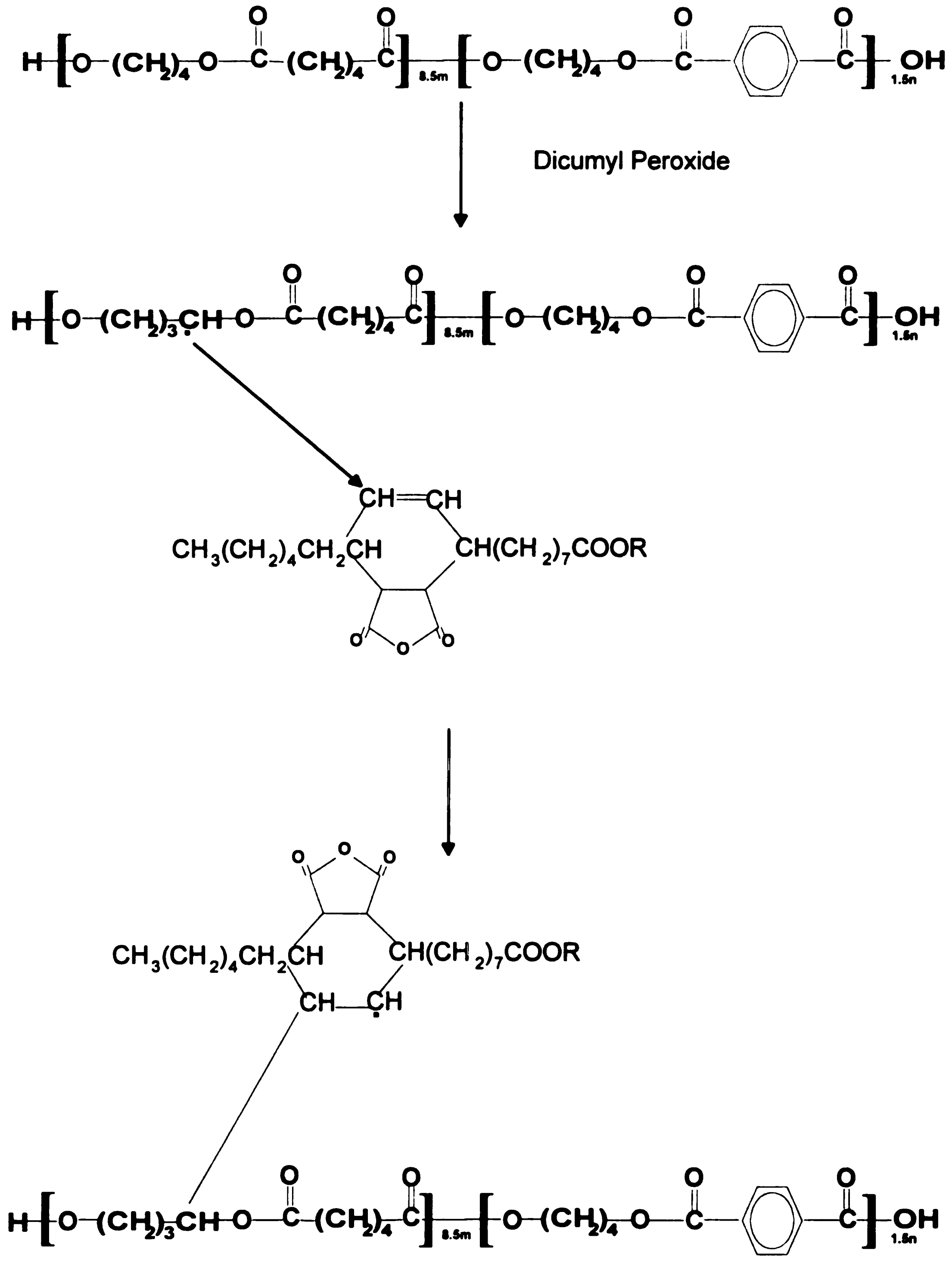


Figure 3.4: Grafting of maleated soybean oil onto Eastar Bio Copolyester

Several parameters were examined to determine the most efficient procedure for performing this process. The first procedure involved simply mixing the MSO with the catalyst, DCP and the copolyester and then feeding this mix to the extruder. This process was unsuccessful because the high viscosity of the MSO inhibited the free flow of the mixture. The next process involved mixing the copolyester with the DCP and then adding the MSO into the extruder through a liquid feed port. This process was partly successful but was not totally successful because it was difficult to pump the viscous MSO with the available peristaltic pump. The final refinement to this process involved heating the MSO and then pumping the less viscous warm MSO into the extruder liquid feed port.

Two screw configurations were tested to determine which configuration would be most effective for this process. The first configuration tested was the configuration used in the starch plasticization process (see Chapter 4). The process did not successfully operate in this configuration. A large zone of kneading blocks nearest the feed throat prevented forward conveying of the MSO. The second configuration eliminated much of this kneading zone and replaced those kneading elements with conveying elements as shown in Figure 3.5.

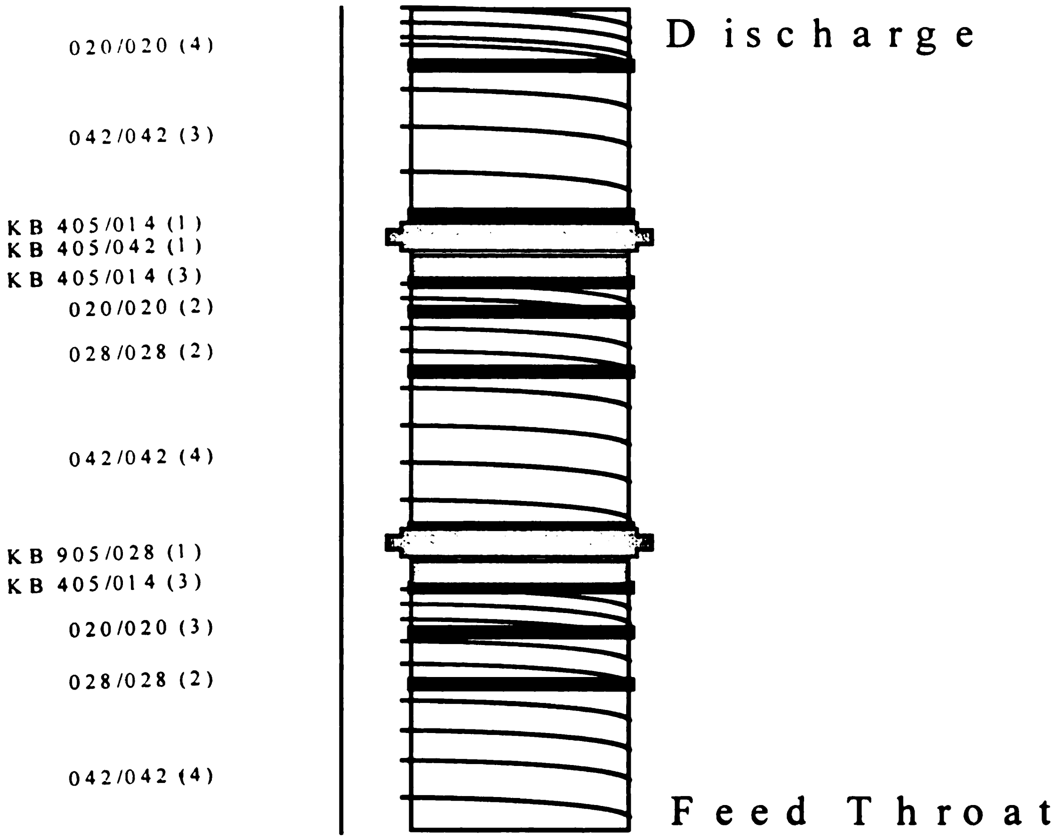


Figure 3.5: Screw configuration for reactive extrusion

The numbers associated with the conveying elements (clear) in Figure 3.5 a/b (c) are a code in which

a = screw pitch (mm)

b = element length (mm)

c = number of elements.

The code for the kneading elements (gray) is aab/bcc where

aa = paddle offset in degrees

b/b = first b is number of paddles on element, second b =0

cc = element length in mm

A final problem that needed to be solved to ensure the success of this process was an equipment problem associated with the extruder. MSO served as a lubricant for the extruder and the extruder would shut down automatically due to extruder under-load. To solve this problem, the temperature profile chosen was lower than the normal processing temperatures for this polymer system, thereby increasing viscosity of the melt and load on the extruder eliminating the extruder under-load problem. The profile used in shown below.

	Zones					
	1 Feed Throat	2	3	4	5 Vent	6
Temperature (°C)	70	175	175	175	120	115

Table 3.3: Temperature profile for reactive extrusion

The entire process was conducted under a blanket of nitrogen gas to prevent any unwanted side reactions. Extruder RPM was 100. Five materials were prepared reactively for further analysis. All mixtures contained 0.3% Dicumyl peroxide. The first material was simply the copolyester and DCP. The second, third and fourth mixes consisted of the copolyester, DCP and 5%, 10%, and 20% MSO. The fifth mix consisted of copolyester and 10% MSO without DCP. These mixes were extruded as described above, run through a water bath and pelletized. The ensuing material was then dried in a vacuum oven for 15 hours and further blended and characterized.

Characterization of maleated soybean oil and the grafted copolyester products.

MSO characterization

Characterization of the MSO included measurement of acid numbers, and Iodine values for reaction performed. To measure acid number, small amount of MSO was dissolved in 1-octanol. This solution was titrated against a standard KOH in octanol solution to a phenopthalein endpoint. The average acid number for the MSO was 82. Based on this acid number the number of moles of maleic anhydride added per mole of soybean oil was determined to be 1.14.

The Iodine value is a measure of unsaturation of fats and oils. To measure Iodine value, the sample material is first dissolved in chloroform. Wij's solution (Iodine monochloride in acetic acid) is added to the flask and incubated for 30 minutes. After incubation, potassium iodide solution is added to the mixture. A nominal amount of water is then added to the solution and the contents are titrated with sodium thiosulfate solution until the yellow color almost disappears. At this point, a small amount of starch indicator solution is added creating a blue mixture. This final mix is titrated to a clear endpoint. The amount of thiosulfate solution can then be used to determine the Iodine number. Iodine numbers were approximately 100 for the MSO. This Iodine value corresponds to about 3.3 double bonds/mole of soybean oil. Further characterization of this product should include GC-MS, and detailed NMR and FTIR spectra of the product to verify the actual structure of the product.

Extraction

Approximately 5g of each material were extracted to determine the grafting efficiency. To do this each material was refluxed in xylene for 4-5 hours. After refluxing the solutions were precipitated into methanol to eliminate any free maleic anhydride. The resulting solids were then washed with warm chloroform to remove any free MSO. The final product was titrated against ethanolic KOH to determine the amount of grafted MSO. Given the amount of MSO added to the extruder, grafting efficiency was determined by dividing the weight percent grafted by the weight percent added. Grafting efficiency for selected materials is shown in Table 3.4.

