Synthesis of polyethylene/starch hybrids using aqueous mini emulsion polymerization

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Synthesis of Polyethylene/Starch Hybrids using Aqueous Mini Emulsion Polymerization

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May 26, 2010

A thesis submitted in partial fulfillment of the requirement for the Degree of Master in Material Science and Engineering

MASTER OF SCIENCE IN MATERIAL SCIENCE AND ENGINEERING

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Brinda B. Shah                                                              MM/DD/YY
I want to dedicate my work to my parents Mr. Bharat Shah and Mrs. Maya Shah and my brother Anand Shah, without their love and trust I would not be the person I am today. And then to my husband Mayank Mehta who has shown unconditional support so that I could achieve my goals.
ACKNOWLEDGEMENTS

The one person who is responsible for all of this and deserves all my thanks and respect is my advisor, Dr. Massoud (Matt) Miri. It is because of his care, and valuable guidance and support that I have been able to complete what I aimed for. He has been like a father to me when I was away from my home and my family during my M.S program. Being his student has taught me to be a perfectionist and far-sighted individual.

I would also like to thank my thesis committee members Dr. Changfang Ge and Mr. Larry Webb for giving me their valuable time and suggestions for improvements. I also would like to thank Dr. Richard Hailstone and Dr. Jeffery Lodge for investing their time in helping me.

I want to acknowledge all my co-workers in Dr. Miri’s research group who have been helping me throughout my thesis and supporting me when things were not in my favor. I am deeply thankful to the stockroom staff for providing me with all the necessary equipments and materials, especially on short notices.

I want to thank my family in New Jersey who have been taking care of me and supporting me in every aspect of this journey and all my friends I made here who took care of me knowing that I was a stranger.
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LIST OF ABBREVIATIONS

LDPE: Low Density Polyethylene
HDPE High Density Polyethylene
LLDPE: Linear Low Density Polyethylene
FTIR: Fourier Transform Infrared Spectroscopy
DSC: Differential Scanning Calorimetry
TGA: Thermo Gravimetric Analysis
HES: Hydroxyethyl starch
PLA: Polylactic acid
PHB: Polyhydroxy butyrate
PET: Polyethylene terephthalate
PE: Polyethylene
PS: Polystyrene
PP: Polypropylene
SDS: Sodium dodecyl sulfate
SEM: Scanning Electron Microscopy
TEM: Transmission Electron Microscopy
Sustainability regarding the most produced plastic, polyethylene, was the main motivation factor behind research of this thesis. The aim was to synthesize hybrids of polyethylene and starch in an aqueous mini emulsion polymerization process using single-site catalysts. Two types of water soluble starches were applied: potato and hydroxyethyl starch. A trifluoromethane bearing nickel enolate catalyst and a 5-halo 3-methoxy salicylaldiminate nickel pyridyl catalyst (with Cl and Br as halogen atoms) were used as polymerization catalysts, the latter two known to results in higher molecular weight polymer. The first catalyst turned to be sufficiently active with increased loads of starch and resulted in hybrids containing between 7.5 and 92.3 % starch. The salicylaldiminate catalysts only led to traces of polyethylene since the applied ethylene pressure of ca. 7.5 bar in the glass reactor was not sufficiently high to polymerize in aqueous solution. The hybrids were characterized using IR spectroscopy, TGA, density measurements, DSC, SEM and TEM. For the determination of the starch content the aqueous latex samples had to be washed with acetone to remove the surfactant (sodium dodecyl sulfate,) and co-surfactant (hexadecane). The SEM and TEM showed that the starch was uniformly distributed in the hybrids. Biodegradability tests were carried out with three different types of fungi, Aspergillus, Trichoderma, and Myrothecium for 21 days. Aspergillus turned out to be the most active in the metabolization of the starches with hydroxymethyl starch being degraded more rapidly than potato starch. The biodegraded samples were also characterized by IR, TGA, and DSC and SEM, verifying that the starch and soap were metabolized by the fungi whereas the polyethylene
was not. The crystallinity of the polyethylene was slightly increased as a result of the biodegradation.
CHAPTER 1

INTRODUCTION
1.1 Polyethylene

Polyethylene is the most produced polymer globally. It is utilized for many applications such as in packaging, electrical insulations, construction and daily consumer products. Polyethylene is a polymer consisting of long, continuous chains of ethylene or ethane (IUPAC name) as the repeating unit. The representation of polyethylene is as below in Figure 1.1:

\[ \text{CH}_2-\text{CH}_2- \]

Figure 1.1: Repeating unit of Polyethylene

Since each carbon atom is tetrahedral (sp\(^3\)), the bond angles are 109.5° approximately. The types of polyethylene mainly used are:

1. High Density Polyethylene (HDPE)
2. Low Density Polyethylene (LDPE) and
3. Linear Low Density Polyethylene (LLDPE)

HDPE is essentially linear, while LDPE and LLDPE are branched. LDPE contains a high degree of both short and long branches, while LLDPE only contains short branched of a certain length. LDPE is typically formed by radically initiated polymerization of ethylene, while LLDPE is made by copolymerization of mostly ethylene with a 1-olefin co monomer, such as 1-butene or 1-hexene, using a coordinative initiator.
The mechanical properties of these polymers depend highly on the molecular weight the branching of polyethylene, the latter having an effect on the crystallinity of the polymer. Due to low degree of branching HDPE have strong intermolecular forces and the highest tensile strength amongst the three. LLDPE has a higher tensile strength than LDPE. A representation of these polyethylenes’s explaining their branching diagrammatically is given in Figure 1.2:

Figure 1.2: Branching in Polyethylene’s

Other basic properties of these polyethylene’s are as listed below in Table 1.1:
Table 1.1: Properties of types of polyethylene’s \(^{(1)(2)(3)}\)

<table>
<thead>
<tr>
<th>Type</th>
<th>Density (g/cm(^3))</th>
<th>Melting point (°C)</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HDPE</td>
<td>≥ 0.941</td>
<td>135</td>
<td>&gt;90</td>
</tr>
<tr>
<td>LLDPE</td>
<td>0.915–0.925</td>
<td>120</td>
<td>35-60</td>
</tr>
<tr>
<td>LDPE</td>
<td>0.910–0.940</td>
<td>115</td>
<td>50-60</td>
</tr>
</tbody>
</table>

The recycling symbol of HDPE, LDPE and LLDPE are given in the Figure 1.3 below, but the symbol for LDPE includes LLDPE also:

![Recycle Symbols of HDPE, LDPE/LLDPE](image)

Figure 1.3: Recycle Symbols of HDPE, LDPE/LLDPE

The production data of polyethylene in the United States from 2004-2007 are shown in Table 1.2.
Table 1.2: Production of Polyethylene in the U.S \(^{(4)}\)

<table>
<thead>
<tr>
<th>Polyethylene</th>
<th>2004</th>
<th>2005</th>
<th>2006</th>
<th>2007</th>
</tr>
</thead>
<tbody>
<tr>
<td>Linear Low density Polyethylene (in metric tons)</td>
<td>5640</td>
<td>5395</td>
<td>5919</td>
<td>6069</td>
</tr>
<tr>
<td>High density Polyethylene (in metric tons)</td>
<td>7960</td>
<td>7328</td>
<td>7966</td>
<td>8334</td>
</tr>
<tr>
<td>Low Density Polyethylene (in metric tons)</td>
<td>3763</td>
<td>3558</td>
<td>3586</td>
<td>3628</td>
</tr>
</tbody>
</table>
1.2 Coordinative catalysts

In 1953 Karl Ziegler discovered that a combination of titanium tetrachloride and aluminum triethyl acts as a catalyst for the formation of HDPE. This catalyst represents a heterogeneous system. Such coordinative catalysts are used for the synthesis of many linear polyolefin’s, predominantly HDPE, LLDPE and polypropylene (PP). Below in Figure 1.4 the evolution of these Ziegler-Natta catalysts is described.
Figure 1.4: Major Milestone in the Evolution of Ziegler-Natta catalyst

- 1953/1954
  - K. Ziegler and G. Natta
  - TiCl₄ / AlEt₃ and γ-TiCl₃ / AlEt₂Cl

- 1960's/70's
  - Solvay, Union Carbide etc.
  - Supported Z.-N. Catalysts
  - on MgCl₂ modified with C₆H₅COOEt

- 1978
  - H. Sinn and W. Kaminsky
  - Metalloocene Catalysts = Single-Site Catalysts
    - with Methylaluminoxane = MAO

- 1985
  - W. Kaminsky, J. Ewen
  - Chiral Metalloocene Catalysts

- 1987
  - Ostoja - Starzweski (Bayer)
  - Klabunde and Ittel (Dupont)
  - Nickel catalysts for ethylene polymerizations

- 1988
  - G. Hlatky, H. Turner
  - Borane Cocatalysts
  - Eg: B(C₆F₅)₃

- 1995
  - M. Brookhart
  - Late Transition Metal Catalysts: α-Diimine Complexes of Ni and Pd
  - Eg:

[Chemical structures and formulas are displayed in the diagram.]
Metallocene catalysts represent the new generation of commercial Ziegler-Natta type catalysts. The metallocene catalysts are also the first generation of homogeneous, single-site catalysts, because they represent defined compounds rather than their predecessors, the heterogeneous Ziegler-Natta catalysts, which have multiple active sites on their crystals. Metallocenes are homogeneous catalyst because of the presence of at least one cyclopentadienyl ring them soluble in aromatic solvents. Some of the advantages of single-site catalysts over Ziegler-Natta catalysts are as follows:

- Higher productivity (kg polymer/gram catalysts)
- Better control over molecular weight distribution and polydispersity index
- Good control over co monomer incorporation and more uniform co monomer distribution
- Making more types of new polymers available such as syndiotactic polystyrene, or cycloolefinic copolymers

In Figure 1.5 a typical example of a chiral metallocene catalyst which produces isotactic polypropylene is shown.
Figure 1.5: Typical metallocene catalyst is shown, which can be used to produce isotactic polypropylene (5).

