# BIOBASED MATERIALS FROM STARCH: TRANS-ESTERIFICATION BLENDS WITH COMMERCIAL POLYMERS

By

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#### ABSTRACT

## BIOBASED MATERIALS FROM STARCH: TRANS-ESTERIFICATION BLENDS WITH COMMERCIAL POLYMERS

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With ever-growing plastic pollution, there has been a significant push to find alternate green materials. These green products are expected to generate less or zero carbon footprint, which has directed efforts towards using natural resources as raw materials. Starch stands out as one of the natural resources which hold potential to produce the alternate plastics.

In this study, Starch has been explored for its use as a thermoplastic material. The contrasting natures of starch have been studied, namely amylose and amylopectin dominated starches. Further thermoplastics made from these starches were reactively extruded with current commercial grade plastics to produce sustainable plastic solutions. The manufacturing using reactive extrusion, downstream processing and characterization (eg. FTIR, TGA and soxhlet extraction) of thermoplastic starch and PBAT or PETG blends was established. These blends were designed to contain 30% starch by weight.

The more linear, high amylose content thermoplastic starch (MTPS) produced blends with PETG with acceptable decline in mechanical properties as compared to regular amylose content thermoplastic starch (RMTPS). On the other hand, RMTPS had higher grafting efficiency (56%) than MTPS (35%) when it was reactively extruded with PBAT. In addition, the covalent nature of the grafted bond was established in starch grafted PBAT using acid hydrolysis and glucose detection.

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#### **Chapter 1: Introduction**

There has been a growing concern about plastics ever since initial trends on global warming were reported. Climate change has been a widely debated topic with focus on plastic pollution. A recent paper on marine plastics pollution highlighted the fact that it has affected land and oceans alike (Monteiro, Ivar do Sul, and Costa 2018). The present model of plastics production is not sustainable and researchers around the world have realized it. While there has been a push for developing biodegradable plastics, cost of these polymers has always been a concern. This paper is a step towards solving the problem.

Recent data on corn production show that 82.7 million acres of corn were harvested and an average price of \$3.25 per bushel was assessed (as reported by USDA). Residual corn was at 37.6% of total corn production with most of it used in feed and a substantial portion going to waste. This can in fact be an opportunity to solve the problem of plastic pollution by incorporating starch in plastics.

Starch should be preferred as a substitute due to its ability to provide a carbon neutral path in generation of plastics. Replacing the petro-fossil carbon with biobased carbon in plastics and other polymer materials intrinsically offers a zero material carbon footprint value proposition (Narayan 2012). Starch provides a way to replace the petroleum carbon with its own, biobased carbon.

This thesis deals with the use of starch in making thermoplastics of the future, giving a greener route to the plastics industry and opening possibilities for research in new topics such as development of Biobased PETG composites. Chapter 2 covers the background necessary for this thesis, including the idea behind mixing of two polymers, compatibilization mechanism, and key reaction used in this thesis as well as the technique of reactive extrusion.

Chapter 3 discusses the materials used in preparation of blends including the main raw materials, key additives such as plasticizers, initiators and compatibilizers.

Chapter 4 initiates discussion on preparation of base resin, the thermoplastic starch. The chapter cover in-depth analysis on preparation of two different grades of thermoplastic starches. This includes process conditions as well as parameters necessary for scale-up of the process.

Chapter 5 throws a light on the techniques used for material characterization. These techniques are common to all the blends manufactured and mentioned in the thesis. The techniques have been discussed with appropriate theoretical knowledge.

Chapter 6 applies the material characterization techniques discussed in the previous chapter, on thermoplastic starches. This chapter also discusses the results obtained by the analysis.

Chapter 7 & 8 discuss the preparation, characterization and analysis on blends of base resin with PBAT and PETG. In addition, Chapter 8 also touches on mechanical properties of the graft polymer of base resins with PETG.

Chapter 9 ends the thesis with discussion on method of identification of starch in a grafted polymer and establishment of covalency in graft polymer.

### **Chapter 2: Background**

## 2.1 Methods of mixing polymers

*Polymer blends* – They may be defined as intimate mixtures of two kinds of polymers, with no covalent bonds between them. Historically, the oldest and simplest method involves mechanical blending, where a plastic and a non-crosslinked elastomer are blended either on open rolls or through extruders.

*Graft polymers* - In the graft copolymerization method, the first polymer portion is dissolved in the plastic monomer, and polymerization is affected. During the polymerization, some or all the second polymer becomes joined to the first.

A graft copolymer has the form



Figure 2.1 Graft polymer structure

The symbol -g- may be employed, as in poly(butadiene-g-styrene). The first polymer mentioned forms the backbone chain, and the second the branches. (Manson and Sperling 1976)

There are other types of methods, not discussed here, may result in :

- A. Block polymers
- B. Interpenetrating polymer networks (IPNs)

Advantages of why two or more polymers may be mixed involve:

- A. A good compromise between desirable properties of two or more homopolymers.
- B. Lowering of cost for similar engineered polymers.
- C. Extending the performance of expensive resins.
- D. Improvement in properties of a deficient resin.
- E. Improvement in processability.

#### 2.2 Compatibilization mechanisms

In most cases, melt mixing two polymers results in blends which are weak and brittle; This is because the incorporation of a dispersed phase in a matrix leads to the presence of stress concentrations and weak interfaces, arising from poor mechanical coupling between phases. It is readily understood that compatibilization can in principle interact in complex ways to influence final blend properties. It may either reduce interfacial tension in the melt, increase the adhesion at the phase boundaries or stabilize the dispersed phase against growth during annealing. The methods by which compatibilization can be achieved may be:

- A. Achievement of thermodynamic miscibility.
- B. Addition of block and graft copolymers.
- C. Addition of functional/reactive polymers.
- D. In situ grafting/polymerization (reactive blending)

A comparatively new method of producing compatible thermoplastics blends is via reactive blending, which relies on the in-situ formation of copolymers or interacting polymers. This differs from other compatibilization routes in that the blend components themselves are either chosen or modified so that reaction occurs during melt blending, with no need for addition of a separate compatibilizer.

Although batch-type melt mixers may be used for reactive blending, continuous processing equipment such as single- and twin-screw extruders are often preferred. As well as the advantages of continuous production, these units generally have better temperature control, and can be designed to allow for removal of unwanted reaction products by devolatilization. (Folkes and Hope 1993)

## 2.3 Transesterification reaction

Etherification and esterification of polysaccharides represent the most versatile transformations as they provide easy access to a variety of bio-based materials with valuable properties.

In new approaches for esterification of polysaccharides via transesterification, the vinyl esters of the carboxylic acids are predominantly exploited. During the conversion, the instable vinyl alcohol is formed and is immediately transformed into acetaldehyde, shifting the equilibrium towards the product side (Heinze 2006).



Figure 2.2 Acetaldehyde – Vinyl alcohol equilibrium

### 2.4 Reactive extrusion

Reactive extrusion (REX) is a manufacturing method that combines the traditionally separated chemical processes (polymer synthesis and/or modification) and extrusion (melting, blending, structuring, devolatilization and shaping) into a single process carried out onto an extruder.

Discontinuous equipments (mixers) are widely used for formulation processes, for instance, in elastomer processing or polyvinyl chloride stabilization and plasticizing, and it seems useful to consider the mixing chamber as a potential reactor for highly viscous systems. Adjustable residence time, power consumption control, mixing efficiency related to blade geometry and rotation speed, are basic advantages of these equipments, which exist on a laboratory and industrial scale. However, a few inconveniences should be mentioned: temperature and pressure control of the viscous mixture, difficulty in continuous feeding of liquid or volatile products, material extraction, etc.

Continuous equipments, like single- or twin-screw extruders have to be adapted to simultaneously process reactions in the melt, using sealed vent chambers, liquid injection ports, various kinds of pressure and temperature sensors, secondary solid or melt-feed ports, and must deal with the continuously changing nature of the reactive melt. Single-screw extruders are best suited for the simpler jobs like melting, plasticizing and discharging melt for the continuous production of pipes, films, etc. Although both single and twin-screw extruder configurations are used in reactive extrusion processes, twin-screw ones are increasingly being favored over the single-screw ones, as they can tackle the more complex tasks involved in reactive systems.