Weight % MSO added	**5%**	**10%**	**10%(no DCP)**	**20%**
Grafting Efficiency	*58%*	*38%*	*23%*	*30%*

Table 3.4: Grafting efficiency of reactive extrusion

Based on the results in Table 3.4 grafting efficiency is a nearly a linear function of theoretical MSO concentration. The results from the 10% MSO blend without DCP show that DCP increases grafting efficiency but is not necessary to achieve grafting of the MSO to the copolyester. The 10% material was chosen for blending with starch for further study because of ease of preparation and middle range grafting efficiency.

Further understanding of this grafting reaction and verification of the structure of the actual product is needed. Studies of the effects of DCP concentration on efficiency need to be performed. Quantitative solution FTIR of the extracted materials could be performed to verify the grafting efficiency. Finally, GC MS, NMR and FTIR spectra of the product should be obtained to verify the product structure.

Intrinsic Viscosity

The intrinsic viscosity measurements were carried out at 30°C in a constant temperature bath using a Ubbelohde viscometer. The pure and grafted samples were dissolved in methylene chloride and diluted to the required concentrations. These intrinsic viscosity measurements were performed for four materials: EBC, EBC-g-MSO10B, EBC-g-MSO10G, EBC-DCP. The intrinsic viscosity was determined by using the Kraemer equation:

$$[\eta] = \frac{1}{c}\ln\left(\frac{\eta}{\eta_0}\right)$$

Plots of the right had side of the equation versus viscosity yield a y intercept equal to the intrinsic viscosity. These plots were constructed for the four test materials and are shown in Figure 3.4. It can be seen that the intrinsic viscosity goes up for the MSO grafted material (EBC-g-MSO10G) when compared to the 10% MSO blended material (EBC-g-MSO10G) or the copolyester itself (EBC). This increase in intrinsic viscosity and in turn molecular weight may be attributed in part to the presence of Dicumyl peroxide as evidenced by the great increase in intrinsic viscosity for the EBC-DCP material. These increases in intrinsic viscosity can be related directly to increases in molecular weight. The materials, then, in order of increasing molecular weight would be: EBC<EBC-g-MSO10B<EBC-g-MSO10G<EBC-DCP. MSO10G indicates 10% by weight MSO was added to the extruder during the reactive extrusion process. MSO10B indicates 10% by weight MSO was added to extruder during the reactive extrusion

process, but without the presence of Dicumyl peroxide. This terminology will be used throughout. Characterization to be done on these materials could include doing Gel Permeation Chromatography (GPC) to determine absolute molecular weights.

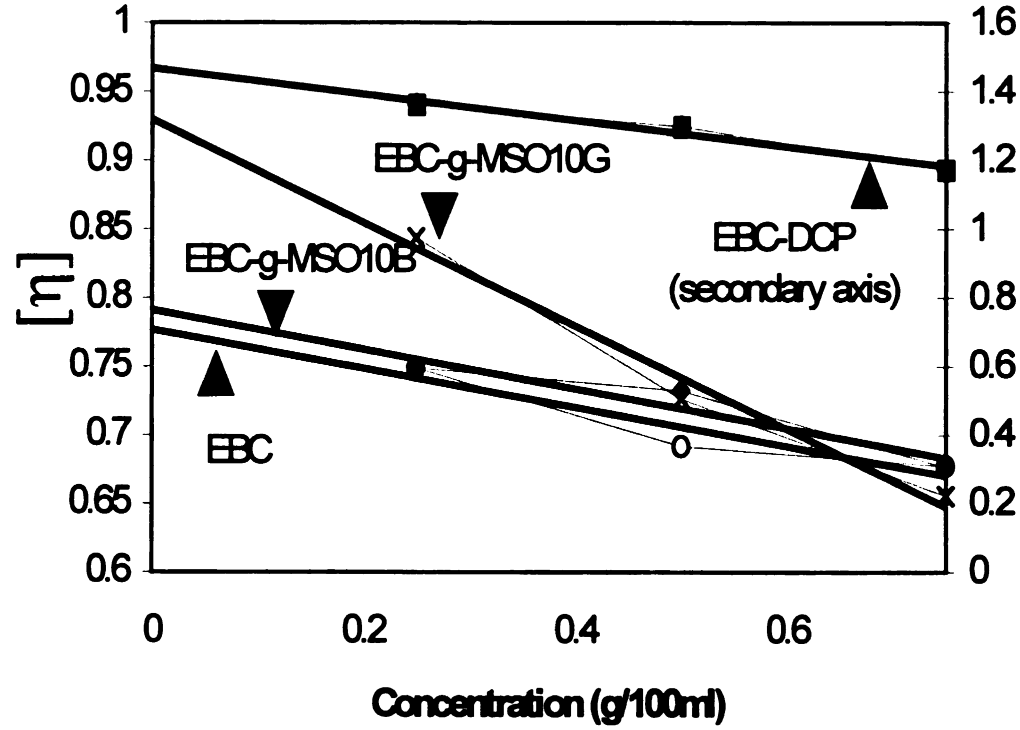


Figure 3.6: Intrinsic Viscosity Determination for Eastar Polyesters

CHAPTER 4

Preparation of Materials

Preparation of Thermoplastic Starch

(TPS) Thermoplastic starch was prepared by mixing 5 parts polycaprolactone (Tone 787, Union Carbide) with 80 parts corn starch (Silver Medal Pearl, Cargill) and 20 parts glycerol (Carrier Stephens). The thermoplastic starch was prepared using the process developed by Krishnan (Krishnan, 1998). Dry starch and other additives were blended to form the solid feed mixture that was fed to the extruder feed throat using an Acrison gravimetric feeder at a set point of 8.0lb/hr. Liquid glycerol was fed to the extruder immediately downstream from the feed throat using a Masterflex peristaltic pump and Tygon tubing at 2.0 lb/hr. The glycerol was fed from a plastic bottle set on a balance during the processing. Plasticizer feed rate was checked by monitoring weight loss on the scale. A vent port was opened on the extruder to allow water to escape, preventing a foamed product. The temperature profile is shown below.

	Zones					
	1 Feed Throat	2	3	4	5 Vent	6
Temperature (°C)	50	90	110	130	140	150

Table 4.1: Extruder temperature profile for starch plasticization

Extruder RPM was maintained at 120. Strands leaving the extruder were allowed to air cool before pelletizing. The screw configuration was chosen to ensure adequate shear to break up the crystalline domains of the starch. This configuration is shown below. The numbers associated with the elements are the same as those in Fig 3.3

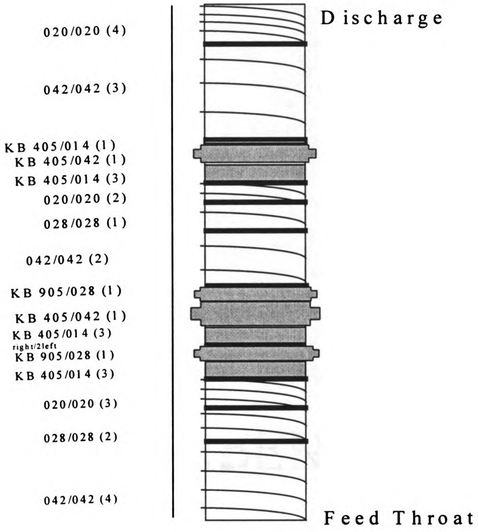


Figure 4.1: Screw configuration for starch plasticization

Environmental Scanning Electron Microscopy clearly demonstrates that plasticization disrupts the crystalline structure of the starch, creating a more thermoplastic material. Figure 4.2 is an ESEM photograph of starch, while Figure 4.3 is an ESEM photograph of Thermoplastic starch. There is a definite reduction in particle size and structure caused by the plasticization process.

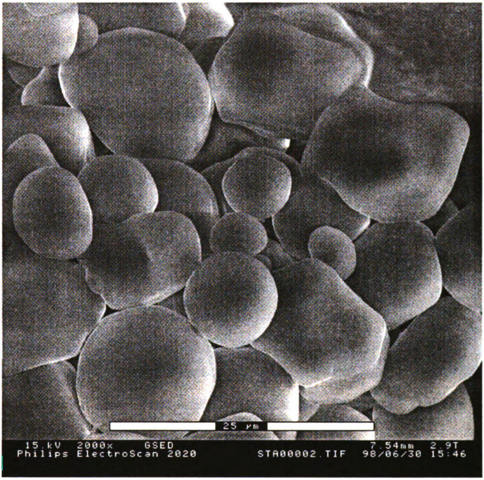


Figure 4.2: ESEM of Starch Granules

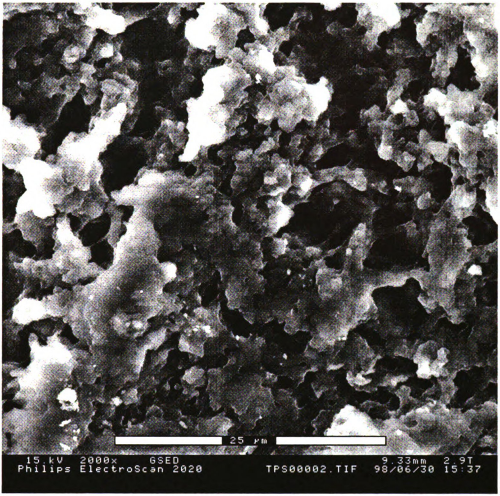


Figure 4.3: ESEM of Thermoplastic Starch

Reactive Blending of Thermoplastic Starch with Grafted Copolyester

Compounding of the copolyester and the MSO-g-EBC with thermoplastic starch, and other materials was done using the ZSK 30 twin screw extruder at 200 RPM.. The compounded materials were passed through a cold water bath, pelletized, and vacuum dried for 15 hours. The screw configuration used was the same configuration used for the reactive extrusion (Figure 4.3). The temperature profile used is shown in Table 4.3.

	Zones					
	1 Feed Throat	2	3	4	5 Vent	6
Temperature (°C)	80	175	175	170	175	140

Table 4.2: Temperature profile for compounding with thermoplastic starch.

Three basic blends were made with EBC and EBC-g-MSO10G. These materials were blended with thermoplastic starch in ratios of 70:30, 60:40, and 50:50. A fourth blend was prepared with both the EBC and EBC-g-MSO10G that consisted of 48% polyester, 32% thermoplastic starch, and 20% Kay-o-cel fiber. The final blend consisted of a ratio of 65:5:30 EBC:EBC-g-MSO10G:TPS. All materials after drying were injection molded for tensile testing and/or characterized further.

Injection Molding of Test Bars

A Cincinnati Millicron Vista Sentry 85 ton injection molder was used for molding materials into ASTM D638 type specimens. Molding conditions used for most of the blends are shown below.

Temperature	Zone 1	Zone 2	Zone 3	Nozzle
	175	175	175	175
Inject time: 5s Pack: 5s Hold: 5s Cooling: 30s				

Table 4.3: Conditions for injection molding of specimens

Most materials molded such that the material fed well and filled the mold readily. Only the material containing 20% MSO could not be injection molded. This material would not actually feed into the injection molder. The MSO provided a lubricating action that reduced the friction with the screw that is needed to convey material forward. The material containing 10% MSO also proved difficult to mold but it was not impossible to mold. Most of the materials molded were stuck to the sprue side of the mold. To eject these materials from the mold manual intervention was required. To remedy this problem a mold heater could be purchased and the side opposite the sprue could be heated. Attempts were made to optimize the cooling time to solve this problem but proved largely unsuccessful. Cooling time should be high enough to allow solidification and some part shrinkage, but low enough to prevent solidification of the material at the nozzle.