The mechanism of how these catalysts work is diagrammatically explained below in Figure 1.6. This mechanism is based on the Cossee-Arlman mechanism (6). The active species in the polymerization is the cationic alkyl-metallocene complex. The MAO co-catalyst is believed to,

i) alkylate the metallocene, forming the active complex,

ii) scavenge for impurities,

iii) stabilize the cationic center in an ion-pair interaction and

iv) possible prevent bimetallic deactivation processes from occurring.
Figure 1.6: Mechanism of metallocene based polymerization

Metallocene have one major drawback that they are highly oxophilic and generally are not stable with compounds containing electronegative atoms, such as water or polar monomers, e.g. acrylates. This drawback leads to the intense research for other Single-Site catalysts, which would be stable even in the presence of polar compounds. In Figure 1.7 three such post-metallocenes, which are based on nickel as central atom stable to polar compounds and we used in this work are shown:
Figure 1.7: Examples of Metallocenes catalysts

The first catalyst from the left is an in-situ formed catalyst, which makes low molecular polyethylene\(^7\). The 3, 5-diiodo-salicylaldiminate catalyst leads to high molecular polyethylene\(^8\). The catalyst shown on the right, bearing a chlorine in the 5-position and a methoxy-group in the 3-position, also forms higher molecular weight polymer and was synthesized recently in our group\(^9\). These catalysts are resistant to water and good candidates for aqueous emulsion polymerization. These single-site catalysts polymerize monomers in a similar manner as metallocenes. In addition, they can cause branching of polyethylene due to chain-walking. This essentially means that unlike the metallocenes these catalysts move along the polymer chain during the polymerization process and upon continued polymerization result in the formation of branches.
1.3 Polymer Blends and In-situ polymerization and Aqueous Emulsion Polymerization

There are two major methods by which blends of plastics with fillers can be produced:

(1) The polymer can be combined in a mixer or extruder, including melt interactive techniques.

(2) The polymerization can be performed in the presence of the filler.

The first method is most commonly applied. Its major advantage is that the polymer is already available and its synthesis need not be modified. The second method, also termed in-situ polymerization, has the advantage that a higher uniformity of the polymer with the filler can be achieved or reactions between the two ingredients can be performed\(^{(10)}\).

The melt interactive is a popular technique used to make composites of polyethylene and starch and however it works on a macromolecular stage. On the other hand, in-situ polymerization works out the interaction between the matrix and filler on a micro level.

In a composite the matrix has strength less than that of the filler so the matrix just transfers its stresses onto the filler.
The matrices used may be soft or rigid:

(a) Flexible matrices can be used for deformable products. When this is the case, the matrix is mainly an elastomer. It has almost nothing to do with the mechanical strength, but acts solely as a binder for the fibers.

(b) Rigid matrices form products that are not deformable, but they provide a degree of strength to the composite material, especially in the crosswise direction of the fibers.

In in-situ polymerization during the initial phase, it uses the deformability properties of a composite material with a thermosetting matrix in its unpolymerized state, while preserving its great mechanical properties obtained after polymerization.

The definition for emulsion is: "A stable colloidal suspension as milk, consisting of an immiscible liquid dispersed and held in another liquid by a substance called an emulsifier". Aqueous Emulsion Polymerization is a special type of radical polymerization with the emulsion containing water, monomer and surfactant. It is one of the most common oil-in-water emulsions in which the oil droplets (monomer) are emulsified in the continuous phase of water with surfactants.
Figure 1.8: Mini-Aqueous Emulsion Polymerization
An ultra-sonicator is used to make fine droplets in the aqueous emulsion they are at a micrometer level and below. In the Figure 1.8 above there is the water the continuous phase and the fine droplets are surrounded by the surfactant (also known as micelles) so that they do not disperse back into the water or coagulate with each other. The polymerization is taking place as shown in the zoomed droplet which contains the organic solvent and the catalyst. The product of the polymerization is latex. The latex particle size is usually 50-200nm.

Advantages of this process are listed as below:

- It is an environmentally friendly process.
- High molecular weight polymers can be made at fast polymerization rates.
- The continuous water phase is an excellent conductor of heat and allows the heat to be removed from the system, allowing many reaction methods to increase their rate.
- Since polymer molecules are contained within the particles, viscosity remains close to that of water and is not dependent on molecular weight.
- The final product can be used as is and does not generally need to be altered or processed
- This process can be operated as batch, semi-continuous or continuous process

It also has certain disadvantages:

- Surfactants and other polymerization adjuvant remain in the polymer or are difficult to remove
- For dry polymers, water removal is an energy-intensive process
- Emulsion polymerizations are usually designed to operate at high conversion of monomer to polymer. This can result in significant chain transfer to polymer.
Applications point of view of how this end-product (latex) can be used will now be discussed\(^{(11)}\).

Areas of interest in which this dispersion technology is most delivered to are as follows:

- Packaging and Paper
- Carpet
- Fabric and Fiber
- Automotive – glass producers and fabricators
- Coatings

In the packaging industry, these benefits are distributed under two categories:

1) Polyolefin performance

   - Especially suitable for pet food bags, pizza boxes, sandwich wrappers
   - Oil and grease resistance even after creasing
   - Moisture barrier
   - Ability to coat in patterns
   - Dimensional stability to coated recycled board

2) Enhanced processability

   - Compatible with most conventional processes for applying water-based coatings
   - Heat sealability to various polar and non-polar substrates
   - Laminating adhesive layer on films and foils
   - Good adhesion between paper, foil and plastic layers
   - New tie layer and primer possibilities
   - Very low heat seal initiation temperatures
- Resource reduction due to much thinner coating applications
- Higher line speeds
- Low temperature flexibility
1.4 Plastic Pollution

Mass production and consumption cycle of polyethylene lead to major problems of plastic pollution at a global level. One of the most common pollution problems is due to the disposal of plastic bags. Less than one fifth of all grades of polyethylene is recycled leading to most of the plastic ending up in the landfills. The inverted pyramid shown in Figure 1.9 explains a stepwise scenario of how lethal these bags are for the environment.

![Inverted pyramid diagram]

**Figure 1.9: Inverted pyramid**

Plastic has amazing benefits but there a major issue with its disposal. The waste of polyethylene bags also gets into other areas of the environment including the oceans. It has been called the
“most harmful trash”. The six-pack ring holder for the beverages is a relief for us, because we are able to carry six cans at a time but this ring holder when disposed into the ocean becomes a deadly noose for a fish or a bird. A sea turtle eats the plastic bag as if it would be a tasty jelly-fish but the plastic is indigestible.

Figure 1.10: Matrix of the effects by plastic bag pollution
1.5 Biodegradability

Some of the solutions to plastic pollution which have been experimented are:

(1) Landfill: It is a method by which all the waste plastic is collected and then dumped in the soil. It is a big problem because the plastic there does not degrade. It stays there on the average for around half million years. Consequentially the landfill is just filling up and it is also very difficult to find new landfill sites.

(2) Plastic litter: Plastic items individually dropped, wind borne or deliberately tipped into rivers and the sea is a huge environmental problem

(3) Burning Plastic: Incinerators are used to burn all the plastic, which emits water, particulates and green house gases. A variation at lower temperatures is the pyrolysis of plastic at medium to high temperatures. It is a big climate problem and has also been a controversial issue because of its one advantage of reducing the waste matter to 95-96% of its original volume. However, the residues of ashes which often contain toxic material represent another waste issue.

(4) Recycling: It is a three-step process. The first step involves collecting and reprocessing materials for recycling. These materials must be separated from other trash and prepared to become new products. Manufacturing of new products from recycled materials is the second step. The final step is the consumer's purchase and use of the recycled product. So recycling is one the most quoted solution to this problem. It also encouraged and well advertised but attempts at expanding this effort are less than effective. Below is the Figure 1.1 representing how much plastic has been recycling in the United States:
Thus the recycling rate is around the same for many years but the rate of production of the plastics is increasing by leaps and bounds due to the market demands. Most of the polyethylene used in commercial applications ends up in landfills or in the oceans. Thus the motivation is to make polyethylene, which is “biodegradable” and “sustainable”.

Sustainability is defined as a characteristic of a process or state that can be maintained at a certain level indefinitely. It is an effort of how to make human economic systems last longer and have less impact on ecological systems, and particularly relates to concern over major global problems relating to climate change and oil depletion. The three components essential for Sustainability are environmental, economic and social. The sustainable development is a pattern
of resources where human needs are met while preserving the environment so that it is available for future generations also. Environmental sustainability is the process of making sure current processes of interaction with the environment are pursued with the idea of keeping the environment as pristine as naturally possible. Figure 1.12 below is the sustainability diagram which explains us what we should be aiming for to make this possible.