The advantages of Twin screw are (Lambla 1995):

- A. The increased surface/volume ratio by the continuous creation of new, thin surface layers which enhance mixing, reaction, and heat-transfer.
- B. Solvent-less polymerization and other chemical modifications of polymers are possible, since the extruder can handle the high viscosity of polymers, leading to a high concentration in reactive species.
- C. Savings in raw materials and solvent-recovery systems.
- D. the adjustment of the screw design, especially in modular equipment, allows different residence times and degrees of mixing.
- E. The modular design offers enormous flexibility, including sequential reaction processes by multiple injection ports and segregation of the different barrel sections, through dynamic sealing devices, which prevent back-mixing of a product with its reactants.

There are a few inconveniencies in using an extruder as a chemical reactor (Lambla 1995):

- A. Most extruders are custom made, as they must be designed specifically for a defined chemistry, considering the resistance to corrosive reagents, and the screws' optimized design is insufficiently understood.
- B. Engineering considerations, based on the type of extruder (single-or twin-screw, selfwiping or not, length over diameter ratio (L/D), number of reactive zones, etc.) and process parameters have also to be considered.
- C. Limited residence time, characteristic of these continuous devices, is one of the main disadvantages, regarding kinetic considerations.

Manufacturability

Instrumentation used to control the melt-extrusion process also provides significant insight into the performance of the formulation. Key measurements of torque, temperature, and pressure provide information on material flow behavior within the process section. Torque values are an indicator of the amount of energy that is being imparted into the materials being processed. Formulations exhibiting increased levels may have high melt viscosities and require the addition of a plasticizer. Similarly, one can also identify if an excessive number of mixing sections are present on the extruder, leading the elevated torque levels. Elevated melt pressure and temperature may also provide information about formulation flow while also identifying if die bore crosssectional area is insufficient for the flow rates used in manufacture. (DiNunzio et al. 2012)

## **Chapter 3: Materials**

## 3.1 Starch

Starch is a carbohydrate of high natural abundance next to cellulose and chitin. It is the most common constituent of human diet, where it accounts for the major share of energy required for the sustenance of life. Starch is one of the cheapest and most abundant natural carbohydrate biopolymers and is compatible with hydrocolloids and other water-soluble polymers. Therefore, it can be an effective component in multifunctional systems. (Kalia and Sabaa 2013)

Molecular formula	$(C_6H_{10}O_5)_n$
Monomer molar weight	162.14 g/mol
Gelatinization temperature	70-80°C
Solubility	Liquid ammonia, aqu. sol. Of cupriethylenediamine,
	fused chloral hydrate, N-ethylpyridinium
	chloride/pyridine (1 /l), W (hot, pressure)
Appearance	White powder
Density	Variable
Degradation Temperature	275°C

## Table 3.1 Data for starch

Starch granules consist of two major polyglucans, namely, branched amylopectin and essentially linear amylose. In all non-mutant starches, amylopectin is the major component and is responsible for the internal structure of starch granules, which is the native, semi-crystalline form of starch (Nakamura 2015).

### 3.1.1 Amylopectin

Amylopectin is generally the major component of starch and constitutes 65-85 % of the matter in the starch granules. However, in some mutant plants, the amylopectin content is much higher – it can even reach 100 % – and the sample is then known as "waxy starch."



Figure 3.1 Structure of amylopectin with 1-4 and 1-6 linkages

Amylopectin consists of numerous short chains of  $\alpha$ -(1,4)-linked D-glucose residues. The chains are interlinked through their reducing end side by  $\alpha$  -(1,6)- linkages. Together the chains form a very large macromolecule with an average molecular weight (Mw) in the order of  $10^7$ – $10^8$  (Nakamura 2015).

## 3.1.2 Amylose

Amylose is usually the second most abundant component of starch, accounting for typically 20–30 % of its weight. In contrast to the more abundant, highly branched amylopectin, amylose is generally recognized as a linear or slightly branched molecule.

The linear nature confers unique properties on amylose, among which is the ability to form complexes with iodine. The formation of the iodine–amylose complex provides the means to determine the amylose content in starch granules by colorimetric, potentiometric, or amperometric methods (Nakamura 2015). The average molecular weight of amylose is in the order of  $10^{5}$ - $10^{6}$ .



Figure 3.2 Structure of amylose with 1-4 linkage

## **3.2 Plasticizers**

Plasticizers are substances added to polymers to improve their softness, stretchability, and processability. There are two types of plasticizers - External and internal. The former reduces the interaction between the polymer chains, which can be observed physically in the reduction of the glass transition temperature, whereas principle of latter is applied in case monomer units are built into the polymer chain, acting as irregularities in the otherwise regular chain structure and thus causing a decrease in the glass transition temperature compared to the unmodified homopolymer (Braun et al. 2013). The external plasticizers that can be used for plasticizing starch are glycerol, sorbitol and water.

#### 3.2.1 Glycerol

Glycerol is the 1,2,3-propanetriol. The term glycerine or glycerin applies to commercial products, which have at least 95 wt% of glycerol. It is a polar, viscous, transparent liquid at ambient temperature, soluble in water and polar media and insoluble in hydrocarbons and other non-polar media (Mota, Peres Pinto, and de Lima 2017).



Figure 3.3 Structure of glycerol

Molecular formula	C <sub>3</sub> H <sub>5</sub> (OH) <sub>3</sub>
Molecular weight	92 g/mol
Melting point	17.8°C
Density at 20°C	1.261 g/ml
Degradation temperature	225°C
Solubility	Acetone

Table 3.2 Data for Glycerol

## 3.3 Additives

Additives are an essential part of polymer compounding processes. Some of the reasons why additives may be used are (Brewis, Briggs, and Pritchard 2012):

- A. Antiblocking agents: These substances prevent plastics films from sticking together, and are used to facilitate handling or for other reasons.
- B. Compatibilizer: Substance, usually polymeric, which when added to a mixture of two rather dissimilar polymers, enables them to become more intimately mixed than before.
- C. Filler: Particulate additive, designed to change polymer physical properties (e.g. fire resistance, modulus, shock resistance) or to lower cost.
- D. Plasticizer: Additive designed to space out the polymer molecules, facilitating their movements and leading to enhanced flexibility (lower modulus) and ductility. Widely used to convert PVC from the rigid to the flexible variety. Can sometimes be polymeric.

## 3.3.1 Maleic Anhydride

Maleic anhydride (MA) is chemically 2,5-furandione, or cis-butene-dioic anhydride. It is also known by other names such as toxilic anhydride, maleic acid anhydride, or malic acid anhydride. It is a white hygroscopic solid and forms orthorhombic crystalline needles (Trivedi and Culbertson 1982).



Figure 3.4 Structure of maleic anhydride

Molecular formula	C4H2O3
Molecular weight	98.06 g/mol
Melting point	52.8°C
Density	1.48 g/ml (Solid)
Degradation temperature	220°C

Table 3.3 Data for Maleic Anhydride

## **3.4 PBAT**

PBAT (polybutylene adipate terephthalate) is a biodegradable random copolymer. The copolyester of adipic acid, 1,4-butanediol and dimethyl terephthalate. As a "drop-in" polymer, PBAT resembles LDPE in its properties. Global annual production capacities are currently around 100,000 tons. Typical applications are packaging (e.g. plastic films and bottles), coatings (e.g. of paper and cardboard) and foam. A major advantage of PBAT is its compostability (Gerard 2016).



Figure 3.5 Structure of PBAT

Melting point	115°C
Density	1.26 g/ml
Degradation temperature	425°C
Solubility	Dichloromethane, THF

Table 3.4 Data for PBAT

## **3.5 PETG**

Glycol modified PET or also known as PETG is a modification of Polyethylene Terephthalate (PET), a very common commercial grade plastic. PETG is synthesized by replace a portion of glycol component of PET with cyclohexanedimethanol (CHDM). The cyclohexanedimethanol ([4-(hydroxymethyl) cyclohexyl] methanol, IUPAC) is a colourless solid glycol for modification of fibers and polyesters. The incorporation of various content of CHDM within aromatic polyesters can lead to the development of different kinds of glycol modified co-polyesters with properties ranging from amorphous to highly crystalline (Paszkiewicz et al. 2017). The PETG used in our studies is completely amorphous.