CHAPTER 5

Properties of Biodegradable EBC-g-MSO Blends

Examination of morphology by Environmental Scanning Electron Microscopy

Surface morphology of a sample can be examined using scanning electron microscopy-SEM. This technique was used to examine the morphology of not only the TPS, but also the TPS blends. A normal SEM image is formed when secondary electrons for atoms of the sample are given out as a result of inelastic scattering by the electron beam. Topography of a sample can be easily seen. The projecting areas of samples give out large number of scattered electrons and appear brighter while low lying areas do not allow electrons to escape and appear darker.

Electrons are detected in typical SEM by and Everhart-Thornley detector. This detector operates at a chamber pressure between 10^{-5} and 10^{-7} Torr. At pressures higher than this, the electric field between the detector and sample breaks down make the detector inoperable. The inherent limitations of SEM, therefore, are imaging of only vacuum tolerant and electrically conductive materials. Conventional SEM can overcome these limitations by application of conductive coatings or by extensive sample prep.

Environmental Scanning Electron Microscopy permits one to view samples with minimal sample prep. These samples can be nonconductive and vacuum intolerant. By employing a much more sensitive detector and an advanced vacuum pumping system that separates a high pressure specimen chamber from the low pressure electron source the sample chamber can be maintained at 20Torr. These advantages provide great versatility in viewing many samples with minimal preparation.

An Electroscan 2020 scanning electron microscope was used to obtain the SEM pictures. Samples were prepared for viewing by taking a raw pellet of material and sticking it to the specimen holder. This holder was then placed in the specimen chamber. After chamber evacuation, computer images were saved for further analysis.

ESEM photographs of the copolyester itself reveal nothing unusual. The surface is uniform and homogenous as seen in Figure 5.1. However the addition of thermoplastic starch at 30% to the mix results in a very heterogeneous blend with starch particles being clearly visible in the ESEM photograph (Figure 5.2).

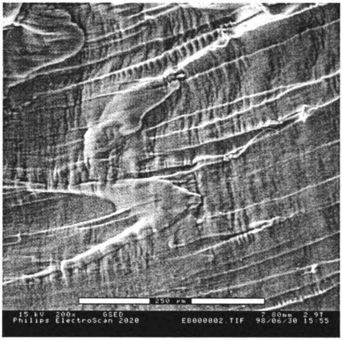


Figure 5.1: ESEM of Eastar Bio Copolyester

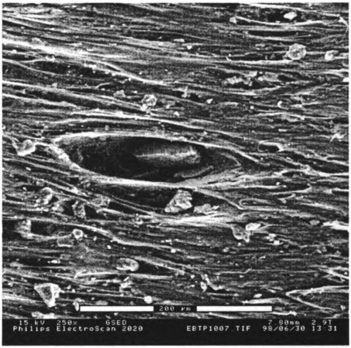


Figure 5.2: EBC:TPS 70:30 blend, note the small starch particles clearly visible.

Comparison of three 70:30 blends reveals some interesting characteristics. The three blends to be compared are EBC:TPS, EBC-g-MSO10G:TPS in 70:30 ratios and EBC:EBC-g-MSO10g:TPS in a 65:5:30 ratio. Panoramic pictures of the three blends reveal striking morphological differences. In the EBC:TPS blend, Figure 5.3, thermoplastic starch granules are clearly visible laying on the surface of the polyester matrix. In the EBC-g-MSO:TPS blend, Figure 5.4, the thermoplastic starch granules are still visible but, they are not as obviously segregated from the polyester matrix. In the EBC:EBC-g-MSO10G:TPS blend the thermoplastic starch granules are not visible at all. This morphological trend indicates that compatibilization is occurring with the addition of the grafted polyester.

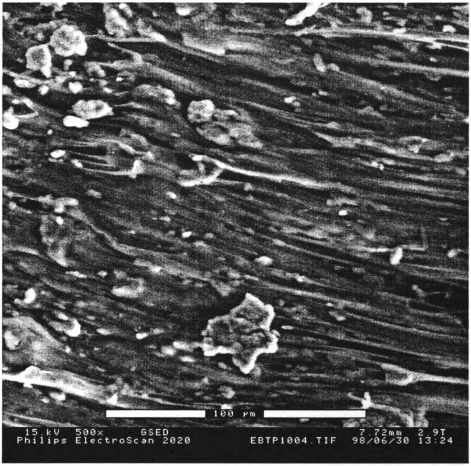


Figure 5.3: EBC:TPS; 70:30 blend, note large TPS particles (lighter color) laying on the surface.

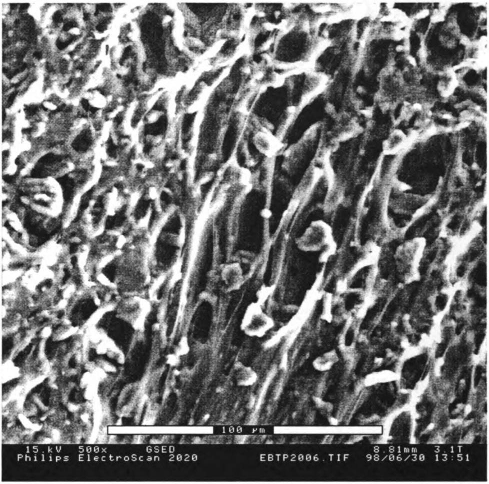


Figure 5.4: EBC-g-MSO10G:TPS; 70:30 blend, note thermoplastic starch particles are partially integrated into the grafted polyester matrix

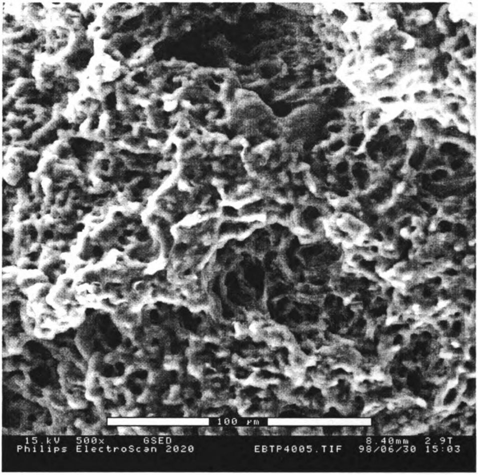


Figure 5.5: EBC:EBC-g-MSO10G:TPS; 65:5:30 blend, note no thermoplastic starch particles are visible.

Close up photographs of each of these three 70:30 blends reveals that in the case of the EBC:TPS blend, Figure 5.6, there is no adhesion between the starch particles and the polyester. In the EBC-g-MSO10G:TPS blend, Figure 5.7, though, adhesion is seen between the thermoplastic starch particles and the grafted copolyester. In contrast, in the EBC:EBC-g-MSO10G:TPS blend, Figure 5.8 the thermoplastic starch particles are barely distinguishable from the polyester matrix, indicating a higher level of adhesion and particle integration. This morphology being exhibited by the last blend indicates that compatibilization is occurring for this mixture. Physical property testing to be discussed later also supports this hypothesis.

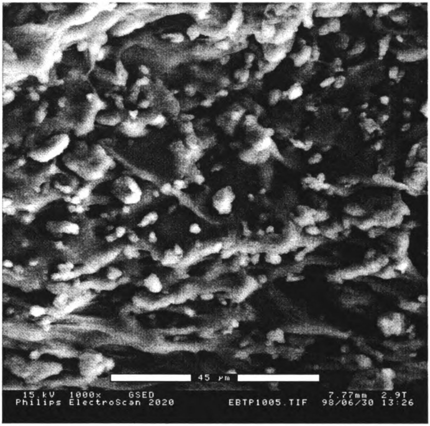


Figure 5.6: EBC:TPS;70:30 blend, note no adhesion of thermoplastic starch particles to matrix

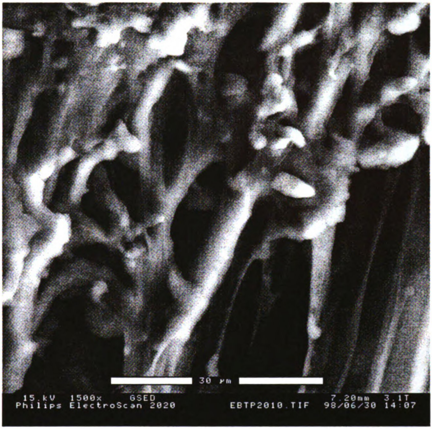


Figure 5.7: EBC-g-MSO10G:TPS;70:30 blend, note some adhesion of thermoplastic starch particles to the matrix

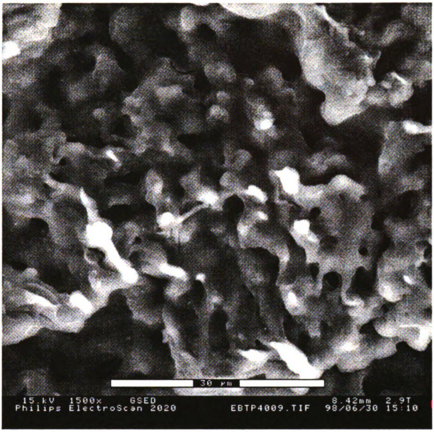


Figure 5.8: EBC:EBC-g-MSO10G:TPS; 65:5:30 blend, note thermoplastic starch particles are no longer readily distinguishable from the polyester matrix

Tensile Testing

Tensile tests were conducted using a UTS testing machine to determine stress, strain, and Young's Modulus for all samples. The blends lacking starch were tested at 1 in/min or 0.5 in/min for the modulus measurement. These samples exhibited high elongation, therefore, stress at break was not measured. Stress at high elongation was measured for comparison purposes. To prevent bar slippage during the test, the UTS clamps were tightened frequently. The starch containing blends were generally tested at 2 in/min for breaking and 1 or 0.5 in/min for modulus measurement. Conditioning of all samples was performed at 50% relative humidity and 75°F for at least 40 hrs prior to testing. At least six specimens of each material were tested The first group of materials tested were the polyesters and modified polyesters: EBC, EBC-g-MSO5G, EBC-g-MSO10G, EBC-g-MSO10B, and EBC:DCP. The second set of materials tested consisted of nine blends and EBC. The nine blends are:

70:30 - EBC:TPS and EBC-g-MSO10G:TPS
60:40 - EBC:TPS and EBC-g-MSO10G:TPS
50:50 - EBC:TPS and EBC-g-MSO10G:TPS
65:5:30 - EBC:EBC-g-MSO10G:TPS
48:32:20 - EBC:TPS:Fiber and EBC-g-MSO10G:TPS:Fiber

Of the materials in the first set the EBC:DCP exhibited the highest tensile strength at break (Figure 4.9). This is not surprising since this material also exhibited the highest intrinsic viscosity and therefore the highest molecular weight of this group of materials. This material was also the only material to break during the tensile test. The other materials stretched to high elongation without breaking. This high elongation caused problems since the test bars tended to slip in the clamps. This slippage was fixed by tightening the clamps in mid-test. This tightening caused the spikes seen in Figure 5.9.