Figure 1.12: Sustainability Diagram

Increasing demand of biodegradable polymers has strongly developed especially in the last decade because of their performance and availability. It has also driven an increased interest for sustainability development.
A material is deemed biodegradable if it undergoes degradation by biological activity under specific environmental conditions to a defined extent and within a given time. To be designated as compostable, a material has to biodegrade and disintegrate in a composting system under standard test methods. A material in order to be defined biodegradable has to fulfill the following criteria by the European Standardization Committee \(^{(14)}\):

- **Biodegradation**: over 90% compared with standard (cellulose) in 180 days under conditions of controlled composting using respirometric methods (ISO 14855)
- **Disintegration**: over 90% in 3 months (ISO FDIS 16929)
- **Ecotoxicity**: test results for aquatic and terrestrial organisms (*Daphnia magna*, worm test, germination test) as for reference compost
- **Absence of hazardous chemicals** included in the reference paragraph

For North America, similar criteria have been established under ASTM-6400-99. It is important to know the difference between the following three types of plastics \(^{(15)}\):

**Compostable plastic**: plastic capable of undergoing biological decomposition in a compost site as part of an available program, such that the plastic is not visually distinguishable and breaks down to carbon dioxide, water, inorganic compounds, and biomass, at a rate consistent with known compostable materials (e.g. cellulose) and leaves no toxic residue

**Biodegradable plastic**: plastic which will degrade from the action of naturally occurring microorganism, such as bacteria, fungi etc. over a period of time. Note, that there is no requirement for leaving "no toxic residue", and as well as no requirement for the time it needs to take to biodegrade.
Degradable plastic: plastic which will undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties. Please note that there is no requirement that the plastic has to degrade from the action of "naturally occurring microorganism" or any of the other criteria required for compostable plastics.

Polyhydroxybutyrate (PHB) is one such example of bioplastic which can rapidly biodegrade and thus is sustainable to the environment. It is produced by micro-organisms in response to physiological stresses. It is a product of carbon assimilation from starch. Some properties of PHB are as follows:

- Water insoluble and relatively resistant to hydrolytic degradation. This differentiates PHB from most other currently available biodegradable plastics, which are either water soluble or moisture sensitive
- Biocompatible and hence is suitable for medical applications
- Melting point 175°C., and glass transition temperature 15°C
- Tensile strength 40MPa, close to that of polypropylene
- Sinks in water (while polypropylene floats), facilitating its anaerobic biodegradation in sediments
- Nontoxic
Figure 1.13: Pyramid materials that are Earth environmentally friendly\(^{(16)}\)
1.6 Starch

Biodegradable polymers are made from renewable raw materials like potato, wheat, maize. Starch is organic filler that can be used in combination with a synthetic polymer to make it biodegradable \(^{(17)}\). It has received maximum attention in the preparation of biodegradable plastics. Figure 1.13 above shows that polymer/starch blends are considered because of their biodegradability very environmentally friendly \(^{(18)} \ (19) \ (20) \ (21) \ (22) \ (23) \ (24) \ (25)\). Starch basically contains large and long chains of the monosaccharide glucose. The two types of main molecules that are always present in starch irrespective of its source are the amylose and amylopectin. The amylose usually present is 25-20\% in amount and the amylopectin in 75-80\%.

![Figure 1.14: Structure of Amylose\(^{(26)}\)](image)
Figure 1.15: Structure of Amylopectin\textsuperscript{(26)}

Starch is cheap, readily available in abundance and considered a renewable resource. Thus it proves a very useful raw material in the concept, because its presence in the plastic implies less use of synthetic polymer made from oil. The two types of starch used for the biodegradable polymer in this are potato starch and hydroxyethyl starch. Plastics made from potato starch are a promising material for the packaging industry and as is one of the well known materials for producing biodegradable polymers. Hydroxyethyl starch (HES/HAES) is a nonionic starch derivative.
The potato starch is hydrophilic while hydroxyethyl starch is hydrophobic for the water. Starch based biodegradable plastics can have starch content ranging from 10% to 90%. The starch content needs to exceed 60% for the plastic to significantly start breaking down. Biodegradation of starch based polymers is a result of enzymatic attack at the glucosidic linkages between the sugar groups leading to a reduction in chain length and the splitting off of sugar units (monosaccharide, disaccharides and oligosaccharides) that are readily utilized in biochemical pathways. At lower starch contents (less than 60%) the starch particles act as weak links in the plastic matrix and are sites for biological attack. This allows the polymer matrix to disintegrate into small fragments, but not for the entire polymer structure to actually bio-degrade.
1.7 Biodegradable polymers

Biodegradable polymers have gained tremendous popularity in recent years. Researchers have very high expectations from these “green plastics” to perform their intended function as bags, packages or film barriers within a reasonable timeframe, essentially disappear in the form of environmentally acceptable degradation products and that they will replace the synthetically produced petroleum based plastics. There are three types of polymers which material scientists are currently focusing on (28):

I. Conventional plastics (Class I) which do not biodegrade because microorganisms in the soil are not able to penetrate their smooth surfaces. These usually have an impenetrable petroleum based matrix

II. The Class II would be a partially degradable polymer where the natural fibers would be surrounding the conventional matrix described above. The goal is that this class would biodegrade at a rapid rate than the conventional class. The micro-organisms will be able to digest the natural fiber polymer leaving a weak residue of polymer with rough and open edges

III. Class III stands for the polymer which will be completely biodegradable because the polymer matrix is composed from natural sources. Micro-organisms can completely feed on these polymers and eventually just leave carbon-dioxide and water as by-products.
The examples of conventional plastics are polyethylene, polypropylene, polystyrene etc. Plastics belonging to second class are thermoplastic starch blends and example for class three would be Polylactic acid (PLA) and PHB.

Polyethylene is widely used for packaging applications and recognized for its resistance to biodegradation. Starch is known to be used as a filler to increase biodegradation rate of synthetic polymers and starch can be biodegraded by micro-organisms such as bacteria and fungi. Starch interacts well with water and degrades by hydrolysis. Hence the blends of polyethylene and starch are quite researched on. These blends would belong to Class II and their advantage over Class III is that these polymers have lower melting temperature which highly limits their applications in various fields.

Nonetheless, PLA belonging to class three faces hurdles, including its high density (1.25 g/cc) relative to PP (0.946 g/cc) and PS (1.05 g/cc). It also has high polarity, making it difficult to adhere without tie-layers to non-polar PE and PP in multi-layer structures. Add to that poorer heat resistance than PET and limited barrier against moisture and gases. But the greatest stumbling block is PLA’s cost, currently an average of $1.30/lb versus $0.5/lb of polyethylene. PLA has not been able to replace polyethylene in the packaging industry. Both PLA and PHB being wholly biodegradable are considered as synthetic polymers.

It is ludicrous to expect them to fully replace the conventional polymer anytime soon but they do have a very positive, mainly because of the benefit that they come from the renewable resources.
Table 1.3: Origin, degradability and properties of some plastic film products (29)

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Polyethylene</th>
<th>Poly (ε-caprolactum)</th>
<th>Polylactic acid</th>
<th>Polyethylene/Starch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic (Non-renewable monomer feedstock)</td>
<td>X</td>
<td>X</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Synthetic (Renewable monomer feedstock)</td>
<td></td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Natural (obtained from plants)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Natural (by fermentation of renewable monomer feedstock)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nondegradable</td>
<td>X</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Degradable/Not compostable</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Degradable/Compostable</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Favorable film properties (strength, melting temperatures, water resistance)</td>
<td>X</td>
<td></td>
<td>X</td>
<td>X</td>
</tr>
</tbody>
</table>
INITIAL RESEARCH PLAN AND PROBLEM SETTING

We set as our primary objective to synthesize polyethylene via catalysis by an environmentally friendly process and to make the polymer biodegradable at the same time. The polymerization process was to become more environmentally friendly by using water as solvent and performing an aqueous mini emulsion polymerization. To achieve the latter we planned to perform the polymerization in the presence of starch as biomass filler. That is the polymerizations were to be performed in-situ rather than blending the starch with polyethylene. We therefore have used the term hybrids rather than blends produced by the presented in-situ process.

We selected two types of starch, potato starch and hydroxyethyl starch. The potato starch is soluble in water at 60°C thus making it hydrophilic to water. Though hydroxyethyl starch possesses –OR group, it is also hydrophilic. We assume that because of this hydrophilic character there may be better formation of the starch/polyethylene hybrids. In addition we were hoping from some synergy in terms of the biodegradability of the polyethylene because of its assumed smaller particle size.

Typically after drying the latex the solid polymers were to be characterized primarily by IR, DSC, TGA, SEM and TEM. In addition for SEM and TEM films were to be pressed. The dried polymers were to be submitted for biodegradability studies by exposing them to a series of fungi. The formation of spores and deterioration of the films was to be monitored over time.
CHAPTER 2

EXPERIMENTAL
2.1 Apparatus Preparations

All the apparatus and the procedures of any experimental work are done under argon. Argon is an inert gas used, which replaces all the air present in any chemical, reagent or experimental apparatus. Typically three vacuum/argon cycles are done on each flask or reactor to remove most of the air. For more sensitive materials the containers are also heated to about 70°C. This vacuum and argon is supplied from a dual manifold. The inert gas argon is about 99.9% pure while the vacuum comes from the high vacuum pump. The oil bubbler acts as a vent for the argon and the cold nitrogen trap helps from contamination of the vacuum pump. This manifold is very important to do any work which requires absolutely no air in the system and the materials used. The representation of this manifold is shown in Figure 2.1. Schlenk lines are attached to the double-oblique stopcocks which allow choosing between vacuum and argon.
Figure 2.1: Schlenk System for working under no-air (inert) atmosphere
2.2 Reagent Preparations

All chemicals were obtained from Sigma Aldrich, except for the TMEDA NiMe\textsubscript{2} which was purchased from MCAT GmbH, Germany. The reagents and solvents had to be deoxygenated before use in the polymerization system. The water was degassed and distilled under argon. Toluene and diethyl ether were dried over sodium/benzophenone, in the case of latter solvent with the addition of tetraglyme and then distilled. The distillation of toluene with a still is shown in Figure 2.2. Anhydrous hexadecane and pyridine were degassed several times. The Celite was dried overnight at 240\textdegree C under a vacuum of ca. 200mtorr. The TMEDA and catalysts were stored in a glove box (M Braun Unilab) and stored at -35\textdegree C.
Figure 2.2: Toluene Distillation in laboratory\textsuperscript{(30)}

Many transfers required use of a needle/cannula. A similar representation to show the needle transfer is given in the Figure 2.3.
Synthesis of the CF3-bearing Nickel Enolate Catalyst

**Catalyst 1**

The synthesis of the CF3 bearing nickel enolate catalyst was performed after a procedure given in the literature reference$^{(32)}$. The ligand was synthesized according to a procedure another reference.
Synthesis of the 5-Chloro-3-Methoxy Catalyst

Catalyst 2

5-chloro-2-hydroxy-3-methoxy salicylaldiminate nickel dimethyl pyridine catalyst. The synthesis procedure is given in detail in Nikhil Kolhatkar’s M.S thesis (9). I also prepared the Schiff base ligand and the catalyst for the polymerizations in this work according to the procedure.