Figure 3.6 PETG molecule in transition state



Figure 3.7 PETG block co-polymer

### **Chapter 4: Blend preparation of MTPS**

Preparation of blends in twin screw extruder was the first step in the experimental protocol. The raw material starch had to be moisture free (<0.1%) and additive maleic anhydride to be in right particle size before they could be fed to the extruder. Wherever necessary, they had to be mixed with catalyst, additive and plasticizer before being fed to the extruder. In many experiments, plasticizer was fed to the extruder directly using a pump. The extrudate was collected and palletized to form resins which could be used for further experiments and analysis. Figure 4.1 shows the steps involved in experimental procedure.



Figure 4.1 Experimental procedure for making MTPS

## 4.1 Drying

Due to mild hygroscopic nature of starch, it tends to absorb moisture if kept in open environment for long durations. Moisture is not preferred in our reactive extrusion experiment as it can interfere with glycerol reactivity and create pressure resulting in foaming of extrudate at the die face. Foaming also interferes with palletization of extrudate later. To overcome this barrier, starch was dried overnight (minimum 8 hours) at 70°C in a convective oven. The material was kept in aluminum trays such that thickness of the layer was not more than 5 cm. Reabsorption of water was avoided by using the dried starch towards the start of experiment.

4.1.1 Analyzing moisture content in starch (Sair and Fetzer 1942)

A. Distillation with Toluene

25 to 35 g of starch is tared into distillation flask containing 5 to 8 g asbestos (previously dried in air oven at 100°C). Sufficient toluene (around 100 ml) is added to fill the traps and cover the sample. The flask is then placed in oil bath and distillation is continued until no increase in recovered water is shown.

B. Oven drying

3 to 5 gm of sample is weighed and kept in air oven at 100°C for 24 hours to measure weight loss which attributes to percentage moisture content in starch.

#### 4.1.2 Water determination using Karl-Fischer titration (Scholz 1984)

The reaction of sulphur dioxide with the alcohol producing a mono alkyl ester of the sulphurous acid is a basic requirement for the Karl Fischer reaction. Thus, the Bunsen reaction is prevented and the stoichiometric course of the KF reaction is ensured. The monoalkyl ester of the sulphurous must be neutralized, as the alkyl sulphite anion actually reacts in the Karl Fischer solution.

Alcohol is reacted with Sulphur dioxide in presence of a base to give hydroiodic acid salt and alkylsulfate salt. The intermediate oxidation reaction consumes water. Volumetric titration can be done where iodine is added mechanically to a solvent containing sample. Water is quantified by volume of KF reagent consumed.

 $ROH + SO_2 + R'N \longrightarrow 2[R'NH]I + [R'NH]SO_4R$ 

### 4.2 Mixing

Before feeding the starch onto the feeder, it was mixed with finely powdered MA when making MTPS. MA was powdered using pestle and mortar. It is important to use dust mask while grinding operation as prolonged exposure to fine MA particles can develop allergy in human body. The mixture was well mixed to disperse MA evenly in the dried starch.

#### 4.3 Extrusion

Extrusion was one of the most important steps of the experiments. This is where the blend materials were mixed, and grafting reaction occurred.

The extruder used was a Century co-rotating intermeshing twin screw extruder. Figure 4.2 shows a schematic diagram of the extruder. The diameter of each screw is 30 mm and the transport length of the extruder is 1260 mm. There are two feed ports on the extruder, one is at the first heat zone through which solids can be fed while the second port is an injection port used mainly for liquids. There is a vent port on 8<sup>th</sup> heat zone. The die that was used has one hole of 3 mm diameter. The temperature was measured at 10 points in the barrel including the die face, defining the conditions in zone 1 through 9 and the die.

The screw elements used are a combination of kneading and conveying elements. The numbers associated with conveying elements in Figure 4.2 a/b are a code in which

a = screw pitch (mm)

b= element length (mm)

The numbers associated in kneading block elements in Figure 4.2 d/c/b are a code in which

d = paddle /disk offset in degrees

b = element length (mm)

c = number of disks



Figure 4.2 Schematic of Century CX-30 Extruder

The extruder was purged and cleaned with LDPE before and after each run. The temperature of barrel and die was kept at 140°C with screw speed of 120 RPM. After purging, the temperatures were brought to the required temperature profile for extrusion. This was done because the extruder could be cleaned better when the LDPE was relatively more viscous which could push out the less viscous polymer already in the extruder. When LDPE coming out of the extruder was clear, it was assumed that no other material (except LDPE) was in the extruder. This generally took about 400-500 g of LDPE. Now the screws were stopped, and the feeder throat was cleaned using a vacuum cleaner to remove any leftover LDPE resins. The dried material was fed in batch of about 400 g and rest of the material was stored in the oven to prevent reabsorption of moisture.

Due to its powdered nature, starch starts clogging on the feeder and does not go through into the barrel section. To avoid this problem, it was stirred continuously with a spatula to ensure free flow. As the gelatinization of starch occurs around 70°C, the starting temperature of the profile is kept at the same temperature. The profile used in extruder is shown below.

Zone	1	2	3	4	5	6	7	8	9	Die
	Feed							Vent		
T (°C)	70	90	110	120	130	140	150	150	150	140

#### Table 4.1 Temperature profile for reactive extrusion to form MTPS

If temperatures are increased over 150°C, the extrudate starts turning darker in color while grafting also decreases, this is a problem when blending MTPS with other polymeric materials later. It may affect reactivity and color of final resins thereby affecting the applications.

Feeder is set at feeding material at 80 g/min while the injection port feeds glycerol at 20 g/min. Due to viscosity of glycerol, it is hard to feed it through injection port at room temperature. Therefore, it is kept on a heating plate at 60°C to reduce the viscosity and fed through a peristaltic pump. The total input to the extruder is at 100 g/min or 6 kg/h. Screw speed of the extruder is at 120 RPM. The increase or decrease in screw speed does not affect the torque and therefore the power consumed as the system is starve fed, meaning that volume of material inside the extruder is less than free volume available. Although this does affect the rate at which extrudate comes out and is essential to control when doing simultaneous palletization.
# 4.4 Scheme of Reaction



Figure 4.3 Maleation of Starch using Maleic Anhydride



Figure 4.4 Hydrolysis of starch to form hemi acetals



Figure 4.5 Glucosidation of starch to form thermoplastic starch

# **4.5 Pelletization**

The extrudate coming out of the extruder was pelletized using brabender pelletizer. It is important to match the speed of outflow to feeder speed of palletizer to maintain continuous pelletization. It is also important to cool down the extrudate to make sure it is brittle enough to get pelletized. The MTPS extrudate was air cooled as it cannot be cooled in water due to its hygroscopic nature. Therefore, it becomes important to identify the minimum length of extrudate coil before it can enter the palletizer.



Figure 4.6 Simultaneous process of palletization

Following calculations were done using the principles of heat transfer to identify the correct length (L) of extrudate.

Diameter of die (2r)	3.1 mm
Temperature of extrudate (T <sub>i</sub> )	140°C
Ambient temperature $(T_{\infty})$	24°C
Temperature of palletization (T <sub>p</sub> )	80°C
Density of thermoplastic starch	$1.4 \text{x} 10^3 \text{ g/m}^3$
Thermal conductivity (Morley and Miles 1997)	0.388 W/m-K
Specific heat capacity (Tan et al. 2004) (C <sub>p</sub> )	1.99692 J/g-K
Absolute viscosity (Souza and Andrade 2001)	1 g/m-s

#### Table 4.2 Data of extrudate for palletization calculation

Equations used in calculation for heat transfer through natural convection were:

1.  $Gr = \beta g \Delta T L^3 / \vartheta^2$  (Grashof number) 2.  $\beta = 2/(T_i + T_{\infty})$ 3.  $\Delta T = T_i - T_{\infty}$ 4.  $\vartheta = \frac{\mu}{\rho}$  (Kinematic viscosity) 5.  $\Pr = C_p \mu / k$ 6.  $Nu = 0.68 + \frac{0.67(GrPr)^{0.25}}{(1+(0.492/\Pr)^{\left(\frac{9}{16}\right)})^{4/9}}$  (Churchill & Chu, 1975) 7.  $Nu = hl_c/k$  (Ic is characteristic length of cylinder = r/2) 8.  $t = \frac{\rho V C p}{hAs} ln \frac{T_i - T_{\infty}}{T_p - T_{\infty}}$  (assuming lumped capacitance; As is cross area) 9.  $t = \frac{L}{speed}$ 10.  $speed = \frac{flow rate}{density \times As}$ 

Using all the above equations and values and keeping L as variable, it was determined that minimum length required to cool down the extrudate was 0.357 m or approximately 40 cm. This length was about 10 cm less than length normally required to cool down the extrudate which is due to higher specific heat capacity values of MTPS and RMTPS than theoretical.