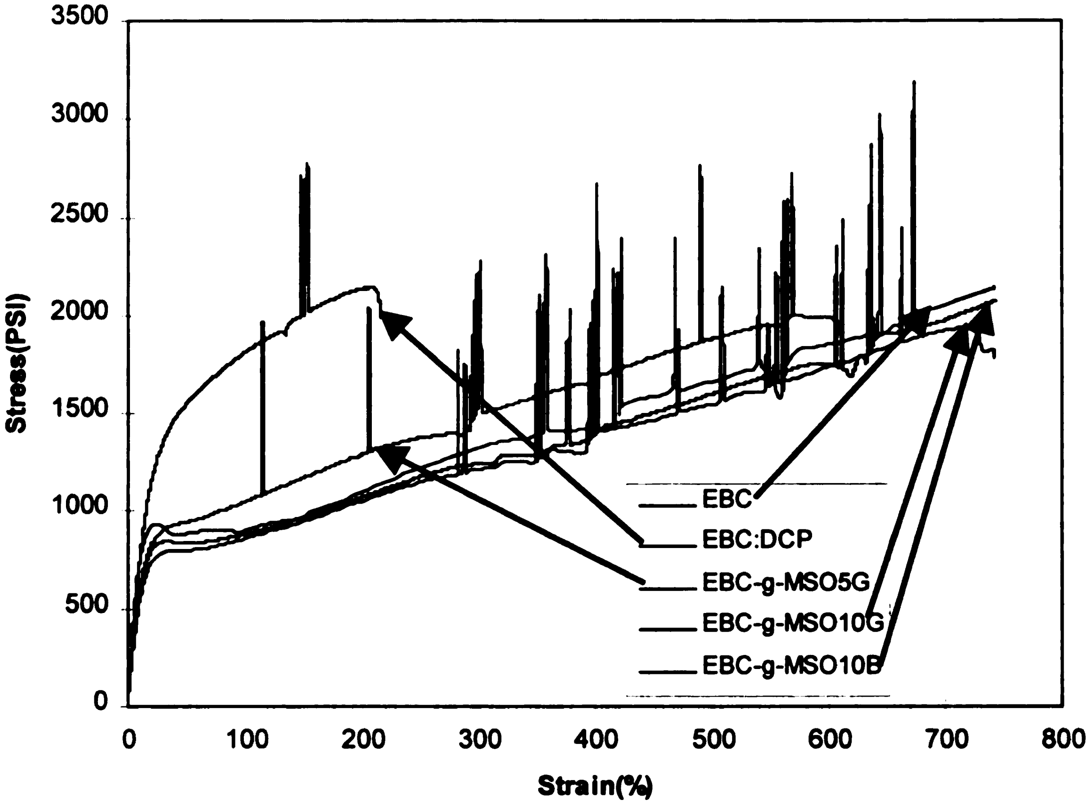


Figure 5.9: Tensile test results for modified copolyesters

The fact that physical properties correlate well with intrinsic viscosity measurements indicates that the grafting reaction was successful. This additional strength could also be a function though of crosslinking caused by the presence of Dicumyl peroxide. Intrinsic viscosity data support this theory. Further characterization of this group of materials by NMR and FTIR techniques in attempts to elucidate the structures will provide great help in determining the actual graft structure and provide another check for the grafting efficiency.

Strength at Break or High elongation was examined for 70:30, 60:40, and the 50:50 EBC:TPS, and EBC-g-MSO:TPS blends. As seen in Figure 5.10, the blends containing EBC-g-MSO10G outperforms the blends containing EBC in the same ratios All blends broke except for the EBC:EBC-g-MSO:TPS; 65:5:30 blend and EBC itself, therefore ultimate tensile strengths of these materials can't be compared to the other materials. Since these materials are already stronger than there counterparts are at break there break strength is also stronger than the other materials break strengths. Compatibilization of the EBC-g-MSO:TPS blends occur but are not as effective as the EBC:EBC-g-MSO:TPS blend. This indicates that a small amount of the grafted copolyester is a better compatibilizer than large amounts. This small amount of modified copolyester is most likely at the interface between the two phases serving in the same fashion as a graft copolymer does to compatibilize this system.

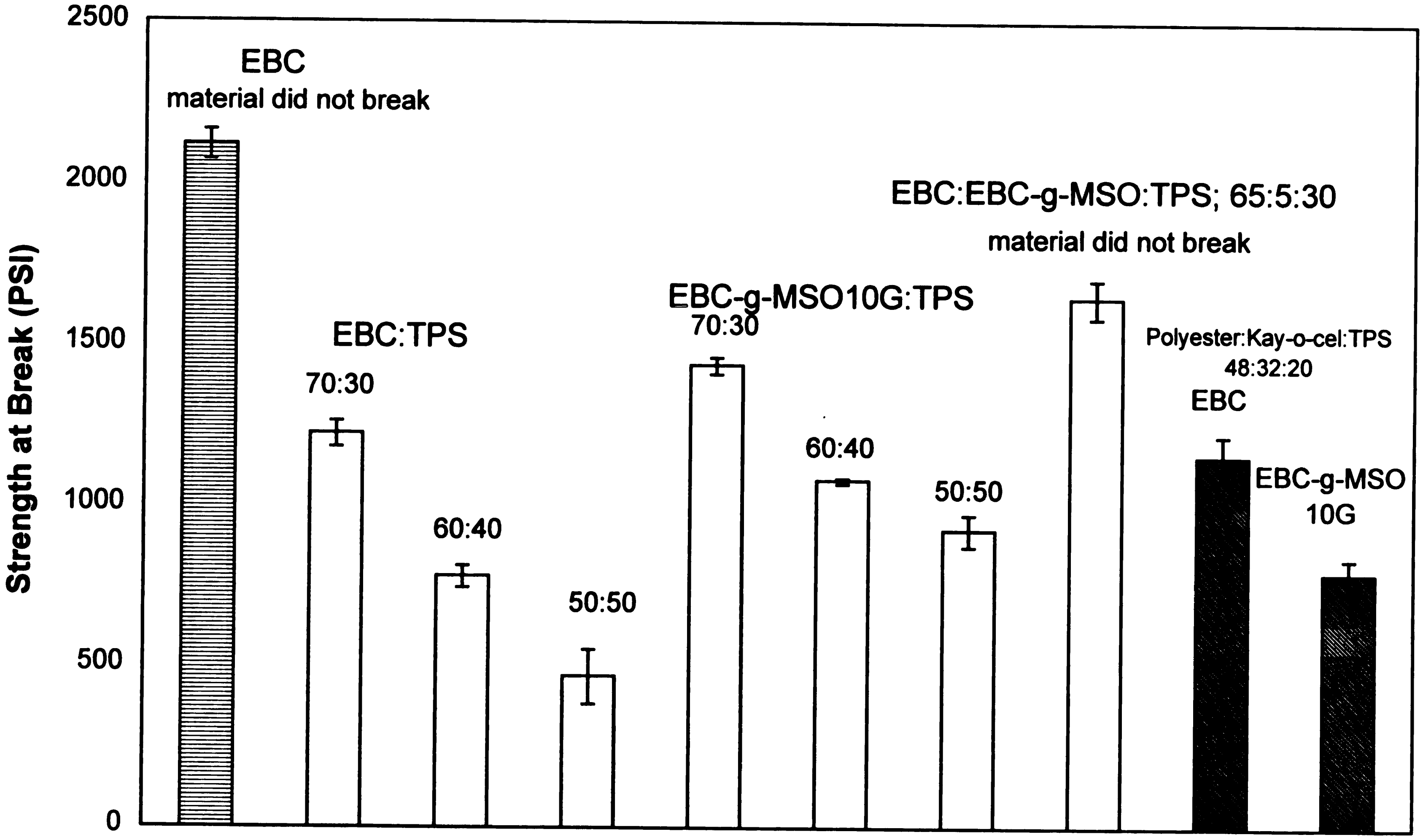


Figure 5.10 Tensile Strength at break for Polyester Blends

Error bars indicate one standard deviation. This fact coupled with the ESEM pictures would indicates compatibilization is occurring with the addition of EBC-g-MSO10G. The observation also that the EBC:EBC-g-MSO10G:TPS; 65:5;30 blend was even stronger than the EBC-g-MSO:TPS; 70:30 blend is also supported again by the ESEM pictures. The only situation in which the EBC outperforms the EBC-g-MSO10G is when fiber is added. The tensile strength at break as a function of concentration is shown in Figure 5.11. Increasing levels of starch, though helpful for biodegradability are detrimental to the material properties.

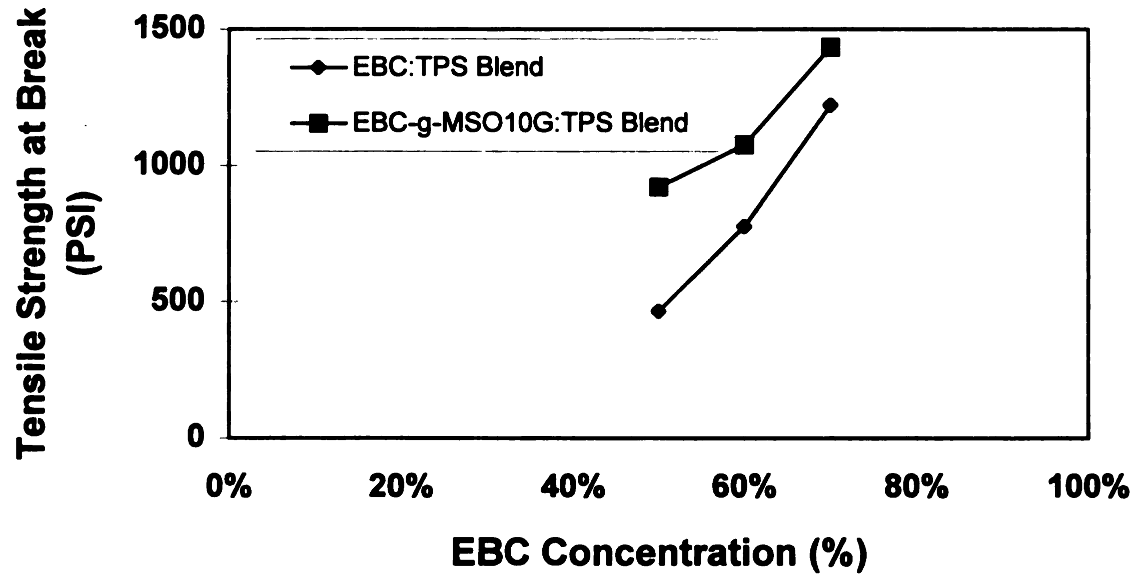


Figure 5.11 Tensile testing of modified polyester: thermoplastic starch blends

Biodegradability Testing Under Composting Conditions

Four materials were tested for biodegradability under composting conditions. These materials were EBC, EBC-g-MSO10G, EBC-g-MSO10G:TPS;70:30, and, EBC-g-MSO10G:TPS:Fiber; 48:32:20. Carbon content of each sample was determined using a Perkine Elmer CHN analyzer. Thirty grams dry weight sample was added to 180g dry weight compost. Water was then added to all samples as needed to reach the centrifuge moisture equivalent described in ASTM D-424-79. These mixtures were then placed into two liter glass bottles for testing. Each sample was tested in triplicate and subjected to the conditions described below. The duration of the test was 65 days.