Step 1: Making of the Schiff-base ligand

Figure 2.5: Synthesis of Salicylaldiminate ligand, (A) 5-chloro-2-hydroxy-3-methoxy benzaldehyde, (B) 2,6-diisopropylaniline, (C) salicyl ligand

Step 2: Formation of Salicylaldiminate catalyst
In a similar manner also a 5-bromo analog catalyst was produced. Further details on this are given elsewhere \(^9\).

Potato starch dissolved in water

The potato starch was dissolved in distilled and degassed water. In a 250ml 3-neck round bottom flask the water was transferred into the flask with needle transfer method and the required amount to potato starch was mixed into it. The apparatus was heated up to 60°C and stirring for 12 hours. Most of the potato starch would dissolve in water.
2.3 Polymerization Procedure

![Polymerization Apparatus Diagram]

**Figure 2.7: Schematic of the polymerization apparatus (The Buchi Reactor)**

All the aqueous emulsion polymerizations are done in the reactor shown above in the Figure 2.7.

The reactor is cleaned thoroughly prior to usage so that there is no contamination with ingredients from previous runs. There are three solvents used for the cleaning and the reactor is filled up to the brim:

- Concentrated hydrochloric acid and water in the ratio of 25:75 for 15min
- Distilled water for 10min
- Methanol for 10min
The bath is turned on and the reactor is set to 70°C so that all the solvent evaporates. Then vacuum-argon cycles are done on the reactor. The reactor temperature for polymerization is then kept at 60°C. About 150ml ml of the prepared solution of potato starch was added to the reactor. A 500ml 3-neck Schlenk flask is filled with argon. Around 185 ml of water followed by 6.06gms sodium dodecyl sulfate and 7.875ml of hexadecane is added in the 500ml 3-neck flask. The mixture is kept in a water bath stirring at 60°C for half an hour. The mixture is sonicated with an ultra sound sonicator for 2 min at amplitude of 90%. The sonicator produces the micelles in the water solution. The solution froths in excess because of the soap. The solution is then transferred into the reactor. It is stirred at 800 rpm for even heat transfer in the solution. Around fifty milligrams of the catalyst is transferred from the glove box in a 100 ml Schlenk flask and 10ml of toluene is added to the catalyst, for example in case of the CF₃-nickel enolate the solution of 63 mg Ni(COD)₂ and 41 mg ligand was added, with stirring for 10-15 min. After the catalyst has dissolved in the toluene it is transferred to the reactor and then the ethylene flow is started which initiates the polymerization. The temperature and the ethylene consumption versus time are monitored by a computer program LabView Measurements. The polymerization was run typically for an hour and then ethylene flow is stopped. The reactor is cooled down and the ethylene pressure is released from the reactor. About 10ml of methanol is added to quench the product; the polymer latex is then transferred into a brown bottle and refrigerated.
Modified procedure for polymerization with hydroxyethyl starch:

The bath is turned on and the reactor is set to 70°C so that all the solvent evaporates. Then vacuum-argon cycles are done on the reactor. The reactor temperature for polymerization is then kept at 60°C. A 500ml 3-neck Schlenk flask is filled with argon. Around 185 ml of water followed by 4.04gms sodium dodecyl sulfate and 5.25ml of hexadecane is added in the 500ml 3-neck flask. The mixture is kept in a water bath stirring at 60°C for half an hour. At the end of 25th minute, around 1-6 grams depending on the requirement is added as a solid powder to the above stirring solution and after additional 5 minutes this solution is sonicated into the reactor. Around fifty milligrams of the catalyst is transferred from the glove box in a 100 ml Schlenk flask and 10ml of toluene is added to the catalyst, for example in case of 5-chloro-3-methoxy it is 50 milligrams and there is no ligand for this catalyst with stirring for 10-15 min. After the catalyst has dissolved in the toluene it is transferred to the reactor and then the ethylene flow is started which initiates the polymerization. The temperature and the ethylene consumption versus time are monitored by a computer program Lab view Measurements. The polymerization was run typically for an hour and then ethylene flow is stopped. The reactor is cooled down and the ethylene pressure is released from the reactor. About 10ml of methanol is added to quench the product; the polymer latex is then transferred into a brown bottle and refrigerated.
2.4 Characterizations

To use polymer powder for most of the characterization a part of the latex proportions is dried at about 50°C in the oven for two days.

I. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR is a chemically specific analysis technique which identifies chemicals, compounds and substituent groups. The samples were polymer powders. The spectra were recorded using a FTIR Biorad Series FTS 3000. The wavelength range in which the IR was recorded was 4000-400 cm\(^{-1}\). The numbers of scans were 16-30 and the resolution was 4-2 cm\(^{-1}\).

II. Differential Scanning Calorimetry (DSC)

DSC is a very useful tool from the point of view of studying phase transitions for polymers. The DSC curve can be used to determine melting point, crystallization temperature, glass transition temperature, melting enthalpy and crystallization enthalpy. It will tell you about how crystalline or amorphous the sample is. The model used is the TA Instrument model DSC 2010 to analyze all the samples.

About 5-15m of sample was weighed out in a hermetic aluminum pan bottom and closed with seal on the top and they were pressed together. The sample or the reference pan is also made in the same exact way but there is no sample in the pan.
They are both placed in the furnace of the DSC chamber. The liquid nitrogen flow maintained in the machine is about 25 ml/min. The procedure for the DSC runs is as mentioned below:

1. Ramp 20.00 °C/min to 180 °C
2. Isothermal for 1.00 min
3. Mark end of cycle 1
4. Ramp 20.00 °C/min to 20 °C
5. Isothermal for 1.00 min
6. Mark of end cycle 2
7. Ramp 20.00 °C/min to 180 °C
8. Mark end of cycle 3

III. Thermo Gravimetric Analysis (TGA)

TGA is used to determine weight percent change of the sample with increasing temperature and provides information about composition analysis and thermal stability. The model used is TA Instrument model TGA 2050. A platinum pan is used for the all polymer samples because of its high melting temperature. About 15-20mg of sample is in the platinum pan. The sample is powdered form and not films. The procedure is as follow:

- Select nitrogen gas
- Ramp from 10.00 °C/min to 900°C
- Isothermal for 2min
The nitrogen gas flow rate is about 90-115 cm$^3$/min.

IV. Pressing of the films

Films were pressed and it was found that they started burning when they were pressed. Films were pressed from the following materials to determine which material is volatile to burn out: Starch and SDS. They both did not burn individually so they were ruled out and then the only ingredient left was hexadecane. The dried polymer was put in a small reactor and vacuum was pulled on it overnight heating the reactor to 60°C. The films pressed after the removal of hexadecane did not burn.

To prepare films a Carver Laboratory Press Model M was used. About 2 g of dried polymer were piled up on a one square inch area and sandwiched between aluminum foils. The polymer was placed into the press, which had been heated to ca. 120°C, which is about the melting point of the polymer. The sample was pressed initially at 1000 psi for 2 min and at 40,000 psi for ca. 10 minutes. The sample was then cooled under running water. The films obtained are very fragile.

V. Density Gradient Measurement

Density gradient measurement has advantages like simplicity of equipment, reduced time of analysis and accuracy in readings when the particles have a small difference in their
density. The column was made using two solutions: (1) ethyl acetate ($\rho = 1.594 \text{ kg/m}^3$) and (2) carbon tetrachloride ($\rho = 0.894 \text{ kg/m}^3$) with a density difference of 0.7. As the process of diffusion is slow and gradual; solutions were mixed before hand and then added to form a concentration gradient. The equipment was calibrated using polymers of given densities, like polystyrene, polymethyl methacrylate and high density polyethylene. Densities of both polymer powders and films were determined using a correlation graph of density versus milliliters of cylinder for accuracy of up to two decimal places.

VI. Scanning Electron Microscopy (SEM)

SEM is a microscope where the sample is targeted with beam of high-energy (5 to 40 keV) electrons and the sample is scanned. These electrons interact with the atoms of the sample and they develop a scanned pattern in which the topography, electrical conductivity, composition, morphology and crystallographic information can be determined. The types of particles emitted from the specimen are secondary electrons, back scattered electrons (BSE), characteristic x-rays, light (cathodoluminescence), specimen current and transmitted electrons. It needs a special type of detector for all these particles, which is not incorporated in one machine. For the work reported here only the secondary electrons were used to form the image. One can identify particle size down to 1-5nm as it can provide that good a resolution. Magnification over 6 orders of magnitude ranging from x25 – x25000 can be achieved. The sample if it is non-conductive metal has to be coated with Au-Pd.
VII. Transmission Electron Microscopy (TEM)

TEM is a microscope where the sample is targeted with electron beam (100 keV or greater) where the electrons are transmitted through the sample to form an image. The image formed from the interaction of electrons with the specimen is magnified and focused on an imaging device. It is capable of higher spatial resolution than the SEM, but does not require especially thin films (< 100 nm). It is also useful in chemical identity, crystal structure, crystal orientation and many others. The sample image cannot have a 3-D appearance because TEM’s do not have large depth-of-field like SEM’s. The other methods for sample preparations include chemical etching, mechanical milling, ion etching and others.