# **Chapter 5: Materials characterization**

After preparing the blend/s in extruder, the extent of reaction or grafting was measured using Soxhlet analysis and was further characterized using FTIR spectroscopy. The extract and residue of extraction were characterized by thermal analysis (TGA). Hydroxyl value determination was done as a measure of free hydroxyl content. Finally, Validation of starch was done using acid hydrolysis and glucose determination.

# 5.1 Soxhlet extraction

The apparatus for Soxhlet extraction consists of a solvent reservoir, extractor body, an electric heat source (e.g. an isomantle) and a water-cooled reflux condenser. The type of extraction is Solid-Liquid extraction. The solid sample is placed in a dried porous cellulose thimble (Whatman) which is in the inner tube of the extractor body. The extractor body is then fitted to a round bottomed flask containing the chosen solvent and to a reflux condenser. By heating the solvent with an isomantle (electric heating device) the solvent will gradually become a vapor and pass vertically through the tube. As the solvent vapor continues to rise it eventually meets the reflux condenser where the solvent vapor condenses and descends into the extractor body. Within the extractor body is located the sample-containing thimble which now slowly fills with solvent. The passage of warm solvent through the sample-containing thimble extracts any organic compounds contained within it. Once the thimble section is full, solvent with extract is siphoned to round bottomed flask (Dean 2009).



Figure 5.1 Apparatus for Soxhlet extraction

The application of Soxhlet extraction involves itself in determination of extent of reaction. The amount of grafting can be calculated by using selective extraction. For example, if polymer A and B react and produce graft polymer A-g-B, then a solvent is selected such that one of A or B is soluble in it while other is not. If the reaction has occurred, then some or all part of the soluble polymer will stay back and not get dissolved in the solvent. It may also happen that all soluble polymer comes out while some of the insoluble polymer also now dissolves in the solvent. Then, the grafting is calculated as a percentage of increase in residue or extract's weight to original composition of soluble polymer.

## Mathematically, if

Sample weight	W
Percentage of soluble polymer in original sample	X
Extract	E
Residue	R
Soluble polymer in original sample ( <i>P</i> )	W*x/100
Insoluble polymer in original sample	W*(1-(x/100))
Weight gain/loss ( $\Delta W$ )	$ E - (W^*x/100) $
	Or
	$ R - (W^{*}(1 - (x/100))) $

# Table 5.1 Soxhlet extraction calculation

Then, Percentage grafting is given by

% grafting = 
$$\Delta W * \frac{100}{P}$$

#### 5.2 Thermo-Gravimetric Analysis (TGA)

Thermogravimetry (TG) is a technique in which the mass of the Definition of sample is monitored against time or temperature while the temperature of thermogravimetry the sample, in a specified atmosphere, is programmed. To enhance the steps in the thermogravimetric curve, the derivative thermogravimetric (DTG) trace is frequently drawn. This is the plot of the rate of mass change, with time, dm/dt (Haines 1995).

The results may depend on:

- A. Sample Size
- B. Atmospheric conditions
- C. Type of Pan
- D. Heating rate

TGA measurements were conducted under nitrogen using a Hi-Res TGA 2950 apparatus from TA Instruments. In a typical experiment, a sample (10-15 mg) was placed in an aluminum pan and was heated at 10°C/min ramp. The same profile was used for all the experiments. Care was taken not to touch the sample pans by hand.

Analysis of the TGA and DSC curves was carried out using TA Instruments Universal Analysis software. The software was used to measure:

- A. Change in weight between onset and offset of DTG curve.
- B. Degradation temperature by estimating temperature at DTG peak.

#### 5.3 Fourier Transform – Infrared Spectroscopy (FT-IR)

An FT-IR can be used to do the unknown analysis. It helps in find what molecules might be present in each sample. The peak positions in an infrared spectrum correlate with molecular structure, which is part of why infrared spectroscopy is useful.

When performing a spectral comparison, or what is sometimes called identity testing, the two samples might be compared to see if they are same. It is easier to compare spectra than finding information about an unknown spectrum (Smith 2011).

In this thesis, FT-IR has been used for comparing spectra, to analyze the effects of grafting by comparing the spectra before and after soxhlet extraction. The sharpness of peaks give qualitative information about the effectiveness of reaction.

### 5.4 Hydroxyl value

A hydroxyl value is the number of milligrams of a potassium-hydroxide equivalent to the acetic acid needed to acetylate 1 gram of sample. To measure the hydroxyl value of Starch and its thermoplastic blends, ASTM D4274 test method A will be used. This test method uses Acetic anhydride and Pyridine to carry out the acetylation reaction in a pressured bottle which when titrated against Sodium Hydroxide with phenolphthalein as indicator can be used to determine the hydroxyl value of the sample.

Since the reaction converts starch and its thermoplastic blends into acetylated products, they can be dissolved in THF and run through gel permeation chromatography to find respective molecular weights. Change in molecular weights after every step of extrusion is a key factor to study the strength of extruded products.

Acetylation reagent is made using 12.7 ml of Acetic Anhydride and 100 ml of Pyridine in a dark colored bottle as the reagent is photosensitive. 20 ml of the reagent is pipetted into each pressure bottle. The samples are run in duplicates.

Sample weight is calculated by determining the approximate hydroxyl value of the sample. For example, for starch –

Approximate hydroxyl value = functionality\*56100/molecular weight= 3\*56100/162.14 = 1038 mg KOH / g StarchThen,Sample weight = 561\*0.98/approximate hydroxyl value (g)= 561\*0.98/1038 = 529.6 mg

A blank and a test flask is prepared in duplicates. Test flask contains the sample weight determined by above formulae. The pressured bottles are kept on water bath at a temperature of 98 degrees Celsius for 2 hours. After 2 hours, the bottles are taken out and allowed to cool down at room temperature. Once cooled, crushed ice is added to the bottles to arrest the reaction. The resulting solution is titrated against sodium hydroxide and corresponding hydroxyl values are calculated. Overall scheme of reaction is shown below –

Titration

$$\begin{array}{c} O \\ H_{3}C \\ \hline O \\ H_{3}C \\ \hline O \\ O \\ H \end{array} + Na^{O} H \begin{array}{c} Pyridine \\ \hline Pyridine \\ H_{3}C \\ \hline O \\ O \\ O \\ H \end{array} + H_{3}C \\ \hline O \\ H_{3}C \\ \hline O \\ H \end{array} + H_{0} \\ - H \\ \\ - H$$

Figure 5.2 Hydroxyl value titration scheme

#### 5.5 Validation of soxhlet results by determining starch content using acid hydrolysis

### Acid hydrolysis of starch

One of the earliest methods of acid hydrolysis of starch were published in 1903 where the authors used HCl as catalyzing agent to hydrolyze starch into glucose by breaking glucosidic linkage. The validation of the reaction was done using optical rotation analysis and is published in DOI: 10.1021/ja02012a001. Following this study, many publications have dealt with optimizing the reaction time for acid hydrolysis of starch. This optimization mainly involved varying parameters such as Temperature, Reaction time, concentration of acid and concentration of reaction solution. It was also realized that Sulphuric acid was better preferred over HCl because rate of conversion of glucose to gluconic acid was faster when latter was used.

### Acid hydrolysis of starch containing polymer

Acid hydrolysis of native starch products is more direct method of conversion to glucose. Taking the base from this method, it was hypothesized that it could be used for determining the presence and quantifying the amount of starch present in starch containing polymers. A study on estimating yields of reducing sugar in cassava bagasse (DOI: 10.1590/S1516-89132002000300018) forms a base for a similar hypothesis where if a graft polymer comprised of some polymer and starch and the polymer portion has much lower reactivity for acid hydrolysis, then all of the starch in the graft polymer could be converted to glucose to estimate percentage starch content in the graft polymer.