Test Apparatus

The experimental test apparatus (Figure 5.12) employed a Siemens Ultramat 22P carbon dioxide analyzer (Siemens AG, Germany) to measure CO_2 production from the samples. The analyzer was calibrated using certified 3.83% CO_2 from AGA Industries. Airflow was regulated by Mott Metallurgical (Farmington, CT) flow restrictors to 60 mL/min.

Test Conditions

Biodegradation of polymer blends under composting conditions was measured by the ASTM D-5338-92 method. This method exposes samples to a mature compost in a controlled temperature chamber. The temperature set points for this experiment were 35° C for the first 24 hours and 58° for until test conclusion. This test method measures the percent of test material converted to CO_2 by microbial activity by determining the difference in CO_2 production between the test vessels and a set of vessels containing no test material (blanks).

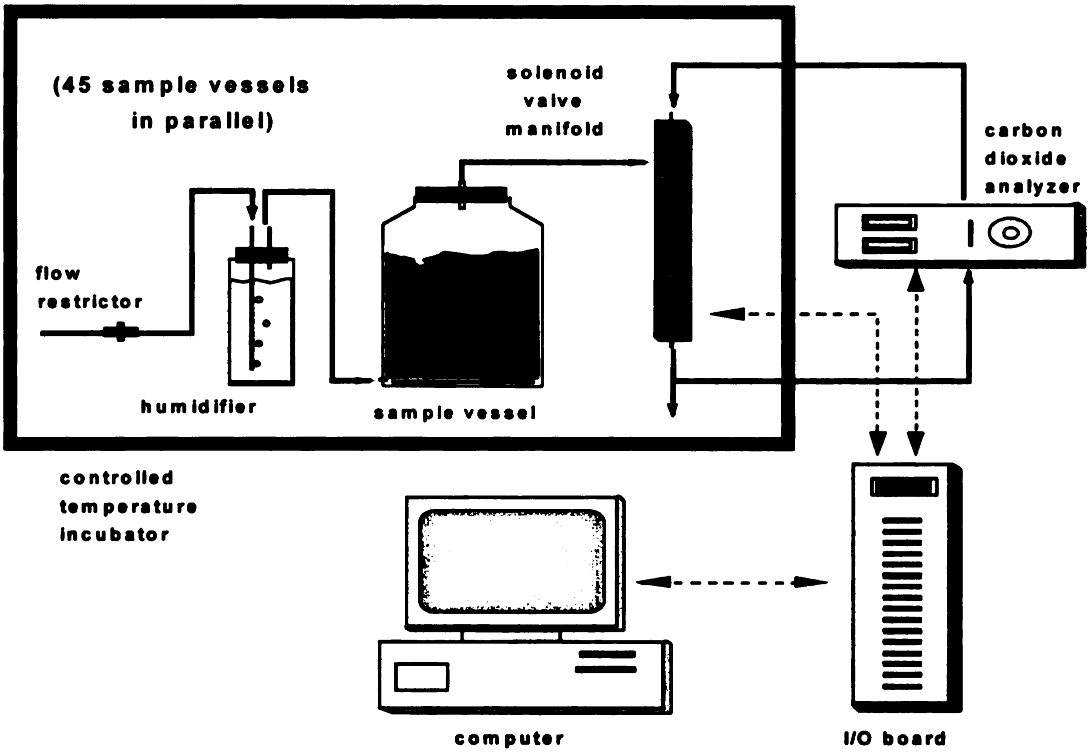


Figure 5.12: Biodegradability Testing Apparatus

The results of the biodegradability testing are displayed in Figure 5.13. ASTM standards dictate that a material reach 80% biodegradability in approximately 180 days. Conversion to CO_2 is increased 10% compared to EBC alone, by grafting MSO to EBC. Blending EBC-g-MSO10G with thermoplastic starch at 30% increases conversion by 25%. The addition of fiber increases conversion by 48%..

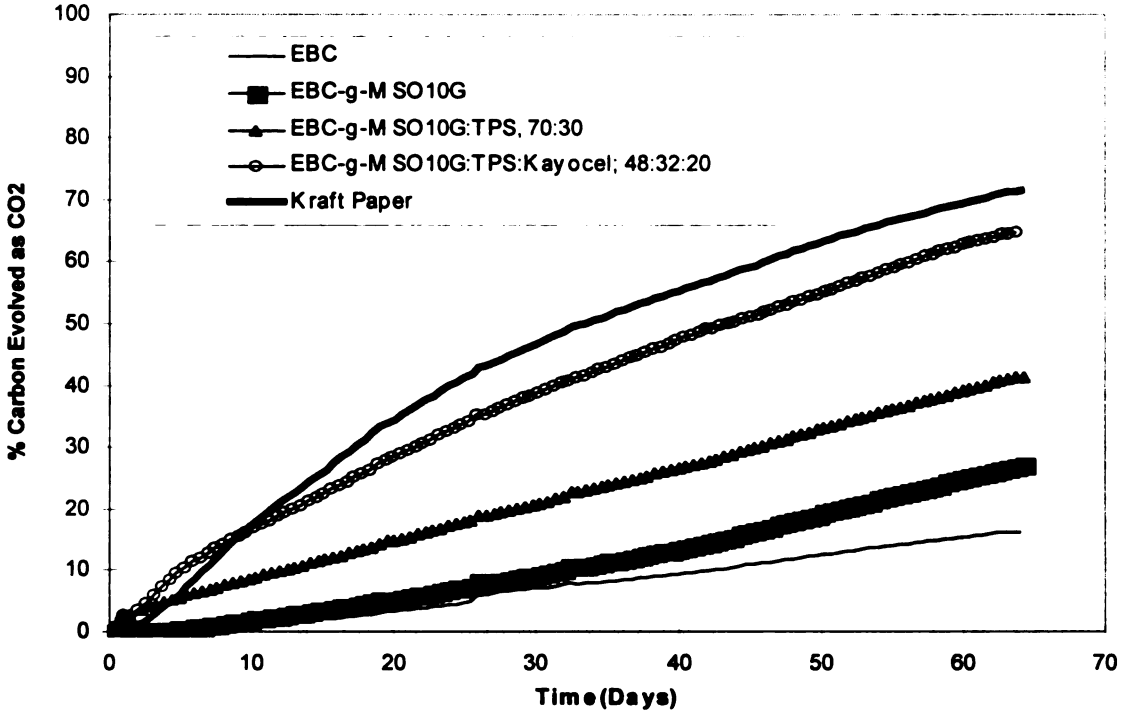


Figure 5.13: Biodegradability Testing Results

The first derivative of each biodegradation curve was determined and using a polynomial based on this curve predictions were made concerning the biodegradability of each material. Eighty percent conversion of sample to carbon dioxide was predicted to occur at 330 days for EBC, 215 days for EBC-g-MSO10G, 120 days for EBC-g-MSO10G:TPS; 70:30, and 78 days for EBC-g-MSO10G:TPS:Fiber; 48:32:20. The polyester and grafted copolyester do not meet international standards, but the addition of thermoplastic starch and fiber improve biodegradability of these blends to the point where international standards are met.

CHAPTER 6

Preliminary Process Design

Process Description

A flow diagram (Figure 6.1) and material and energy balances (Table 6.1) of a reactive extrusion and compounding process for two different resins was determined from experimental data. The basis for the design was:

- 5 million pound per year of total resin.
- 2.5 million pound per year of resin containing 70% EBC-g-MSO10G and 30% TPS
- 2.5 million pound per year of resin containing 48% EBC-g-MSO10G, 32% TPS and 20% Fiber.
-Stream factor of 0.9

This plant will contain two extrusion lines, E1 andE2. The two final products will be produced on line E2. Thermoplastic starch and EBC-g-MSO10G will also be produced on line, E1. Hourly production rates for this design were based on equal usage of the extruder for each product produced in it- production time for each product was 3942 hours. The EBC-g-MSO line will be maintained under a nitrogen blanket to prevent unwanted side reactions during extrusion. Storage will be provided for two weeks inventory of all required materials and products produced, S1-S10. Kinetic studies of the grafting reaction have not been performed, so it was assumed that extruder residence time and temperature affects scaled up with equal effect.

All reactants will be stored in carbon steel storage tanks. Pelletized and powdered materials will be conveyed to gravimetric feeders for feeding into the extruder by

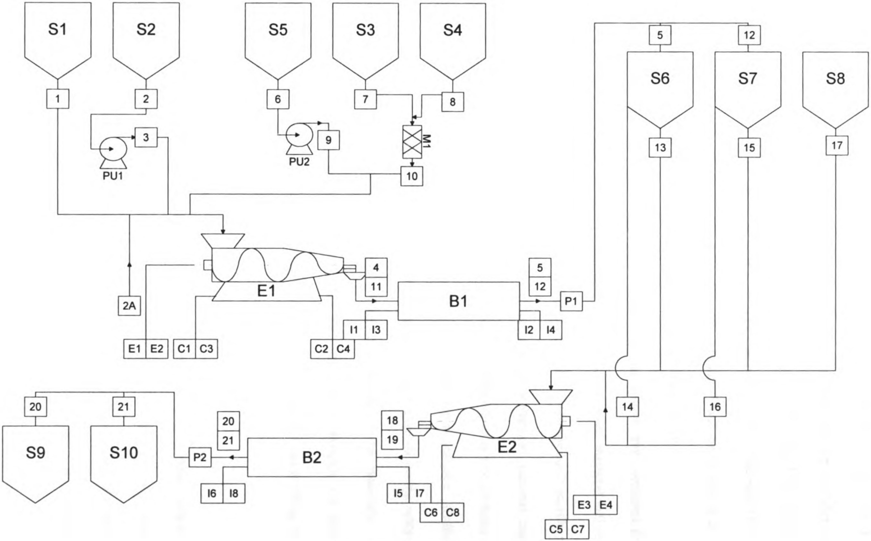


Figure 6.1: Process Flow Diagram

pneumatic conveying systems. Feeders have been omitted from the process flow diagram for simplicity. Flow of liquid reagents, streams 2 and 6, pumped to the extruders will be controlled by feedback loops containing the appropriate pump-PU1 and PU2, and a liquid flow meter. maleated soybean oil, stream 2, will be heated to 70°C to increase the ease of pumping. Polycaprolactone, stream 6, and starch, stream 7 will be mixed in a tumble mixer prior to addition to the extruder in making thermoplastic starch.

In all production lines except for the thermoplastic starch line, extruded material will be cooled by passing through a water bath, B1 and B2. Cooled material will be dried using a twelve inch air wipe, and then pelletized, P1-P2. Thermoplastic starch will be passed through a stream of chilled air, prior to pelletizing. Pelletized material may need further drying, however estimates concerning the extent of drying have not yet been made.