TEM was done on the polymer samples in the latex form. It helped in determining the particle sizes of the polyethylene and the starch. Staining was also tried with TEM but the agent was so strong than it dissolved the copper grid.

VIII. Biodegradablility studies

To study whether polyethylene-starch composites biodegradability tests were done on the films containing different starch percentages. The test was done in a Petri- dish with solid plating media and three fungal strains were used. All these strains were stored as spore suspensions and they were harvested in the laboratory itself. Their names are as follows:

- Aspergillus
- Trichoderma
Myrothecium

A carbonless agar medium is prepared which is applied to the composite films. The pH of this medium is 5.5. This medium lacks the carbon on which the fungal strains could feed themselves and they do not even possess any ability for agarolytic activity. Everything utilized in the experiment is disinfected and the experiments are carried out in a Biogard Safety hood to avoid contamination with any other bacteria or fungi. The films are pre-weighed and then applied to the agar medium by gently tapping them into the agar as they are fragile. The films are then inoculated with 0.1 ml of a spore suspension. The inoculation is done at room temperature for 25-40 days period in an incubator during which they are monitored and photos are taken at various time intervals with a dissecting microscope with camera attachment. The films with the fungi are also observed under SEM to find holes in the films indicating starch consumption by fungi.

Tests are also done on these films using mycelia biomass. The mycelia are large inter twined strands of Asperigillus. They are larger than the spores and are expected to consume more starch from the films than the above experiment. The films are inoculated with the mycelliums for about a period of 28 days at 27°C and are monitored at various time intervals.

Mechanism of Biodegradability:

The biodegradability of starch stems mainly from the oxygen atoms connecting successive ring structures, and the oxygen atom within each ring. Starch interacts strongly with water and degrades by hydrolysis. Microbes consume starch and this leads to porosity and formation of voids in the plastic, leading to an increase in the surface area and permeability of the
polyethylene matrix, and provides susceptible groups for its biodegradation. When added in low amounts (6-15%) starch remains isolated in the matrix and is not susceptible to the microbes for degradation. When it is added larger amounts (>40%) rapid and complete biodegradation occurs.
CHAPTER 3

RESULTS AND DISCUSSION
### 3.1 Polymerizations

#### Table 3.1: Polymerization Data

<table>
<thead>
<tr>
<th>Run #</th>
<th>Catalyst(^a)</th>
<th>Ligand or Type of Biomass</th>
<th>Amount of Biomass (g)</th>
<th>Calculated Starch % (kg PE/mol. Catalyst/hr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CF(_3)-Ni(COD(_2))</td>
<td>Soluble potato starch</td>
<td>1.35</td>
<td>14.70</td>
</tr>
<tr>
<td>2</td>
<td>5-Cl,3-CH(_3)O</td>
<td>Soluble potato starch</td>
<td>1.00</td>
<td>≥ 99.00</td>
</tr>
<tr>
<td>3</td>
<td>3,5-I(_2)</td>
<td>Soluble potato starch</td>
<td>1.00</td>
<td>≥ 99.00</td>
</tr>
<tr>
<td>4</td>
<td>5-Cl,3-CH(_3)O</td>
<td>Soluble potato starch</td>
<td>1.10</td>
<td>≥ 99.00</td>
</tr>
<tr>
<td>5</td>
<td>CF(_3)-Ni(COD(_2))</td>
<td>Hydroxyethyl starch</td>
<td>0.50</td>
<td>7.50</td>
</tr>
<tr>
<td>6</td>
<td>CF(_3)-Ni(COD(_2))</td>
<td>Hydroxyethyl starch</td>
<td>2.00</td>
<td>15.70</td>
</tr>
<tr>
<td>7</td>
<td>CF(_3)-Ni(COD(_2))</td>
<td>Hydroxyethyl starch</td>
<td>2.00</td>
<td>13.90</td>
</tr>
<tr>
<td>8</td>
<td>CF(_3)-Ni(COD(_2))</td>
<td>Hydroxyethyl starch</td>
<td>4.00</td>
<td>83.50</td>
</tr>
<tr>
<td>9</td>
<td>CF(_3)-Ni(COD(_2))</td>
<td>Hydroxyethyl starch</td>
<td>4.00</td>
<td>76.30</td>
</tr>
<tr>
<td>10</td>
<td>CF(_3)-Ni(COD(_2))</td>
<td>Hydroxyethyl starch</td>
<td>6.00</td>
<td>92.30</td>
</tr>
<tr>
<td>11</td>
<td>CF(_3)-Ni(COD(_2))</td>
<td>Hydroxyethyl starch</td>
<td>6.00</td>
<td>85.90</td>
</tr>
<tr>
<td>12</td>
<td>5-Cl,3-CH(_3)O</td>
<td>Hydroxyethyl starch</td>
<td>2.00</td>
<td>≥ 99.00</td>
</tr>
<tr>
<td>13</td>
<td>5-Br,3-CH(_3)O</td>
<td>Hydroxyethyl starch</td>
<td>1.00</td>
<td>≥ 99.00</td>
</tr>
<tr>
<td>14</td>
<td>5-Br,3-CH(_3)O</td>
<td>Hydroxyethyl starch</td>
<td>2.00</td>
<td>≥ 99.00</td>
</tr>
</tbody>
</table>

---

\(^1\): Total volume: runs 1-4 300 ml, runs 5 – 19: 200ml, Temperature: 60°C; Stirring speed: runs 1-4 600rpm, runs 5-19 1000rpm, Reactor pressure: runs 1-6: 5.5 bar, runs 7-19: 7.6 bar., Run time: 60 min, except for runs 2-4.

\(^a\): CF\(_3\)-Ni(COD\(_2\)) represents the CF\(_3\) bearing nickel enolate catalyst formed in situ, 5-Cl, 3-CH\(_3\)O the 5-chloro-3-methoxy salicyl aldiminate nickel pyridine catalyst, and 5-Br, 3-CH\(_3\)O the bromo analog catalyst, 3,5-Diiodo represents the 3,5-Diiodo salicyl aldiminate nickel pyridine catalyst, the latter produced originally by Mecking et. al.\(^8\)

\(^b\): in case of the in-situ formed catalyst from CF\(_3\)-Ligand and Ni(COD\(_2\)) the catalyst amount is based the ligand as the limiting reagent.
In the above Table 3.1, the percentage starch is based on the portion of starch in the hybrid (not including soap) and it is the average percentage starch obtained from TGA and density gradient measurement analysis.

The nickel enolate bearing the trifluoromethyl-group produces a lower molecular weight polymer \(^{(7)}\). From starch free-emulsion polymerizations we could determine that \(M_w = 6000\) g/mol, \(M_n = 5000\) g/mol, and the polydispersity is narrow with \(1.09\). In contrast the salicylaldiminate \(^{(34)}\) nickel pyridyl methyl produces are known to higher molecular, branched polyethylene \(^{(9)}\). Initially we believed to be able to produce also hybrids with reasonable amounts of polyethylene using the salicylaldiminate catalysts, since the polymer could be easily detected by DSC, IR and TGA (shown in the subsequent sections). However, only traces of polyethylene could be obtained with the salicylaldiminate catalysts in these runs. We explain this by the relatively low amount of ethylene dissolved in the aqueous solution at the low pressures we had to apply using glass vessel reactors.

The yield of the product contains polyethylene, starch and the surfactant and some of the co-surfactant, but the activity should be referred on the amount of the synthetic polymer, which we obtained from TGA and other methods described further below under characterization. The calculation of how the activity is calculated is based on the formula below:

\[
\text{Activity (kg/mol. Catalyst/hr)} = \frac{\text{Amount of polymer}}{\text{Amount of catalyst used x time}}
\]
The amount of polymer in the formula above is based on the amount of starch in the final product. All the polymerization data in the Table 3.1, has been calculated based on the experimental data.
3.2 Measurement Errors and Solutions

As the reaction contains several components (polyethylene, starch, surfactant and co surfactant), determination of the hybrids’ masses and their composition is complex and requires washing of the samples with acetone to remove the SDS and hexadecane. The obtained results for the starch contents have an error of about 10%. These errors are mainly due that some of the starch was lost during the transfer into the reactor.

The most reliable method to determine the starch content required washing of the latex with acetone, which caused removal of most of the soap and hexadecane. We based the starch content on the TGA, IR and density gradient methods that were obtained from these acetone washed samples. The composition of the samples was determined from the mass losses assigned to the starch and polyethylene in the TGA, and secondly by density gradient measurements. They could be further verified to correlation with the ratio of starch/polyethylene from IR spectroscopy.
### 3.3 Activities

Activities of the polymerization runs are depended on the amount of the polymer included in them.

**Figure 3.1:** Activity versus biomass (Hydroxyethyl starch) content for CF$_3$-Ni(COD)$_2$ catalyst
Hydroxyethyl starch was used for most of the runs as the initial biodegradability tests between soluble potato starch and hydroxyethyl starch favored towards the hydroxyethyl starch. It is more readily consumed by the fungi than the soluble potato starch.