Method	Principle	Limitations		
Lane Eynon method (Titrimetric method)	<ul> <li>Known amount of CuSO<sub>4</sub> solution with methylene blue indicator is titrated with carbohydrate solution being analyzed.</li> <li>Reducing sugars present in CuSO<sub>4</sub> and solution turns from blue to white.</li> <li>Calibration curve is made first using a series of known solutions.</li> <li>Applicable to all starch hydrolysis products.</li> </ul>	<ul> <li>Results depend on precise reaction times, temperature, conc. of reagents</li> <li>Not very accurate</li> <li>Susceptible to interference from other types of molecules that may act as reducing agents</li> </ul>		
Munson-Walker method (Gravimetric method)	<ul> <li>Sugar solution Fehling's solution is mixed and heated.</li> <li>Cu<sub>2</sub>O precipitate is formed.</li> <li>Solid is filtered, washed, dried and weighed.</li> <li>From the weight of Cu<sub>2</sub>O obtained, amount of sugar can be determined from empirical tables.</li> </ul>	<ul> <li>Can be less accurate for small samples.</li> <li>Used for glucose. So, extrapolation to starch necessary.</li> </ul>		

Table 5.2 Methods of glucose detection

Table	5.2	(Cont'd)
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Phenol sulphuric acid method (colorimetric method)	Glucose is dehydrated to furfural in presence of H <sub>2</sub> SO <sub>4</sub> Furfural + Phenol → Yellow brown colored product Absorbance is measured at 490 nm	
Anthrone method (colorimetric method)	-Glucose is dehydrated to furfural in presence of H <sub>2</sub> SO <sub>4</sub> -Furfural +Anthrone gives a blue green complex whose absorbance is measured at 620 nm	
GOD-POD method	<ul> <li>-Glucose oxidase (GOD) catalyzes oxidation of glucose to gluconic acid. H<sub>2</sub>O<sub>2</sub> is formed during this reaction.</li> <li>- H<sub>2</sub>O<sub>2</sub> is detected by phenol aminophenazone in presence of peroxidase (POD)</li> </ul>	Detection limit - 100-1000 mg/L

# Table 5.2 (cont'd)

Glucose meters	-various glucose meters available in market (Accu	Detection limit-
	check, precision, optimum lines etc.)	100-1000 mg/L
	- Enzymes are directly impregnated on test strips, small	
	drop of fluid applied directly	
Polarimetry	-Molecules with asymmetric C rotate the plane of PPL	
	(plane polarized light)	
	-Polarimeter measures angle by which this plane is	
	rotated	
	$\alpha = [\alpha] lC$	
	Where-	
	$\alpha$ - measured angle of rotation	
	$[\alpha]$ - optical activity (from literature)	
	l- path length	
	C- Concentration	

# Steps for acid hydrolysis

- Take certain concentration of starch per liter of acid solution (determined from different papers at 2g/l for native starch).
- Prepare 2% H<sub>2</sub>SO<sub>4</sub> solution in a volumetric flask.
- Use a round bottomed flask for the reaction. Put native starch or extract in the round bottomed flask (weight determined using concentration).
- Pour in required volume of 2% acid solution.
- Set oil bath at required temperature.
- Set up the round bottomed flask on oil bath with a reflux condenser.
- Start the reaction and monitor reaction time.
- After the end of reaction, neutralize the reaction mixture immediately to stop the reaction using BaCO<sub>3</sub>.
- Take 1 ml of the neutralized sample in a centrifuge vial and centrifuge it.
- Measure the amount of glucose using YSI glucose analyzer.

#### **Chapter 6: Maleic Thermoplastic Starch analysis**

Maleic thermoplastic starch was made using two kinds of starch: High amylose Hylon VII starch supplied by National Starch (Now Ingredion) and Regular corn starch SMP 1100 supplied by Cargill, Inc. Iowa.

#### A. HYLON VII

The amylose content of this starch is at 70% and therefore has lower molecular weight. The moisture content of this starch was determined at 12% of total weight.

#### B. SMP 1100

The amylose content of this starch is at 25% and has higher molecular weight than high amylose starch. The moisture content of this starch was determined at 10% of total weight.

For ease of reference, Maleic thermoplastic starch made from high amylose starch will be referred as MTPS while that made from Regular starch will be referred as RMTPS.

# 6.1 Temperature Profile and Steady State

The temperature profile for both the starches were kept at fixed one mentioned in the table below. It is important to maintain steady state to ensure reproducibility. During initial processing, system runs at unsteady state till temperatures get stabilized, for this purpose cooling system is needed for the extruder. The unsteady state extrudate is discarded. Once the system was in steady state, the extrudate was fed to pelletizer to obtain resins.

Zone	1	2	3	4	5	6	7	8	9	Die
	Feed							Vent		
T (°C)	70	90	110	120	130	140	150	150	150	140

Table 6.1 Temperature profile for reactive extrusion to form MTPS

#### 6.2 Torque and Specific Mechanical Energy

Specific Mechanical Energy (SME) is a scale-independent measure of the mechanical energy put into the extrudate.

The basic concept behind SME is to measure the energy going into the extrusion system per unit mass in the form of work from the motor. That energy is put into the extrudate through viscous dissipation. That energy is converted primarily into heat in the extruder. There are other reactions that can occur, such as gelatinization of starch or denaturation of protein and some, of course, is lost across the boundary (through the barrel wall) of the extruder. Unfortunately, there are a lot of uncertainties in measuring the mechanical input, so getting an extremely accurate SME is somewhat uncertain.

One of the more straight-forward SME calculations is as follows:

$$SME\left(\frac{kJ}{kg}\right) = P \times (\Delta\tau) \times (\frac{RPMact}{RPMrat}) \times 1/m$$

P = Motor Power (in kW)

 $\Delta \tau$  = Difference between running torque and torque when extruder is empty (in decimal)

RPMact = Actual RPM

RPMrat = Rated RPM

m = mass flow rate (in kg/s)

	RMTPS	R1	R2	R3
Motor power	15	15	15	15
running torque	0.3	0.34	0.34	0.36
empty torque	0.08	0.04	0.05	0.06
RPM act	150	123	122	120
RPM rated	1460	1460	1460	1460
mass flow rate	0.00167	0.001833	0.001833	0.001833
SME (kJ/kg)	203.0186	206.7908	198.2726	201.7471

Table 6.2 Different processing conditions and corresponding Specific Mechanical Energies.

Not one but many variables affect the total energy input or Specific Mechanical Energy in the system. The temperature rise resulted by specific mechanical energy input can be used to determine the specific heat capacity of the material. Mathematically –

$$SME = Cp \times \Delta T$$

Where,

C<sub>p</sub> – Specific heat capacity

 $\Delta T$  – Temperature increase from feed throat to melt temperature

Sample	SME	Ti	Tf	ΔT	Ср
RMTPS	203.0186	24	110	86	2.360682
R1	206.7908	24	111	87	2.376906
R2	198.2726	24	108	84	2.360388
R3	201.7471	24	109	85	2.373496

Table 6.3 Specific heat capacity in kJ/kg-K for MTPS from different processing conditions.

### 6.3 Soxhlet analysis

Soxhlet analysis of resins were done once dried overnight. The solvent used was acetone and grafting of glycerol on starch was measured. Sample size varied from 2g to 5g with triplicate iteration over duration of 48 hours. It was expected that all the free glycerol will be extracted by acetone and subsequently fall into volumetric flask. The contents of volumetric flasks could then be dried to check unreacted glycerol's presence. It is important to have as less of free glycerol possible to ensure good grafting of subsequent blends.

The extract and residue were dried to ensure they were acetone free. Presence of acetone in residue or extract will give flawed results in further analysis and therefore, is not desired.

The average data on different thermoplastic starch samples produced was tabulated and has been listed below.

Sample	1	2	3	4	5	6	7	8
% Grafting	84.036	83.978	84.282	82.601	83.080	83.460	84.445	83.729

Table 6.4 Grafting of glycerol on starch backbone obtained in different runs

The average grafting of MTPS was measured at 83.463 % while that of RMTPS was measured at 84.099 %



Figure 6.1 Individual control chart of grafting for RMTPS and MTPS

# 6.4 Thermogravimetric analysis

A TGA was carried out on all the following samples and analyzed using TI Universal analysis software. The degradation peaks, onset and offset of degradation and composition of components of polymer were identified using the software.

- A. Extrudate
- B. Residue from soxhlet extraction
- C. Extract from soxhlet extraction

The TGA and Differential thermogravimetric (DTG) curves have been plotted below for both MTPS as well as RMTPS samples.