Several assumptions were made in order to close the energy balance. Enthalpy of the materials was considered constant. The mechanical energy exerted on the materials in the extruder by the screws was de-coupled from the heating of the materials. In the balances, this energy was entirely dissipated by water flow through the extruders. Material heating efficiency was assumed 100%. Heat of reaction for the grafting reaction, since it is unknown, was neglected.

Extruder Sizing

Extruders used in this process were all twin screw co-rotating intermeshing machines. The extruder used for grafting and thermoplastic starch production, E1, was a 70mm-screw diameter machine while the machine used for compounding, E2, was also a 70mm machine. These machine sizes were based on manufacturer recommendations

(Krupp Werner & Pfleiderer Corporation). Machine size can be determined, however using appropriate scale up equations.

capacity of b = capacity of a x scale up factor

scale up factor = (screw d of b^3/screw d of a^3)

The maximum throughput for the grafting reaction is not known, however assuming it to be 50 lb/hr in a 30mm extruder, one could calculate the size of extruder necessary for the needed capacity of 748 lb/hr. Using the above equations, the scale factor would be 14.96, while extruder diameter would be 74 mm. This calculation provides good agreement with the 70mm recommendation by the manufacturer. To truly determine appropriate extruder size though, studies must be done in which the absolute maximum capacity of the 30mm is determined. Studies concerning kinetics of the grafting reaction, and residence time distribution of the material in the extruder also need to be done. Completion of these studies would enable an engineer to do pilot plant studies of this process and then further refining of equipment choice for a large scale plant.

Table 6.1 Material and Energy Balances for Production of Biodegradable Resins

Basis	2,500,000	lb/yr	70% EBC-G-MSO 10G 30% TPS			2500000 lb/yr		48% EBC-g-MSO 10G 32% TPS 20% Fiber	
Production Hours	7884								
Stream No.	**1**	**2**	**2a**	**3**	**4**	**5**	**6**	**7**	**8**
Component(lb/hr)	**Eastar Bio Copolyester (EBC)**	**Maleated Soybean Oil (MSO)**	**Catalyst**	**Maleated Soybean Oil**	**EBC-g-MSO 10G**	**EBC-g-MSO 10G**	**Glycerol**	**Corn Starch**	**Polycaprolactone (PCL)**
Eastar Bio Copolyester	598.7	0.0	0.00	0.0	0.0	0.0	0.0	0.0	0.0
Maleated Soybean Oil	0.0	149.7	0.00	149.7	0.0	0.0	0.0	0.0	0.0
Catalyst	0.0	0.0	2.25	0.0	0.0	0.0	0.0	0.0	0.0
Corn Starch	0.0	0.0	0.00	0.0	0.0	0.0	0.0	299.6	0.0
Glycerol	0.0	0.0	0.00	0.0	0.0	0.0	74.9	0.0	0.0
Polycaprolactone	0.0	0.0	0.00	0.0	0.0	0.0	0.0	0.0	18.7
Kayocell	0.0	0.0	0.00	0.0	0.0	0.0	0.0	0.0	0.0
Thernoplastic Starch	0.0	0.0	0.00	0.0	0.0	0.0	0.0	0.0	0.0
EBC-g-MSO	0.0	0.0	0.00	0.0	393.2	393.2	0.0	0.0	0.0
EBC-g-MSO:TPS;70:30	0.0	0.0	0.00	0.0	0.0	0.0	0.0	0.0	0.0
EBC-g-MSO:TPS:Kayocel; 48:32:20	0.0	0.0	0.00	0.0	0.0	0.0	0.0	0.0	0.0
Water	0.0	0.0	0.00	0.0	0.0	0.0	0.0	0.0	0.0
Total	598.7	149.7	2.25	149.7	393.2	393.2	74.9	299.6	18.7

Enthalpy Balance

Stream No.	1	2	2a	3	4	5	6	7	8
Component(lb/hr)	**Eastar Bio Copolyester (EBC)**	**Maleated Soybean Oil (MSO)**	**Catalyst**	**Maleated Soybean Oil**	**EBC-g-MSO 10G**	**EBC-g-MSO 10G**	**Glycerol**	**Corn Starch**	**Polycaprolactone (PCL)**
Temperature (degC)	25	25	25	70	115	25	25	25	25
Cp(BTU/lb-degF)	0.5	0.4	0.4	0.4	0.5	0.5	0.4	0.46	0.48
Enthalpy(BTU/lb)	22.5	18	18	50.4	103.5	22.5	18	20.7	21.6
Enthalpy Flow (BTU/hr)	13470.3	2694.1	40.4	7543.4	40696.3	8847.0	1348.1	6201.3	404.4

Table 6.1 Material and Energy Balances for Production of Biodegradable Resins(cont)

Basis	2,500,000	lb/yr	70% EBC-G-MSO 10G 30% TPS			2500000	lb/yr	48% EBC-g-MSO 10 32% TPS 20% Fiber
Production Hours	7884							
Stream No.	11	12	13	14	15	16	17	18
Component(lb/hr)	Thermoplastic Starch (TPS)	TPS	TPS	TPS	EBC-g-MSO 10G	EBC-g-MSO 10G	Fiber	70% EBC-g-MSO 30% TPS
Eastar Bio Copolyester	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Maleated Soybean Oil	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Catalyst	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Corn Starch	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Glycerol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Polycaprolactone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Kayocell	0.0	0.0	0.0	0.0	0.0	0.0	126.8	0.0
Thermoplastic Starch	393.2	393.2	202.9	190.3	0.0	0.0	0.0	0.0
EBC-g-MSO	0.0	0.0	0.0	0.0	304.4	443.9	0.0	0.0
EBC-g-MSO:TPS;70:30	0.0	0.0	0.0	0.0	0.0	0.0	0.0	317.1
EBC-g-MSO:TPS:Kayocel; 48:32:20	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Water	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Total	393.2	393.2	202.9	190.3	304.4	443.9	126.8	317.1

Enthalpy Balance

Stream No.	11	12	13	14	15	16	17	18
Component(lb/hr)	Thermoplastic Starch (TPS)	TPS	TPS	TPS	EBC-g-MSO 10G	EBC-g-MSO 10G	Fiber	70% EBC-g-MSO 30% TPS
Temperature (degC)	150	25	25	25	25	25	25	170
Cp(BTU/lb-degF)	0.52	0.52	0.52	0.52	0.5	0.5	0.44	0.506
Enthalpy(BTU/lb)	140.4	23.4	23.4	23.4	22.5	22.5	19.8	154.836
Enthalpy Flow (BTU/hr)	55205.5	9200.9	4748.9	4452.1	6849.3	9988.6	2511.4	49098.5

Table 6.1 Material and Energy Balances for Production of Biodegradable Resins (cont)

Basis	2,500,000	lb/yr	70% EBC-G-MSO 10G 30% TPS			2500000	lb/yr	48% EBC-g-MSO 10G 32% TPS 20% Fiber	
Production Hours	7884								
Stream No.	21	C1	C2	C3	C4	C5	C6	C7	C8
Component(lb/hr)	48% EBC-g-MSO 32% TPS 20% Fiber	Chilled Water Supply (CWS)	Chilled Water Return (CWR)	CWS	CWR	CWS	CWR	CWS	CWR
Eastar Bio Copolyester	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Maleated Soybean Oil	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Catalyst	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Corn Starch	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Glycerol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Polycaprolactone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Kayocell	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Thermoplastic Starch	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
EBC-g-MSO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
EBC-g-MSO:TPS;70:30	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
EBC-g-MSO:TPS:Kayocel; 48:32:20	317.1	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Water	0.0	6403.1	6403.1	6403.1	6403.1	6403.1	6403.1	6403.1	6403.1
Total	317.1	6403.1	6403.1	6403.1	6403.1	6403.1	6403.1	6403.1	6403.1

Enthalpy Balance

Stream No.	21	C1	C2	C3	C4	C5	C6	C7	C8
Component(lb/hr)	48% EBC-g-MSO 32% TPS 20% Fiber	Chilled Water Supply (CWS)	Chilled Water Return (CWR)	CWS	CWR	CWS	CWR	CWS	CWR
Temperature (degC)	25	10	50	10	50	10	50	10	50
Cp(BTU/lb-degF)	0.4944	1	1	1	1	1	1	1	1
Enthalpy(BTU/lb)	22.248	18	90	18	90	18	90	18	90
Enthalpy Flow (BTU/hr)	7054.8	115255.5	576277.3	115255.5	576277.3	115255.5	576277.3	115255.5	576277.3

Table 6.1 Material and Energy Balances for Production of Biodegradable Resins (cont.)

Basis	2,500,000	lb/yr	70% EBC-G-MSO 10G 30% TPS			2500000	lb/yr	48% EBC-g-MSO 10G 32% TPS 20% Fiber	
Production Hours	7884								
Stream No.	I1	I2	I3	I4	I5	I6	I7	I8	E1
Component(lb/hr)	Industrial Cold Water In (ICI)	Industrial Cold Water Out (ICO)	(ICI)	(ICO)	(ICI)	(ICO)	(ICI)	(ICO)	Electricity
Eastar Bio Copolyester	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
Maleated Soybean Oil	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
Catalyst	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
Corn Starch	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
Glycerol	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
Polycaprolactone	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
Kayocell	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
Thermoplastic Starch	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
EBC-g-MSO	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
EBC-g-MSO:TPS;70:30	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
EBC-g-MSO:TPS:Kayocel; 48:32:20	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0
Water	1769.4	1769.4	247.3	247.3	1245.0	1245.0	836.1	836.1	0
Total	1769.4	1769.4	247.3	247.3	1245.0	1245.0	836.1	836.1	
Enthalpy Balance									
Stream No.	I1	I2	I3	I4	I5	I6	I7	I8	E1
Component(lb/hr)	Industrial Cold Water In (ICI)	Industrial Cold Water Out (ICO)	(ICI)	(ICO)	(ICI)	(ICO)	(ICI)	(ICO)	Electricity
Temperature (degC)	15	25	15	25	15	25	10	25	-
Cp(BTU/lb-degF)	1	1	1	1	1	1	1	1	-
Enthalpy(BTU/lb)	27	45	27	45	27	45	18	45	-
Enthalpy Flow (BTU/hr)	47774.0	79623.3	6678.1	11130.1	33614.9	56024.9	15050.3	37625.8	-

CHAPTER 7

Economic Analysis

Process Economics

Table 7.1 lists the assumptions that were used in the economic evaluation of the proposed plant. Several of the assumptions made for non-manufacturing labor and utilities can from Peters and Timmerhaus (Peters and Timmerhaus, 1991). The plant will produce 5 million total pounds of resin per year. One half of that resin will be 70% EBC-g-MSO 10G: 30% TPS, while the other half of that resin will be 48% EBC-g-MSO: 32% TPS: 20% Fiber. The plant will operate for 10 years at which time salvage value will be considered 10% of the initial fixed capital investment. The depreciation will be straight-line over the 10-year period for 90% of the fixed capital investment. Labor will be paid $15 per hour. Three operators will be required per shift. Supervision, maintenance, local taxes and insurance will be 8%, 7% and 2% of the fixed capital investment, respectively. Future R & D, marketing, and general sales and administration expenses will be 5%, 5%, and 4% of the total manufacturing cost respectively.