As indicated in Figure 3.1 the activity decreases as the starch percentage increases in polymerizations with the CF$_3$-Ni(COD)$_2$ catalyst.
3.4 Characterization and Biodegradability tests

1. Results on the Fourier Transform Infrared Spectroscopy (FTIR)

The simplest polymer structure would be a chain of methylene units terminated on each end by methyl groups. This is the structure of polyethylene, or PE. Since the polymer is composed almost completely of methylene groups, its infrared spectrum would be expected to consist solely of methylene stretches and bends. Four sharp peaks dominate the spectrum: The methylene stretches at 2,920 and 2,850 cm$^{-1}$ and the methylene deformations at 1,464 and 719 cm$^{-1}$. Due to the crystallinity of polyethylene, the 1,464 and 719 cm$^{-1}$ peak is split, and additional peaks are seen at 1,473 and 731 cm$^{-1}$. LDPE is about 50% crystalline. The crystallinity of a polyethylene sample can be determined from the ratio of the 731 to 719 cm$^{-1}$. 
Figure 3.2: FTIR spectrum of pure polyethylene without starch made by aqueous emulsion polymerization with CF$_3$-Ni(COD)$_2$ catalyst

As seen in the Figure 3.2, the spectrum has all the peaks of LDPE both methylene stretching and deformations marked with arrows. Near the finger print region all the other major peaks belong to the surfactant sodium dodecyl sulfate (SDS), whose spectrum is also shown below in Figure 3.4.

The spectrum of hexadecane, which was used as co surfactant, is quite similar to that of polyethylene, as shown in Figure 3.3. However, hexadecane has sharp side peak at about 2950 cm$^{-1}$, not present in polyethylene. We used DSC diagrams described further below to clearly show that even in the hybrids made with the salicyl aldimate catalyst traces of polyethylene are present.
Figure 3.3: FTIR spectrum of pure hexadecane

Figure 3.4: FTIR spectrum of SDS
The Figure 3.4 above is the spectrum of sodium dodecyl sulfate (SDS). It exhibits a sharp peak between 1250 cm$^{-1}$ and 1200 cm$^{-1}$.

The spectrum of hydroxyethyl starch is also shown in the Figure3.5 below. Starch usually exhibits a sharp peak between 1100 cm$^{-1}$ and 960 cm$^{-1}$. And they also have a large broad band of hydroxyl group in the ranges 3600 cm$^{-1}$ – 3000 cm$^{-1}$.

![FTIR spectrum of hydroxyethyl starch](image)

**Figure 3.5: FTIR spectrum of hydroxyethyl starch**

As shown in Figure 3.5 the peak at ca. 1000 cm$^{-1}$ is narrower than the broad peak above 3000 cm$^{-1}$. 
When the above spectrums are combined, we get a spectrum we should get for is the polyethylene/starch composite which is indeed the case. In Figure 3.6 below you will see the spectrum for polyethylene/starch composite, which includes all the major peaks belonging to polyethylene, SDS and hydroxyethyl starch.

![Figure 3.6: FTIR of polyethylene/starch composite (Run #8 in Table3.1, unwashed)](image)

Figure 3.6: FTIR of polyethylene/starch composite (Run #8 in Table3.1, unwashed)

In Figure 3.7 the same sample is shown after washing with acetone and then dried.
Figure 3.7: FTIR of polyethylene/starch composite (Run #8) in Table 3.1 (acetone washed)

It is apparent from the IR spectrum in Figure 3.7 that the peak at about 1200 cm\(^{-1}\), which was characteristic peak of the soap, is now not present, however, the peaks characteristic for starch and polyethylene can be well detected.

The starch/polyethylene ratio was determined using the FTIR spectrum of each sample. Below in Table 3.2 the data has been displayed:
Table 3.2: Starch/Polyethylene ratio by FTIR spectrums

<table>
<thead>
<tr>
<th>Run #</th>
<th>Catalyst</th>
<th>Amount Ligand or Catalyst (mg)</th>
<th>Type of Biomass</th>
<th>Starch/polyethylene ratio based on IR peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>CF$_3$-Ni(COD)$_2$</td>
<td>45.8</td>
<td>Soluble potato starch</td>
<td>0.4</td>
</tr>
<tr>
<td>2</td>
<td>5-Cl,3-CH$_3$O</td>
<td>50.0</td>
<td>Soluble potato starch</td>
<td>1.44</td>
</tr>
<tr>
<td>3</td>
<td>3,5-I$_2$</td>
<td>38.5</td>
<td>Soluble potato starch</td>
<td>1.68</td>
</tr>
<tr>
<td>4</td>
<td>5-Cl,3-CH$_3$O</td>
<td>21.2</td>
<td>Soluble potato starch</td>
<td>1.34</td>
</tr>
<tr>
<td>5</td>
<td>CF$_3$-Ni(COD)$_2$</td>
<td>31.8</td>
<td>Hydroxyethyl starch</td>
<td>0.1</td>
</tr>
<tr>
<td>6</td>
<td>CF$_3$-Ni(COD)$_2$</td>
<td>61.0</td>
<td>Hydroxyethyl starch</td>
<td>0.4</td>
</tr>
<tr>
<td>7</td>
<td>CF$_3$-Ni(COD)$_2$</td>
<td>45.4</td>
<td>Hydroxyethyl starch</td>
<td>1.2</td>
</tr>
<tr>
<td>8</td>
<td>CF$_3$-Ni(COD)$_2$</td>
<td>41.0</td>
<td>Hydroxyethyl starch</td>
<td>5.0</td>
</tr>
<tr>
<td>9</td>
<td>CF$_3$-Ni(COD)$_2$</td>
<td>43.0</td>
<td>Hydroxyethyl starch</td>
<td>2.7</td>
</tr>
<tr>
<td>10</td>
<td>CF$_3$-Ni(COD)$_2$</td>
<td>41.0</td>
<td>Hydroxyethyl starch</td>
<td>7.4</td>
</tr>
<tr>
<td>11</td>
<td>CF$_3$-Ni(COD)$_2$</td>
<td>44.0</td>
<td>Hydroxyethyl starch</td>
<td>4.3</td>
</tr>
<tr>
<td>12</td>
<td>5-Cl,3-CH$_3$O</td>
<td>51.2</td>
<td>Hydroxyethyl starch</td>
<td>1.81</td>
</tr>
<tr>
<td>13</td>
<td>5-Br,3-CH$_3$O</td>
<td>51.9</td>
<td>Hydroxyethyl starch</td>
<td>1.68</td>
</tr>
<tr>
<td>14</td>
<td>5-Br,3-CH$_3$O</td>
<td>48.0</td>
<td>Hydroxyethyl starch</td>
<td>1.64</td>
</tr>
</tbody>
</table>

The values of the ratios (starch/polyethylene) in the fifth column of the Table 3.2 were later inserted in the correlation of Figure 3.16 to obtain percentage starch values by the method of Fourier Transform Infrared Spectroscopy. The samples pressed as films were subjected to biodegradation and showed a considerable loss in starch and SDS. This is proved by FTIR of samples in Figure 3.8 and Figure 3.9. In the Figure 3.9, most of the major peaks indicating starch and soap, at 1000 cm$^{-1}$ and 1200 cm$^{-1}$, respectively, have disappeared. All the starch filled hybrids exhibit the hydroxyl bulge but hydroxyl group bulge in the range 3600 cm$^{-1}$ – 3000 cm$^{-1}$.
in Figure 3.9 has increased because the biodegradative attack of fungi reducing the polymer to carbon-dioxide and water.

Figure 3.8: FTIR of Run #8 of Table 3.1 before biodegradation tests
Figure 3.9: FTIR of the sample of Run #8 after biodegradation tests

In the Table 3.3 below the percentage transmission for the biodegraded samples has been displayed with samples that had not been washed with acetone and therefore still contained soap. We did not wash those samples because for a potential commercialization it would be more economical not to add the washing step and because the soap would not have caused an issue in applications or biodegradation.
Table 3.3: Percentage transmission of samples from selected runs

<table>
<thead>
<tr>
<th>Run #</th>
<th>% Transmission before biodegradation test for starch</th>
<th>% Transmission after biodegradation test for starch</th>
<th>% Transmission before biodegradation test for soap</th>
<th>% Transmission after biodegradation test for soap</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>1.3</td>
<td>0.8</td>
<td>1.9</td>
<td>0</td>
</tr>
<tr>
<td>6</td>
<td>7.7</td>
<td>0.5</td>
<td>13.1</td>
<td>0.4</td>
</tr>
<tr>
<td>8</td>
<td>13.2</td>
<td>9.2</td>
<td>12.4</td>
<td>2.1</td>
</tr>
</tbody>
</table>

It is observed from the Table 3.3 that the transmission values for both starch and soap have decreased because the microorganisms digested both starch and soap.

Figure 3.10: IR-spectrum of a sample made with a salicyl aldiminate catalyst (Run #2)
The IR spectrum shown in Figure 3.10 is from a sample of a run made with the 5-chloro-3-methoxy salicyl aldiminate nickel pyridine catalyst. The latex had been dried for a day in the hood. The peaks around 2900 cm\(^{-1}\) and between 1400 and 1300 cm\(^{-1}\) resemble those of polyethylene. However, they are actually caused by remaining SDS and hexadecane in the sample, which as shown from the previous IR spectra in this section have very similar peaks. As the subsequent methods more clearly indicate this sample only contains traces (less than 1\%) polyethylene.
2. Results on the Thermo Gravimetric Analysis (TGA)

TGA is another important type of thermal analysis for polyethylene/starch hybrids as it would reveal the actual amount of starch in the hybrids. In Table 3.4 only the TGAs of the acetone washed starch/polyethylene samples have been included. A figure of the TGA of an unwashed polyethylene sample and the TGA of a hybrid made with the salicyl aldiminate type catalyst has been included further below.