Figure 6.2 TGA Curve of High amylose starch showing 11% moisture content, degradation peak of starch at 298.78 degrees and rest composition of starch.



Figure 6.3 TGA curve of pure glycerol showing degradation peak at 226.88 degrees



Figure 6.4 TGA curve of MTPS showing presence of glycerol and starch near respective degradation peaks



Figure 6.5 TGA curve of residue from MTPS acetone extraction showing reduction in amount of glycerol owing to removal during extraction

In above graphs we see that there is a change in concentration of glycerol from extrudate to residue which is an evidence for glycerol extraction. The free glycerol is extracted and goes into solvent reservoir while the bound glycerol is visible in residue. To give a better picture of this analysis, DTG curve is studied.



Figure 6.6 DTG curve comparison of MTPS extrudate and residue showing removal of free glycerol



Figure 6.7 DTG curve comparison of RMTPS extrudate and residue showing removal of free glycerol

# 6.5 FT-IR Analysis

An ATR FT-IR analysis was done on reactants, products, residues and extracts. Studying the spectra helps in visual analysis of reaction. By identifying peaks for a given sample, the change in resultant products can be studied as an effect of reactants. For example, by conducting an FT-IR of glycerol and starch sample, it can be predicted which bonds and therefore which peak should arise in the MTPS.



Figure 6.8 FTIR spectra - Reaction between glycerol and high amylose starch to result into MTPS



Figure 6.9 FTIR spectra - Reaction between glycerol and regular starch to result into RMTPS



Figure 6.10 FTIR spectra - Soxhlet extraction of MTPS to give residue and glycerol (extract)



Figure 6.11 FTIR spectra - Soxhlet extraction of RMTPS to give residue and glycerol (extract)

Sample	Peak (cm <sup>-1</sup> )	Description			
Glycerol	3294	Intermolecular bonded -OH			
	2935	Intramolecular bonded -OH			
	2879	Alkane stretch -CH			
	1413	Alkane bending -CH <sub>2</sub>			
	1330	Alcohol bending			
	1050	Primary stretching -OH			
Starch	3324	Intermolecular bonded -OH			
	2935	Alkane stretch -CH			
	1375	Alcohol bending			
	1650	Aromatic -CH overtone			
	1000	Primary -OH			
	1140, 770	Stretch -CO bend			

Table 6.5 Peak measurement data on FT-IR of glycerol and starch.

The key difference between starch and MTPS is seen at  $1715 \text{ cm}^{-1}$  where a -C=O stretch peak arises due to covalently bonded Maleic anhydride. Rest of the spectra remains nearly the same for starch, MTPS and RMTPS samples.

# 6.6 Hydroxyl value

The hydroxyl value for both thermoplastic starches was found out using Pyridine, Acetic anhydride and Imidazole. The unit for hydroxyl value is in (mg of KOH per g of acetic anhydride). This is equivalent to (mg of KOH per g of sample. To find the free hydroxyl groups, a multiplication factor of 17/56100 can be used where 17 denotes molecular weight of OH group and 56.1 the molecular weight of KOH, 1000 being the conversion from mg to g.

The hydroxyl values and corresponding free hydroxyl groups have been tabulated below -

Sample	Hydroxyl value	Free hydroxyl
	(mg KOH / g Sample)	(per 100g sample)
MTPS	800	24
RMTPS	1000	30

# Table 6.6 Hydroxyl values of Thermoplastic starches

Higher number of hydroxyl groups are available for trans-esterification reaction in RMTPS than in MTPS. This may be attributed to the higher degree of hemi-acetal formation in regular starch than linear high amylose starch.

# **Chapter 7: Plasticized starch blend with PBAT: Preparation and analysis**

The basis of this thesis is to study the trans-esterification reaction between starch and other polyesters. The study on graft polymerization can help contribute to commercial use of starch. While the thermoplastic starch has moderate to high hydrophilic nature, forming an ester of the compound helps make the graft polymer hydrophobic and therefore better for commercial applications.
### 7.1 Preparation of R/MTPS-g-PBAT

Once MTPS with more than 80% grafting was prepared, it was dried overnight to forego moisture content. Similarly, PBAT was dried to remove moisture. The dried MTPS and PBAT were mixed in 30:70 ratio and fed through the feeder. The feed rate was maintained at 100 g/min or 6 kg/h for the mixture by calibrating it. Alternatively, two feeders or a feeder and a side feeder can be used.

### 7.2 Process Conditions

The processing conditions for MTPS-g-PBAT blend are given below:

- A. Screw Speed = 120 RPM
- B. Feed rate = 6 kg/h
- C. Maximum temperature of heating barrel =  $160^{\circ}$ C
- D. Screw design = Alternating set of conveying and kneading
- E. Extruder type = Twin-screw intermeshing co-rotating
- F. Vent port = Open
- G. Cooling of extrudate = Water trough

Zone	1	2	3	4	5	6	7	8	9	Die
	Feed							Vent		
T (°C)	90	110	120	130	140	150	160	160	160	150

Table 7.1 Temperature profile for reactive extrusion of MTPS and PBAT

#### 7.3 Scheme of reaction between MTPS and PBAT

A reaction between MTPS and PBAT happens through trans-esterification. For transesterification to occur, a hydroxyl site is required. MTPS has three available hydroxyl sites and therefore, there are three possible routes for this reaction to happen. The cleavage of PBAT will occur at the C-O linkage in the O=C-O section to facilitate trans-esterification.

The first route may involve exchange at inherent primary alcohol. That is, ester will form at the site of alcohol group present in starch before MTPS formation. This will give the graft polymer and alcohol terminated PBAT as a by-product. This has been marked number 1 in the Figure presented ahead.

The second route may involve removal of glycerated terminal group of MTPS to give the graft polymer and reduction of glycerated terminal group to glycerol and alcohol terminated PBAT as by-products. This has been marked number 2 in the Figure ahead. Existence of this route may be verified by conducting a soxhlet analysis on extrudate with acetone. If total amount of glycerol in the soxhlet analysis is more than free glycerol available just in MTPS, then reaction may have taken this route.

The third route may involve exchange at primary alcohol of the glycerated terminal group to give the graft polymer and alcohol terminated PBAT as a by-product. This is number 3 in Figure ahead.



Figure 7.1 Proposed scheme of reaction to form graft polymer MTPS-g-PBAT

### 7.4 Soxhlet analysis

As discussed earlier, soxhlet extraction is a preferential extraction and therefore identifying solvent is a crucial step. Approximately 1 gm of PBAT was taken and dissolved in Dichloromethane (DCM) and Tetrahydrofuran (THF). The time taken to dissolve in DCM was lesser than that for THF, hence it was chosen as a solvent for our experiment.

In MTPS-g-PBAT, MTPS grafts on to the backbone of PBAT and therefore all the grafted portion is extracted in to the solvent. The non-grafted portion that is MTPS remains in the thimble and is classified as residue. The experiment was conducted for 5 gm samples in triplicate for 48 hours and grafting was calculated using mass balance demonstrated earlier in this thesis.

The results obtained have been tabulated and discussed ahead.

Sample	1	2	3	4	5	6
Weight	5.0203	5.0672	5.075	5.1121	4.9779	5.0562
MTPS	1.50609	1.52016	1.5225	1.53363	1.49337	1.51686
PBAT	3.51421	3.54704	3.5525	3.57847	3.48453	3.53934
Extract	4.3512	4.3537	4.4385	4.4551	4.3732	4.4244
Residue	0.6691	0.7135	0.6365	0.657	0.6047	0.6318
% grafting	55.573	53.064	58.193	57.160	59.507	58.348

Table 7.2 Soxhlet extraction data on RMTPS-g-PBAT sample with grafting of  $56.285 \pm 3.22 \%$ 

Sample	1	2	3	4	5	6
Weight	5.0013	5.0562	5.0562	5.1003	5.0398	5.0012
MTPS	1.50039	1.51686	1.51686	1.53009	1.51194	1.50036
PBAT	3.50091	3.53934	3.53934	3.57021	3.52786	3.50084
Extract	4.0274	4.0598	4.0727	4.1213	4.0677	4.0198
Residue	0.9739	0.9964	0.9835	0.979	0.9721	0.9814
% grafting	35.090	34.311	35.162	36.017	35.705	34.589

Table 7.3 Soxhlet extraction data on MTPS-g-PBAT sample with grafting of  $35.164 \pm 0.853 \%$ 

More portions of RMTPS graft on the backbone of PBAT than MTPS. A graft polymer is characterized by a covalent bond between grafted molecules. It is important to note that an RMTPS covalent bond with PBAT will be stronger than MTPS covalent bond with PBAT due to relatively higher molecular weight of RMTPS in addition to more branching present in RMTPS. Therefore, when the solvent tries to pull out RMTPS along with PBAT, it is easier to do so and hence higher grafting percentages are shown for the same composition.