Utility costs will be purchased ate $0.07 per KWH for electrical power, $0.15 per 1000 gallons industrial cold water, $0.25 per 1000 gallons chilled water, and $0.015 per gallon for sewer. Purchased chemical will cost $2.15 per lb. for Eastar Bio Copolyester, $0.60 per lb. for Maleated soybean oil, $3.00 per lb. for Dicumyl Peroxide, $0.145 per lb. for starch, $1.00 per lb. for glycerol, $1.25 per lb. for Polycaprolactone, and $0.10 per lb. for fiber. Chemical costs were obtained directly from suppliers when possible and estimated for maleated soybean oil using estimates based on Seybold (Seybold, 1997).

Plant Capacity Factor	7884 hours per year	
Resin 1: 70% EBC-g-MSO 10G 30% Thermoplastic Starch	2,500,000 lb./year	
Resin 2: 48% EBC-g-MSO 10G 32% Thermoplastic Starch 20% Fiber	2,500,000 lb./year	
Depreciation	9 percent, straight line	
Total Federal Taxes	34 percent	
Working Capital	15 percent of Total Capital	
Plant Lifetime	10 years	
Base Rate Operating Labor	$15 per hour	
Supervision	8 percent fixed capital investment	
Maintenance	7 percent fixed capital investment	
Local Taxes and Insurance	2 percent fixed capital investment	
R & D	5 percent total manufacturing costs	
Marketing	5 percent total manufacturing costs	
General, Sales, Admin Expense	4 percent total manufacturing costs	
Utility Costs		
Purchased Electric Power	0.07	$ per KWH
Industrial Cold Water	0.15	$ per 1000 gallons
Chilled Water	0.25	$ per 1000 gallons
Sewer	0.015	$ per gallon
Purchased Chemicals		
Eastar Bio Copolyester	2.15	$ per pound
Maleated Soybean Oil	0.60	$ per pound
Catalyst	3.00	$ per pound
Corn Starch	0.15	$ per pound
Glycerol	1.00	$ per pound
Polycaprolactone	1.25	$ per pound
Fiber	0.10	$ per pound

Table 7.1: Assumptions for Economic Evaluation

The necessary equipment is described in Table 7.2. Equipment costs were taken from Peters and Timmerhaus (Peters and Timmerhaus, 1991), when possible. Plastics processing equipment costs were obtained directly from vendors. Extruder cost estimates specifically were obtained from Krupp Werner & Pfleiderer Corporation and are quotes based on purchase of ZSK series extruders. Equipment costs when necessary were adjusted to 1998 dollars using a Marshall and Swift Index (Chemical Engineering, May 1998).

Item	**Description**	**Size**	**Purchase Cost(1998 $)**
E1	Twin Screw Extruder	70mm	$ 410,000
E2	Twin Screw Extruder	70mm	$ 410,000
PU1	Pump	9.25gal/hr	$ 2,746
PU2	Pump	7.13gal/hr	$ 2,347
P1	Pelletizer		$ 5,258
P2	Pelletizer		$ 5,258
S1	Storage Tank Carbon Steel	9618 gallons	$ 23,473
S2	Storage Tank Carbon Steel	1399 gallons	$ 8,216
S3	Storage Tank Carbon Steel	3566 gallons	$ 11,854
S4	Storage Tank Carbon Steel	261 gallons	$ 2,347
S5	Storage Tank Carbon Steel	1077 gallons	$ 5,868
S6	Storage Tank Carbon Steel	3586 gallons	$ 11,854
S7	Storage Tank Carbon Steel	4890 gallons	$ 17,605
S8	Storage Tank Carbon Steel	10945 gallons	$ 25,821
S9	Storage Tank Carbon Steel	8671 gallons	$ 22,300
S10	Storage Tank Carbon Steel	9549 gallons	$ 23,473
B1-B2	Cooling Baths	20ft	$ 2,347
	Gas blanketing system	-	$ 3,228
	Feeding Systems		$ 58,684
	Air Wipe	2- 12 inch lip units	$ 4,695
	Total Purchased Equipment Cost		**$1,077,375**

Table 7.2: Equipment List for Resin Production

The total capital investment for construction of the 5 million pound per year resin facility (2.5 million pound per year of two different resins) is shown in Table 7.3. All costs are based on industrial averages for new plant fabrication from the work of Peters and Timmerhaus. The total capital investment is calculated using the equipment cost as a basis and industrial averages for needed accessories. The actual costs and percentages of purchased equipment cost each is shown below in 7.3.

Plant Capacity Factor	7884 hours per year	
Resin 1:	2,500,000 lb./year	
70% EBC-g-MSO 10G		
30% Thermoplastic Starch		
Resin 2:	2,500,000 lb./year	
48% EBC-g-MSO 10G		
32% Thermoplastic Starch		
20% Fiber		
Direct Costs	**As a % of Purchased Equipment Cost**	
Purchased Equipment	100	$ 1,077,375
Purchase Equipment Installation	39	$ 484,819
Instrumentation and Controls	13	$ 96,964
Piping (Installed)	31	$ 3,12,438
Electrical (Installed)	10	$ 172,380
Buildings	29	$ 107,737
Yard Improvements	10	$ 269,344
Service Facilities	55	$ 140,059
Land (if purchase is required)	6	$ 64,642
	Total Direct Plant Cost	**$ 2,725,758**
Indirect Costs		
Engineering and Supervision	32	$ 355,534
Construction Expenses	34	$ 420,176
	Total Direct and Indirect Costs	**$ 3,501,468**
Contractors Fee	5	$ 183,154
Contingency	10	$ 366,307
Fixed Capital Investment		**$ 4,050,929**
Working Capital		**$ 732,615**
	Total Capital Investment	**$ 4,783,543**

Table 7.3 Capital Investment Breakdown.

Table 7.4 shows the manufacturing cost breakdown for the proposed production facility. The variable and material costs determined as part of the material and energy balances are included in this table.

	$/Unit	Units	Cost $/year
Variable Costs			
Industrial Water	0.15	1000 gallon	$ 291
Chilled Water	0.25	1000 gallon	$ 3013
Sewer	0.015	gallon	$ 29,064
Electricity	0.07	KWH	$ 158,41
	Total Variable Costs		$191,009
Material Cost			
Eastar Bio Copolyester	2.15	lbs	$5,708,250
Maleated Soybean Oil	0.6	lbs	$ 177,000
Catalyst	3	lbs	$ 26,550
Corn Starch	0.145	lbs	$ 171,238
Glycerol	1.00	lbs	$ 295,238
Polycaprolactone	1.25	lbs	$ 92,262
Kayocell	0.1	lbs	$ 50,000
	Total Material Costs		**$6,520,538**
Fixed Costs			
Labor	3 operators @$15/hr		$ 236,520
Supervision	8% of FCI		$ 324,074
Maintenance	7% of FCI		$ 283,565
Depreciation	10% Salvage, 9% FCI		$ 364,584
Local Taxes and Insurance	2% FCI		$ 81,019
Total Fixed Costs			**$ 1,289,761**
Total Manufacturing Costs			**$ 8,001,308**
R&D	5% of TMC		$ 400,065
Marketing	5% of TMC		$ 400,065
General, Sales, Administration Expense	4% of TMC		$ 320,052
Total Operating Costs			**$ 9,121,491**

Table 7.4 Manufacturing cost breakdown for 5 million pound per year plant

Fixed costs consist of three operators per shift at $15/hour, and Supervision, maintenance and local taxes and insurance at 8%, 7%, 10% and 2% of the fixed capital investment.

Other costs include R&D, Marketing, and General, Sales and Administration expenses at 5%, 5%, and 4% of the total manufacturing cost respectively. Examination of the table reveals that manufacturing cost is most sensitive to the cost of raw materials. Energy and labor costs are insignificant compared to the cost of raw materials.

There are several methods for determining the selling price for a product. One method, Return on Investment-ROI can be calculated by adding the total manufacturing cost to the required return and dividing this number by the total production. For the situation for which minimum return on investment is 15%, the selling prices are $2.01/lb. for the resin without fiber and 1.47/lb. for the resin with fiber.

Another method for determining selling price for a product is discounted cash flow. This method takes into account the time value of money by establishing a rate of return that can be applied to the yearly cash flow so that the original investment is reduced to zero during the project life. This rate of return is equivalent to the maximum interest rate, after taxes, at which money could be borrowed to finance the project over the project's life under conditions where the net cash flow would be just sufficient to pay the principal and interest accumulated on the outstanding principal. At the end of n years the cash flow compounded based on end of year income will be:

$$F(1+i)^{n-1}+F(1+i)^{n-2}+.....F(1+i) = S \qquad (1)$$

where F = yearly cash flow

i = interest rate

S = future worth of the project

The future worth of the initial investment would be:

$$S' = P(1+i)^n \quad (2)$$

where P = principal investment

Given an interest rate and principle the equation:

$$S - S' = 0 \quad (3)$$

can be solved by a trial and error method. Other terms that can be included in equation (3) include the working capital, and the project salvage value. These terms were not included in the simple economic analysis performed below. The selling price can be varied until a solution to this equation is found. Using this method for the 5 million pound per year plant yields the selling prices at various rates as shown in Table 7.5. The differences in selling price between the two resins is based on different material costs.

Rate of Return	**Selling Price ($/lb.):** **70% EBC-g-MSO 10G** **30% TPS**	**Selling Price ($/lb.):** **48% EBC-g-MSO** **32% TPS** **20% Fiber**
10%	$ 2.23	$ 1.63
20%	$ 2.34	$ 1.70
25%	$ 2.40	$ 1.74

Table 7.5: Selling price based on discounted cash flow

Assuming an average selling price for both products of $2.05/lb., the net present worth, the right hand side of equation (3) was calculated for various interest rates. Figure 7.1 shows several discounted rates and the net present value for the proposed process. The discounted rate, the internal rate of return-IRR, at which the net present value equals zero is 23%. Using this method various alternative manufacturing methods could be compared. The 'best' manufacturing method would have the highest IRR.