### 7.5 Thermogravimetric analysis

TGA and DTG curves were plotted for extrudate to verify the composition of blends, their extracts and residues to verify the grafting percentage. In a typical case, the blend of composition 30 parts of MTPS and 70 parts of PBAT were analyzed. From soxhlet extraction it was realized that solvent pulled all of PBAT and the grafted portion of MTPS. If the portion of MTPS pulled was 'x' amount then the percentage grafting was roughly '100\*x/30' which were in accordance with the soxhlet results. The graphs have been shown ahead.



Figure 7.2 TGA and DTG curves for RMTPS-g-PBAT with 30% RMTPS and 70% PBAT



Figure 7.3 TGA and DTG curves of extract after soxhlet extraction of RMTPS-g-PBAT using DCM as solvent. About 19 parts of starch out of 30 original parts were obtained in the extract which is equal to 60% grafting.



Figure 7.4 TGA and DTG curves of residue after soxhlet extraction of RMTPS-g-PBAT using DCM as solvent. The residue is entirely made of non-grafted RMTPS as expected.



Figure 7.5 TGA and DTG curves for MTPS-g-PBAT with 30% MTPS and 70% PBAT



Figure 7.6 TGA and DTG curves of extract after soxhlet extraction of MTPS-g-PBAT using DCM as solvent. About 10 parts of starch out of 30 original parts were obtained in the extract which is equal to 33% grafting.



Figure 7.7 TGA and DTG curves of residue after soxhlet extraction of MTPS-g-PBAT using DCM as solvent. The residue is entirely made of non-grafted MTPS as expected.

### 7.6 FT-IR analysis

A trans-esterification reaction is an exchange of hydroxyl group with that of an ester. It is hence, expected that carbonyl peak will be generated on the molecule to be esterified. The blend is expected to have carbonyl peak but the efficiency or the grafting of the reaction can be judged only after extraction has completed. The trend was observed for both RMTPS and MTPS and sharpness of the carbonyl peak was a clear distinguisher towards grafting reaction. The FT-IR trends for extracts and residues after the extraction have been represented ahead.



Figure 7.8 FT-IR Spectra of MTPS-g-PBAT after soxhlet extraction. Presence of carbonyl peak at 1700 cm<sup>-1</sup> is a validation of transesterification reaction.



Figure 7.9 FT-IR Spectra of RMTPS-g-PBAT after soxhlet extraction. Presence of carbonyl peak at 1700 cm<sup>-1</sup> is a validation of transesterification reaction.

# 7.7 Hydroxyl value

The hydroxyl values were determined for extracts of both MTPS-g-PBAT as well as RMTPS-g-PBAT. The reaction was done with acetic anhydride in presence of pyridine and imidazole. The values have been presented in the table below.

Sample	Hydroxyl value	Free hydroxyl
	(mg KOH / g Sample)	(per 100g sample)
MTPS-g-PBAT	330	10
RMTPS-g-PBAT	300	9.1

Table 7.4 Hydroxyl values of extracts of MTPS-g-PBAT and RMTPS-g-PBAT after soxhlet extraction.

The significant decrease in hydroxyl value attributes to removal of non-grafted starch (as compared to hydroxyl values of MTPS).

## **Chapter 8: Plasticized starch blend with PETG: Preparation and analysis**

Another trans-esterification reaction which could be done with MTPS involves PETG. PETG is known for its mechanical properties and is used widely in plastics industry. This chapter can be regarded as a starting step towards research on starch and PETG blends. After reactively extruding MTPS and PETG, the blend was studied for grafting efficiency and its mechanical properties.

### 8.1 Preparation of R/MTPS-g-PETG

After drying overnight, the MTPS with 80% grafting or more was reactively extruded with PETG in the ratio of 30:70. The feed rate of the mixture was calibrated and maintained at 100 g/min or 6 kg/h. Before feeding, it was made sure that machine was free of contamination and was purged with PETG.

### **8.2 Process conditions**

The processing conditions for MTPS-g-PETG blend are given below:

- A. Screw Speed = 120 RPM
- B. Feed rate = 6 kg/h
- C. Maximum temperature of heating barrel =  $170^{\circ}$ C
- D. Screw design = Alternating set of conveying and kneading
- E. Extruder type = Twin-screw intermeshing co-rotating
- F. Vent port = Open
- G. Cooling of extrudate = Water trough

Zone	1	2	3	4	5	6	7	8	9	Die
	Feed							Vent		
T (°C)	90	120	140	150	160	170	170	160	160	150

Table 8.1 Temperature profile for reactive extrusion of MTPS and PETG

## 8.3 Scheme of reaction between MTPS and PETG

The proposed scheme of reaction is like the scheme of reaction between MTPS and PETG due to same class of reaction which takes place. The reaction can either be trans-esterification on primary alcohols or removal of glycerol and trans-esterification.



Figure 8.1 Proposed mechanism for reactive extrusion between MTPS and PETG

### 8.4 Soxhlet extraction and analysis

For Soxhlet extraction study on MTPS-g-PETG, DCM was used as a solvent. It was seen that some portion of PETG remained in the residue after the extraction was complete indicating an opposite trend to that seen in MTPS-g-PBAT. This primarily means that PETG molecule grafted on to backbone of starch. The grafting results for MTPS and RMTPS blends are shown in the table below.

Sample	1	2	3	4	5
SW	5.0122	4.983	5.0281	5.0686	5.0505
Extract	2.175	2.2118	2.1644	2.1121	2.1018
Residue	2.8372	2.7712	2.8637	2.9565	2.9487
%Grafting	38.008	36.590	38.506	40.471	40.549

Table 8.2 Soxhlet extraction data on RMTPS-g-PETG sample with grafting of  $38.825 \pm 1.98$  %

Sample	1	2	3	4	5
SW	3.0303	5.1132	4.5539	5.0201	5.1103
Extract	1.0262	1.7743	1.5236	1.7912	1.8357
Residue	2.0041	3.3389	3.0303	3.2289	3.2746
%Grafting	51.622	50.428	52.204	49.028	48.683

Table 8.3 Soxhlet extraction data on MTPS-g-PETG sample with grafting of  $50.393 \pm 1.76 \%$ 

From the above data, it can be inferred that some PETG molecules are covalently bonded to MTPS backbone and are not pulled away by solvent. The molecules which are not bonded to the backbone easily come out and fall in to the solvent reservoir.

#### 8.5 Thermogravimetric analysis

TGA and DTG curves were plotted for extrudate to verify the composition of blends, their extracts and residues to verify the grafting percentage. In a typical case, the blend of composition 30 parts of MTPS and 70 parts of PETG were analyzed. From soxhlet extraction it was realized that solvent pulled all of non-grafted PETG and the grafted portion of PETG and entire MTPS were left behind in the residue. If the portion of PETG pulled was 'y' amount, then the percentage grafting was roughly '100\*y/70' which were in accordance with the soxhlet results. The graphs have been shown ahead.



Figure 8.2 TGA and DTG curves of residue after soxhlet extraction of RMTPS-g-PETG using DCM as solvent. About 33 parts of PETG out of 70 original parts were obtained in the extract which is equal to 47% grafting.



Figure 8.3 TGA and DTG curves of extract after soxhlet extraction of RMTPS-g-PETG using DCM as solvent. The extract is entirely made of non-grafted PETG as expected.



Figure 8.4 TGA and DTG curves of residue after soxhlet extraction of MTPS-g-PETG using DCM as solvent. About 41 parts of PETG out of 70 original parts were obtained in the extract which is equal to 58% grafting.



Figure 8.5 TGA and DTG curves of extract after soxhlet extraction of MTPS-g-PETG using DCM as solvent. The extract is entirely made of non-grafted PETG as expected.

# 8.6 FT-IR analysis

As discussed earlier, a trans-esterification reaction can be characterized by formation of carbonyl peak. It can be further validated by presence of carbonyl peak in the residue after soxhlet extraction. The following FT-IR curves present a validation of the reaction.



Figure 8.6 FT-IR Spectra of RMTPS-g-PETG after soxhlet extraction. Presence of carbonyl peak at 1700 cm<sup>-1</sup> in residue is a validation of trans-esterification reaction.



Figure 8.7 FT-IR Spectra of MTPS-g-PETG after soxhlet extraction. Presence of carbonyl peak at 1700 cm<sup>-1</sup> in residue is a validation of trans-esterification reaction.

## 8.7 Hydroxyl value

The hydroxyl values were determined for extracts of both MTPS-g-PETG as well as RMTPS-g-PETG. The reaction was done with acetic anhydride in presence of pyridine and imidazole. The values have been presented in the table below.

Sample	Hydroxyl value	Free hydroxyl
	(mg KOH / g Sample)	(per 100g sample)
MTPS-g-PETG	290	8.7
RMTPS-g-PETG	310	9.3

Table 8.4 Hydroxyl values of extracts of MTPS-g-PETG and RMTPS-g-PETG after soxhletextraction.

The significant decrease in hydroxyl value attributes to removal of non-grafted starch (as compared to hydroxyl values of MTPS).

# 8.8 Tensile testing

After making injection molded test bars on microtruder, the test bars of area 0.194 sq. inch were tested for tensile properties such as young's modulus, % elongation at break and tensile strength. These properties have been discussed below.

Number	Yield strength	Yield	Young's	Tensile strength	% Elongation
	(psi)	elongation	modulus (psi)	(psi)	at break
1	392.655	2.436	161.188	426.649	148.54
2	397.990	2.216	179.598	430.155	173.11
3	376.701	2.18	172.799	430.155	181.87
4	405.309	2.64	153.526	424.278	168.33
5	396.340	2.31	171.576	426.392	184.48
Average	393.799	2.3564	167.737	427.526	171.266

Table 8.5 Tensile testing data for native PETG



Figure 8.8 Tensile properties of native PETG

Number	Yield strength	Yield	Young's	Tensile strength	% Elongation at
	(psi)	elongation	modulus (psi)	(psi)	break
1	388.041	2.6	149.247	403.814	158.6
2	379.845	2.19	173.445	388.814	153.2
3	377.577	2.432	155.254	393.196	149.6
4	374.278	2.39	156.602	391.031	160.4
5	370.515	2.08	178.132	390.155	156.8
Average	378.052	2.3384	162.536	393.402	155.7

Table 8.6 Tensile testing data for MTPS-g-PETG



Figure 8.9 Tensile properties of MTPS-g-PETG

Number	Yield strength	Yield	Young's	Tensile strength	% Elongation at
	(psi)	elongation	modulus (psi)	(psi)	break
1	371.737	1.899	195.754	390.619	88.4
2	358.845	1.79	200.472	375.103	90.1
3	366.356	2.102	174.289	385.773	118.5
4	353.237	1.823	193.767	378.918	98.3
5	358.155	1.806	198.314	375.876	87.1
Average	361.666	1.884	192.519	381.258	96.5

Table 8.7 Tensile testing data for RMTPS-g-PETG



Figure 8.10 Tensile properties of RMTPS-g-PETG

### Chapter 9: Acid hydrolysis of starch: Validating the presence of starch in samples

Acid hydrolysis of starch is known to give glucose as product. Glucose is a type of sugar with formula  $C_6H_{12}O_6$ . There are numerous ways to detect glucose which have been discussed in earlier sections. This chapter discusses the technique of acid hydrolysis on starch and how it was sued to confirm the presence of starch in MTPS-g-PBAT extracts after soxhlet extraction.

Acid hydrolysis reaction was carried out on samples. Once the reaction time was over, the samples were neutralized using BaCO<sub>3</sub>. The neutralized samples were then centrifuged and tested using YSI glucose analyzer.

# 9.1 Calibration on YSI analyzer

Before running the reaction and analyzing the samples, it was made sure that the glucose analyzer gave acceptable results. For this, a calibration run was done with varying samples. The run has been plotted below.

Concentration of glucose (g/l)	Detected (g/l)
0	0
0.5	0.476
1	1.02
2	2
5	4.97
9	9.36
10	9.93

Table 9.1 Calibration data for glucose analyzer



Figure 9.1 Calibration curve for glucose analyzer

### 9.2 Optimizing the reaction time for starch

It was important to estimate reaction time of native starch to understand the reaction time on the extracts. The acid hydrolysis reactions were carried out on both, high amylose as well as regular corn starch. The reaction temperature was maintained at 140°C and reaction time was found using reaction kinetics.

For given intervals of time, reaction concentration and change in concentration was determined. This helped in determining reaction model of acid hydrolysis of given starch type. The reaction models have been discussed ahead.

## 9.2.1 Reaction kinetics of acid hydrolysis of regular corn starch

Sample	Initial Conc. (g/l)	Final Conc. (g/l)	% conversion	Notes
C1	2.23	1.29	57.95	1-hour reaction
C2	2.21	1.66	75.12	2-hour reaction
C3	2.22	1.81	81.38	3-hour reaction

Table 9.2 Reaction kinetics data for Regular corn starch



Figure 9.2 Reaction plot for acid hydrolysis of regular corn starch. Maxima is predicted at 2.56 hours using differential method of rate determination.

At 2.5 hours, the reaction yield was at 94% which is an acceptable reaction for acid hydrolysis reaction. The drop in concentration after certain time because of suspected formation of gluconic acid.
## 9.2.2 Reaction kinetics of acid hydrolysis on high amylose starch

Sample	Initial Conc. (g/l)	Final (g/l)	% conversion	Notes
H1	2.23	1.39	62.25	1-hour reaction
H2	2.28	1.88	82.63	2-hour reaction
H3	2.22	1.92	86.16	3-hour reaction

## Table 9.3 Reaction kinetics data for High amylose starch



Figure 9.3 Reaction plot for acid hydrolysis of high amylose starch. Maxima is predicted at 2.6 hours using differential method of rate determination.

At 2.5 hours, the reaction yield was at 91% which is an acceptable reaction for acid hydrolysis reaction. As discussed earlier, the drop in concentration after certain time because of suspected formation of gluconic acid.

## 9.3 Validation of starch in R/MTPS-g-PBAT extracts

Sample	glucose at 100% (g/L)	Actual (g/L)	% conversion	Notes
CE1	0.182	0.060	32.93	12 hour reaction
	0.182	0.062	34.03	
CE2	0.182	0.151	82.87	14 hour reaction
	0.182	0.150	82.32	
CE3	<mark>0.182</mark>	<mark>0.163</mark>	<mark>89.46</mark>	15 hour reaction
	<mark>0.182</mark>	<mark>0.165</mark>	<mark>90.56</mark>	
<mark>CE4</mark>	<mark>0.182</mark>	<mark>0.166</mark>	<mark>91.10</mark>	15 hour reaction
	<mark>0.182</mark>	<mark>0.168</mark>	<mark>92.20</mark>	

Table 9.4 Reaction completion data for RMTPS-g-PBAT extracts. 90% completion of acidhydrolysis on RMTPS-g-PBAT extracts occurred in 15 hours.

Sample	glucose at 100%	actual	% conversion	Notes
HE1	0.119	0.055	46.12	10 hour reaction
	0.119	0.058	48.63	
HE2	<mark>0.119</mark>	<mark>0.108</mark>	<mark>90.56</mark>	12 hour reaction
	<mark>0.119</mark>	<mark>0.109</mark>	<mark>91.39</mark>	
HE3	<mark>0.119</mark>	<mark>0.110</mark>	<mark>92.23</mark>	12 hour reaction
	<mark>0.119</mark>	<mark>0.109</mark>	<mark>91.39</mark>	

Table 9.5 Reaction completion data for MTPS-g-PBAT extracts. 90% completion of acidhydrolysis on MTPS-g-PBAT extracts occurred in 12 hours.



Figure 9.4 TGA of post-reaction extract of RMTPS-g-PBAT showing absence of starch



Figure 9.5 TGA of post-reaction extract of MTPS-g-PBAT showing absence of starch.

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