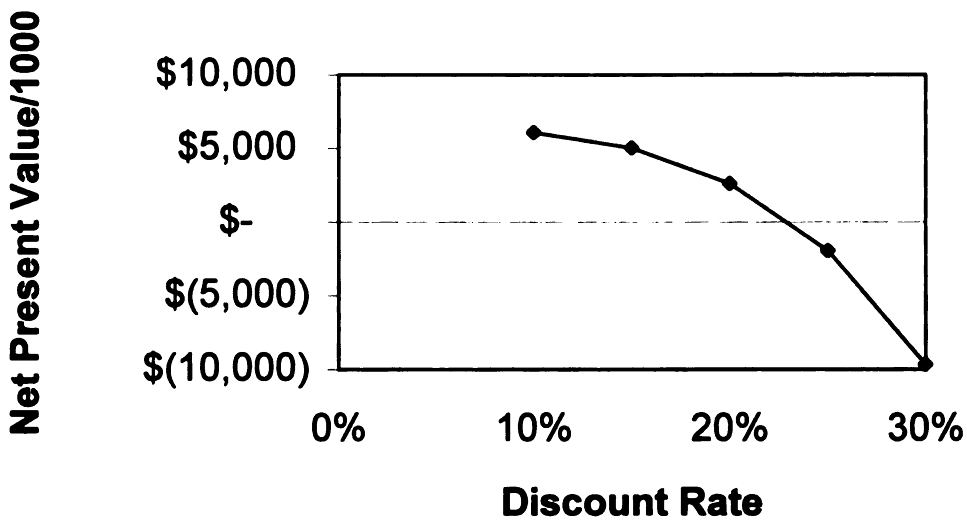


Figure 7.1: Determination of Internal Rate of Return by a discounted cash flow for the proposed process

Sensitivity analysis

A sensitivity analysis was performed for the proposed process. In this analysis the effect of fluctuations of Eastar Bio Copolyester cost, glycerol cost and capital investment on the two product average selling price were examined. The assumptions made for this analysis were:

- Production capacity of 2.5 million pounds per year of each resin
- Return on investment of 15%

The results of this sensitivity analysis are shown in Figure 7.2. The proposed process is highly sensitive to fluctuations in capital investment and Eastar Bio Copolyester costs, and relatively insensitive to all other factors.

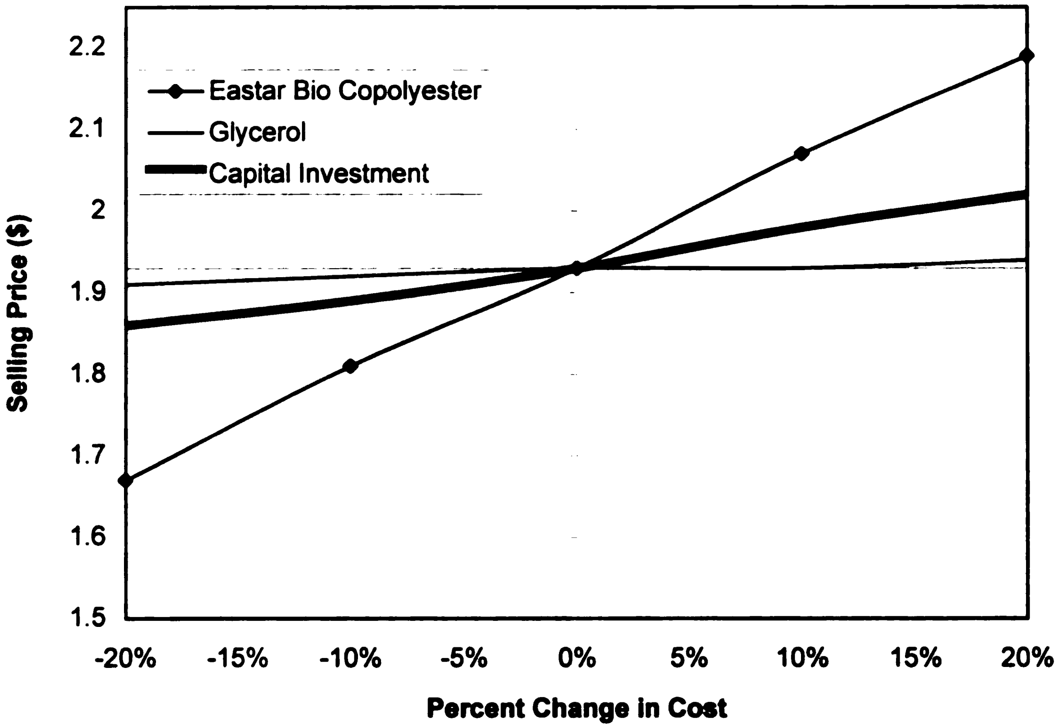


Figure 7.2: Sensitivity analysis for the proposed process

Conclusions

The selling price for 10% discounted cash factor for the 70:30 EBC-g-MSO10g:TPS resin is $2.23/lb while the selling price for the fiber containing blend is $1.63/lb. The average of these two resin costs is $1.93/lb. This average cost is $0.22/lb below the purchase cost of the copolyester itself. Since blend properties are inferior to the polyester properties itself, the small difference in selling price is not great enough to encourage product sales, unless increased rates of biodegradation are desired. Further optimization of product production to greatly improve properties and reduce production cost is necessary if these blends are to be attractive to perspective customers.

Examination of the effects of variation of the amount of grafted copolyester on the product material cost for the 70:30;EBC-g-MSO:TPS blend reveals that not only does the grafting result in a product with superior properties, but it also reduces the material cost and in turn the selling cost as shown in Figure 7.3

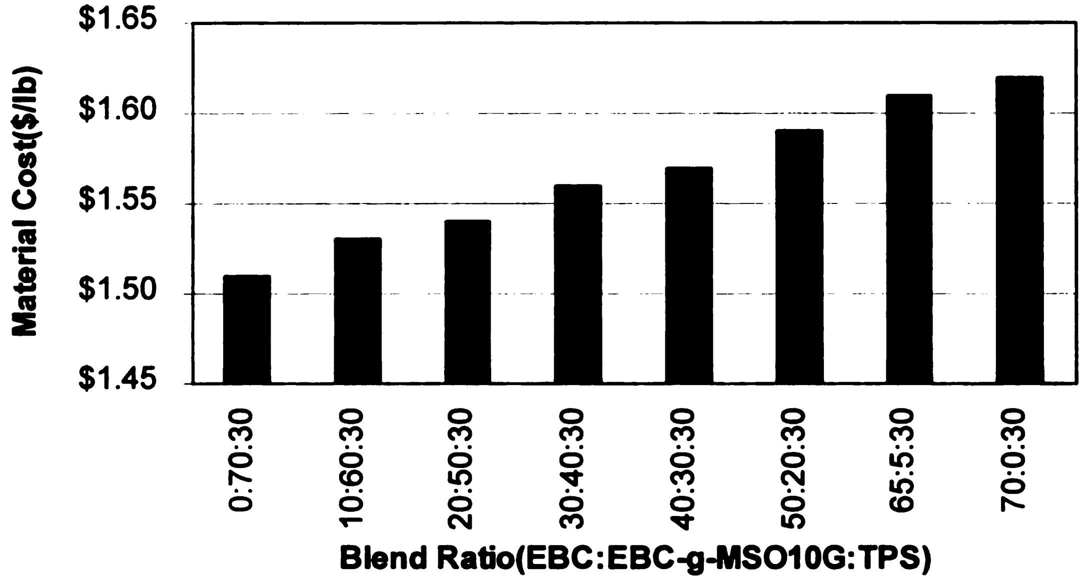


Figure 7.3: Effects of varying graft copolyester amounts on material costs

Though the lowest material costs are for the blend containing entirely graft copolyester, the best properties probably lie somewhere between the extremes. The overall improvement in properties coupled with a reduction in material costs associated with grafting provide a strong impetus for further examination of grafted copolyester as a compatibilizing agent for EBC:TPS blends.

CHAPTER 8

CONCLUSIONS AND RECOMMENDATIONS

Conclusions

The two goals outlined at the start of this work were:

1) the design and engineering of biodegradable starch:copolyester blend. The copolyester used in this blend is Eastar Bio Copolyester (EBC), a biodegradable copolyester containing Adipic acid, Terepthalic acid, and 1,4-Butanediol.

2) the evaluation of maleated soybean oil (MSO) as a compatibilizing agent.

With the above goals in mind and based on the work accomplished the following conclusions can be drawn:

1) Soybean oil can be maleated cheaply and effectively using existing technology.

2) Maleated soybean oil can be grafted to Eastar Bio Copolyester using Dicumyl Peroxide as a catalyst, or with less efficiency no catalyst.

3) Grafting of MSO to EBC is verifiable using common extraction techniques.

4) Thermoplastic starch is easily prepared and reactively blended with EBC-g-MSO10G.

5) Environmental Scanning Electron Microscopy and Tensile testing of the EBC-g-MSO10G:TPS blends reveals direct evidence of blend compatibilization.

6) A process to produce 2.5 million pounds/year of two blends: EBC-g-MSO10G:TPS; 70:30 and EBC-g-MSO10G:TPS: Fiber; 48:32:20 was shown to produce these two resins at an average selling price of $1.93/lb. The addition of grafted copolyester to blends containing copolyester and thermoplastic starch results in a material possessing superior blend properties at a reduced material cost. This fact provides a driving impetus for further study of such blends.

Recommendation for further work

The conclusions above do demonstrate achievement of the outlined goals. The goal of all engineers should be to take an idea and convert it to an economically profitable product. To achieve that end with the product idea examined in this thesis further work must be done. The suggest work will help achieve this goal of converting an idea into a marketable reality.

1) **Further characterization maleated soybean oil and optimization of the maleation reaction.** :

   Determination of the actual structure of MSO using GC-MS, FTIR and NMR techniques will provide insight as to the reactivity of this material in regards to increasing grafting efficiency. Optimization of this reaction will reduce production costs thereby decreasing its price.

2) **Examination of catalyst efficiency and non catalytic grafting**:

   Grafting of MSO to EBC occurs both in the presence and absence of catalyst. Only the 0.3% Dicumyl Peroxide concentration was investigated as a potential catalyst system. Other concentrations of catalyst and other catalysts should be investigated. In addition the mechanism of non-catalytic grafting must be further investigated. Better understanding of the graft reaction will lead to increased efficiency in product production.

3) **Verification of grafting and characterization of the copolyester graft structure.**

   Extraction of the grafted copolyester was performed to verify grafting. Further characterization of this extracted product using appropriate analytical techniques to identify and verify the grafted copolyester structure. With this structure in hand the reaction can be better tailored to produce a better compatibilizing agent.

4) **Production of different blends and examination of effects of varied processing conditions.**

Blending of thermoplastic starch with grafted copolyester should be done for different levels of grafting. Only the 10% by weight grafted copolyester was blended with TPS. Blending of the 5%, 10% non-catalytic, and the 20% by weight materials with thermoplastic starch should be performed to determine which one provides the best compatibilization. A 65:5:30; EBC:EBC-g-MSO10G:TPS blend was found to provide excellent properties. Further blends of this nature should be made to determine if there is an optimum amount of grafted copolyester that should added to a copolyester:thermoplastic starch blend to yield the best properties. In addition processing parameters such as throughput and extruder zone temperatures should be examined to determine if there is an optimum condition at which reactive blending should be performed.

5) **Further Characterization of blends**

Tools such as ESEM, and property testing, and others such as Dynamic Mechanical Analysis-DMA, should be used to determine the extent of compatibilization. Biodegradability testing should be used to screen new materials and as a guide to which application the biodegradable materials are best suited for.

6) **Pilot plant construction and determination of economic viability.**

The construction of a pilot plant is necessary to determine what if any problems there will be associated with scale up. These scale up problems should be addressed prior to completion of accurate assessment of economic viability.

Completion of the further work will create a more accurate picture of the economic viability of the desired product. With this picture more clearly shown, a final decision can be made as to whether the capital investment necessary for large-scale plant construction will return a profit in the desired amount of time.

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