Table 3.4: TGA Calculations

<table>
<thead>
<tr>
<th>Run #</th>
<th>Amount of Biomass (g)</th>
<th>% Starch assumed in blend</th>
<th>% Starch calculated in blend</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.35</td>
<td>8.11</td>
<td>13.79</td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>3.41</td>
<td>8.71</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>21.40</td>
<td>15.17</td>
</tr>
<tr>
<td>7</td>
<td>2</td>
<td>28.20</td>
<td>13.99</td>
</tr>
<tr>
<td>8</td>
<td>4</td>
<td>74.07</td>
<td>85.78</td>
</tr>
<tr>
<td>9</td>
<td>4</td>
<td>73.53</td>
<td>74.75</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>76.53</td>
<td>92.27</td>
</tr>
<tr>
<td>11</td>
<td>6</td>
<td>81.34</td>
<td>92.56</td>
</tr>
</tbody>
</table>

The word assumed in the third column of the Table 3.4 represents the theoretically calculated percentage starch with no loss considered for the amount of starch in the blend while

---

2: runs are made with CF₃ bearing nickel enolate catalyst formed in situ
synthesizing. In the emulsion TGA’s, the starch and the surfactant starts thermally degrading at much lower temperature than the polyethylene, the polyethylene does start melting but there would be no significant weight loss. Its TGA curve can be distinguishly be seen in any TGA shown below in Figure 3.11, below. There is always around 7-10% of ash content at the end of the TGA method. Below in the figure is a TGA of pure polyethylene by Aqueous Emulsion Method which is the base for comparing the phases of all the other TGA’s.

![TGA of pure polyethylene made by aqueous emulsion polymerization](image)

Figure 3.11: TGA of pure polyethylene made by aqueous emulsion polymerization

Figure 3.11 above indicates that initially a weight loss occurs starting at 100°C and lasting to about 300°C. This is due to the presence of the SDS and hexadecane. The polyethylene decomposes starting at ca. 350°C and is totally broken down at 500°C.
The TGA of a polyethylene/starch hybrid is shown below in Figure 3.12.

![TGA Graph]

**Figure 3.12:** TGA of a sample from Run #6, (not washed with acetone, before biodegradation)
Figure 3.13: TGA of a product washed with acetone (Run #6, before biodegradation)

The region in which the weight loss of a particular starch occurs depend also on its origin and some starches may decompose at lower temperatures\(^\text{(23)}\). The following TGA diagrams in Figure 3.13 show that HES is indicated by a weight loss which typically begins at 300\(^\circ\)C and ends at about 400\(^\circ\)C. This loss in weight is due to partial or complete pyrolytic volatilization of the starch and hence we can use it to determine starch content in the sample. Thus based on these TGAs we could also obtain reliable amounts of the polyethylene in our hybrids with the starch. The weight \% starch in the hybrid was obtained by obtaining the fraction the originally used amount of starch in the hybrid with polyethylene.
The TGA’s of the sample subjected to acetone wash gave more accurate regions of starch decomposition which was earlier overlapped with SDS being present in the samples. Hence more accurate data on starch content and polyethylene could be obtained.

![TGA Graph](image)

**Figure 3.14**: TGA of the sample from Run #6 after biodegradation (also shown in Fig. 3.8, acetone unwashed sample)

A comparison can be made between the Figures 3.13 and Figures 3.14 that most of the starch and SDS has been metabolized by the bacteria most likely leaving holes in the polyethylene film which makes it vulnerable for further biodegradation.
Another example of such a case is exhibited in Figure 3.15 and Figure 3.16; this sample contains around 85.9%.

Figure 3.15: TGA of the sample from Run #11 before biodegradation
Figure 3.16: TGA of the sample from Run #11 after biodegradation

Clearly, the Figure 3.16 does not have any starch or the surfactant left in it.

The following graph shows some good agreement between the percentage starch obtained indirectly as described by TGA, and the peak ratios for starch and polyethylene from the IR spectra using the peak at 1460 cm\(^{-1}\) for the starch and the peak at 980 cm\(^{-1}\) for the polyethylene.
Figure 3.17: Correlation between Percentage of starch in hybrids and peak-ratios for starch and polyethylene at 1460 cm$^{-1}$ and 980 cm$^{-1}$

In the following Figure 3.17, a TGA of a hybrid made with a salicylaldiminate catalyst is shown (Run #2). It clearly shows very little decomposition above 400°C indicating almost negligible amount of polyethylene as compared to the TGAs of the hybrids made with the CF$_3$- substituted enolate catalyst.
Figure 3.18 shows the TGA of a sample made with the 5-chloro, 3-methoxy salicylaldiminate nickel pyridyl catalyst. There are two weight losses starting before 200°C, which are mainly due to the SDS and starch in the sample. However, no significant weight loss can be observed beginning at 400°C which would have been characteristic for the presence of polyethylene. This is in agreement with the IR and DSC measurements indicating that only traces of polyethylene are formed with this type of catalyst.
3. Results on the Density Gradient Analysis

To have a higher reliability on the starch contents of the samples we used a third method that can be applied here, because the densities of polyethylene and starch are sufficiently apart, the density gradient column technique\(^{(35)}\).

The Figure 3.19 is a correlation obtained between density and milliliters of cylinder for measuring densities of polyethylene/starch hybrids and pressed films.

![Figure 3.19: Correlation for density gradient measurement system](image)

The main purpose of this measurement system was to obtained percentage starch in the hybrid apart from what was determined by Thermo Gravimetric Analysis. In the table below are the
starch percentages obtained from density gradient measurement and their comparison with thermo gravimetric analysis.

Table 3.5: Density Gradient Measurements

<table>
<thead>
<tr>
<th>Run #</th>
<th>Density of the sample of the blend (kg/m³)</th>
<th>% Starch from Density Gradient Analysis</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyethyl starch</td>
<td>1.457</td>
<td>100.0</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>0.918</td>
<td>0.0</td>
</tr>
<tr>
<td>1</td>
<td>1.002</td>
<td>15.6</td>
</tr>
<tr>
<td>5</td>
<td>0.952</td>
<td>6.4</td>
</tr>
<tr>
<td>6</td>
<td>1.006</td>
<td>16.3</td>
</tr>
<tr>
<td>7</td>
<td>1.018</td>
<td>13.8</td>
</tr>
<tr>
<td>8</td>
<td>1.362</td>
<td>81.3</td>
</tr>
<tr>
<td>9</td>
<td>1.338</td>
<td>77.9</td>
</tr>
<tr>
<td>11</td>
<td>1.345</td>
<td>79.2</td>
</tr>
</tbody>
</table>

The percentage starch values of the Table 3.5 were obtained from the correlation in the Figure 3.17.
In the Table 3.6 Average percentage starch has been calculated based on three results from Thermo Gravimetric Analysis (TGA), Fourier Transform Infrared Spectroscopy (FTIR) and Density Gradient Analysis. In Table 3.1 it can be observed that these values of average percentage starch are close to that of assumed percentage starch.

### Table 3.6: Average Percentage Starch

<table>
<thead>
<tr>
<th>Run #</th>
<th>% Starch from TGA</th>
<th>% Starch from FTIR</th>
<th>% Starch from Density Gradient Analysis</th>
<th>Average % Starch</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroxyethyl starch</td>
<td>-</td>
<td>-</td>
<td>100</td>
<td>-</td>
</tr>
<tr>
<td>Polyethylene</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>13.8</td>
<td>13.8</td>
<td>15.6</td>
<td>14.7</td>
</tr>
<tr>
<td>5</td>
<td>8.7</td>
<td>8.7</td>
<td>6.4</td>
<td>7.5</td>
</tr>
<tr>
<td>6</td>
<td>15.2</td>
<td>15.2</td>
<td>16.3</td>
<td>15.7</td>
</tr>
<tr>
<td>7</td>
<td>14.0</td>
<td>14.0</td>
<td>13.8</td>
<td>13.9</td>
</tr>
<tr>
<td>8</td>
<td>85.8</td>
<td>85.8</td>
<td>81.3</td>
<td>83.5</td>
</tr>
<tr>
<td>9</td>
<td>74.7</td>
<td>74.7</td>
<td>77.9</td>
<td>76.3</td>
</tr>
<tr>
<td>11</td>
<td>92.6</td>
<td>81.4</td>
<td>79.2</td>
<td>85.9</td>
</tr>
</tbody>
</table>
4. Results on the Differential Scanning Calorimetry (DSC)

Thermal analysis of the hybrids were carried out under nitrogen atmosphere at heating rate of 20°C/min using DSC over the temperature range of 20-200°C. In the Table 3.7 below the DSC data of the products are given:

<table>
<thead>
<tr>
<th>Run #</th>
<th>Melt temperature ( (T_m) ) in Peak 1</th>
<th>Heat of fusion ( (\Delta H_f) ) in J/g Peak 1</th>
<th>Crystallinity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>100.01 - -</td>
<td>46.74 Peak 1</td>
<td>15.95 Peak 1</td>
</tr>
<tr>
<td>2</td>
<td>120.96 - -</td>
<td>12.48 Peak 1</td>
<td>4.26 Peak 1</td>
</tr>
<tr>
<td>3</td>
<td>119.2 - -</td>
<td>17.89 Peak 1</td>
<td>6.02 Peak 1</td>
</tr>
<tr>
<td>4</td>
<td>99.13 - -</td>
<td>0.325 Peak 1</td>
<td>0.11 Peak 1</td>
</tr>
<tr>
<td>5</td>
<td>101.80 - -</td>
<td>54.6 Peak 1</td>
<td>18.63 Peak 1</td>
</tr>
<tr>
<td>6</td>
<td>103.88 - -</td>
<td>97.59 Peak 1</td>
<td>33.31 Peak 1</td>
</tr>
<tr>
<td>7</td>
<td>50.48 - -</td>
<td>2.304 Peak 1</td>
<td>0.786 Peak 1</td>
</tr>
<tr>
<td>8</td>
<td>88.56 100.79 116.79</td>
<td>1.73 1.225 14.3</td>
<td>0.59 0.42 4.88</td>
</tr>
<tr>
<td>9</td>
<td>100.37 106.31 114.5</td>
<td>0.761 2.284 0.423</td>
<td>0.25 0.77 0.14</td>
</tr>
<tr>
<td>10</td>
<td>88.32 100.92</td>
<td>2.314 1.915</td>
<td>0.789 0.653</td>
</tr>
<tr>
<td>11</td>
<td>104.51</td>
<td>2.664</td>
<td>0.91</td>
</tr>
<tr>
<td>12</td>
<td>93.96</td>
<td>103.2</td>
<td>35.29</td>
</tr>
<tr>
<td>13</td>
<td>119.38</td>
<td>13.86</td>
<td>4.73</td>
</tr>
<tr>
<td>14</td>
<td>89.07 99.67</td>
<td>0.355 0.701</td>
<td>0.12 0.239</td>
</tr>
</tbody>
</table>

In the above Table 3.7, the melt enthalpy and crystallinity of some samples from Table 3.6 which were subjected to biodegradation tests are given below in the Table 3.8.
Table 3.8: Effects of biodegradation on thermal properties

<table>
<thead>
<tr>
<th>Run #</th>
<th>Heat of fusion before degradation ((\Delta H_f)) in J/g</th>
<th>Heat of fusion after degradation ((\Delta H_{f1})) in J/g</th>
<th>Crystallinity before degradation (%)</th>
<th>Crystallinity after degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak1 Peak2 Peak3</td>
<td>Peak1 Peak2 Peak3</td>
<td>Peak1 Peak2 Peak3</td>
<td>Peak1 Peak2 Peak3</td>
</tr>
<tr>
<td>5</td>
<td>54.6 163.6 18.63</td>
<td>55.85</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>97.6 149.1 33.31</td>
<td>50.88</td>
<td></td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>2.304 2.011 0.786</td>
<td>0.786</td>
<td>0.686</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>0.761 2.284 0.423</td>
<td>3.117</td>
<td>0.25 0.77 0.14</td>
<td>1.064</td>
</tr>
</tbody>
</table>

The percent crystallinity was calculated based on the following formula:

\[
\% \text{ crystallinity} = \frac{\Delta H_f \times 100}{\Delta H_f^*}
\]

In the above formula, \(\Delta H_f\) and \(T_m\) are obtained from the thermographs and the value of \(\Delta H_f^*\) is taken as 293 J/g\(^{(36)}\).

The literature value for \(T_m\) for LDPE is around 115°C. The reason for the discrepancies in the results of the experimental data can be attributed to the thermal history which the polymer has been subjected to during its synthesis. Below is a Figure 3.20 of polyethylene without starch:
Figure 3.20: DSC Thermo gram of pure polyethylene by the process of Aqueous Mini Emulsion Polymerization CF$_3$ bearing nickel enolate catalyst [CF$_3$Ni(COD)$_2$]

Figure 3.20 and Figure 3.21 are the thermographs of Sample # 6 of Table 3.1 before and after biodegradation.

It is interesting that the crystallinity of the sample increases after biodegradation. The bacteria and the fungi during biodegradation feed on the amorphous part of the polymer and hence making it more crystalline after the biodegradation. The melt enthalpy has increased of all the samples after biodegradation. A similar observation was also made by Soula et al (7).
From observing the data a conclusion can be drawn that the crystallinity of the sample increases after biodegradation. The bacteria and the fungi during biodegradation feed of the amorphous part of the polymer and hence making it more crystalline after the biodegradation. The melt enthalpy has increased of all the samples after biodegradation.

Figure 3.21: DSC Thermograph of Run #6 of Table3.1 with 15.7 % starch

![DSC Thermograph](image-url)
Figure 3.22: DSC thermograph of Run #6 after biodegradation for 21 days

Figure 3.22 shows the DSC spectrum of a hybrid made with a salicylaldiminate catalyst run #2. Although the polyethylene in this hybrid only amounts to traces, clearly the peak at 124.28°C can only be explained by its presence (neither starch, nor SDS or hexadecane would produce such a melting peak.
Figure 3.23: DSC thermograph of sample from Run #4 made with salicyl aldiminate catalyst

Figure 3.23 shows the DSC thermograph of the product obtained with the 5-Chloro, 3-methoxy salicyl aldiminate nickel pyridyl catalyst (Run #4). It has a melting point around 123°C clearly indicative of polyethylene (neither SDS nor hexadecane can have this kind of melting peak). In addition smaller endothermic peak also shows in the second heat.
5. Results on the Scanning Electron Microscopy (SEM)

Scanning Electron Microscopy was done on the polymer to determine its particle size and
study the morphology before and after biodegradation studies were done.

Some of the images from the SEM are exhibited as below in the order of the type of
starch used:

A. Soluble potato starch

Images of pure soluble potato starch and a high molecular weight potato starch hybrid
obtained in Run # 2 are shown below in Figure 3.24 and Figure 3.25 respectively:

![SEM imaging of a pure soluble potato starch](image)

Figure 3.24: SEM imaging of a pure soluble potato starch \(^{(37)}\)
Figure 3.25: SEM imaging of a sample from Run #2 from Table 3.1

Because only traces of polyethylene formed it is not even apparent in this image and only the potato starch forming the spherical bodies can be observed.
B. Hydroxyethyl starch

Figure 3.26: SEM imaging of a sample from Run #5 from Table 3.1

The Figure 3.26 is the image of low molecular LDPE with hydroxyethyl starch as the biomass. All the above images of SEM are taken at 20 kV. To obtain an overall view, the magnification was set at 10,000, leading to 2 µm scale bar.

C. Images of hydroxyethyl starch in different forms

To distinguish between starch and polyethylene images of hydroxyethyl starch powder were taken. This powder was used in two ways: (1) Natural form and (2) Milled form
which upon capturing the following images was concluded that there is no difference between them:

![Figure 3.27: (Left) Natural form of hydroxyethyl starch and (Right) Milled form of hydroxyethyl starch](image)

The natural form has lot of agglomeration of particles which just disappears when milled but there is no size reduction in real. Some starch particles have shape similar to polyethylene.
D. Images of pressed films

![Figure 3.28: SEM image of a pressed pure polyethylene film (acetone washed) on the top (left) and pressed film (acetone washed) of Run #8 (top-right), pressed films of hybrids on the bottom – Left: containing 7.5% starch (Run #5) and right: containing 15.7% starch (Run #6).]

The above images in the Figure 3.28 are a view of the cross-section of films. A similar methodology was used previously by Wool \(^{38}\). They are also coated in a sputter with Au-Pd.
These films were pressed at temperature of around 160°C. Images were taken before the films were put to biodegradation test with fungi for 21 days. The two bottom images indicate that the soap produces a more heterogeneous texture.

Figure 3.29: SEMs of pressed films showing a hybrid containing ca. 15.7 % hydroxyethyl starch (Run #6), left: before degradation, right: after degradation with Aspergillus fungi for 21 days.

In the above Figure 3.29 on the right hand shows a close up of a degrading sample, as indicated by the holes in the surface of the hybrid.
Figure 3.30: SEM image of low molecular pressed film with 85.9 % hydroxyethyl starch (Run #11)

In the Figure 3.30 holes are seen distinctly at many places. The cylindrical crystalline parts are the mycelium formed over the film over a period of time from Asperigillus used to biodegrade films.
6. Results on the Transmission Electron Microscopy

TEM was basically used to determine particle size, claimed to be in nanometers.

Images below are some images of the LDPE latex. In the following figures some images of the LDPE latex are shown. From Figure 3.31 it is apparent that the polymer particles are lentil shaped as had been showed earlier by Mecking (36). The polymer particles had on the average a diameter size of about 200 nm.

Figure 3.31: TEM images of a low molecular LDPE with soluble potato starch as biomass at different magnifications (Run #1)
Figure 3.32: TEM image of a low molecular LDPE with hydroxyethyl as biomass (Run #5)

From Figure 3.32 it can be concluded again that only the polyethylene is visible as solid particle and the starch is dissolved and in the background.

In Figure 3.33 are the images of TEM of hybrids with different catalyst are shown.
Figure 3.33: TEM images of polyethylene starch hybrids made with – Left: with CF$_3$-Ni(COD)$_2$ (Run #5), right: with 5-Cl, 3-CH$_3$O

In Figure 3.33 the image of the hybrid on the left contains polyethylene particles; however, the image on the right shows hardly any polymer. The more amorphous shapes depicted in the image on the right is more likely soap.
CONCLUSIONS

Our investigation showed that biodegradable polyethylene starch hybrids can be synthesized using aqueous mini emulsion polymerizations. With the nickel enolate catalyst it was possible to obtain polyethylene in presence of starch at high activities even in when hybrids containing more than 50% starch were obtained. Polymerization activities decreased as the loading of starch in the reaction was increased. The salicyl aldiminate catalysts we applied resulted in only traces of polyethylene. This is likely due to the relatively low concentration of ethylene in the aqueous solution at the low ethylene pressures affordable in the glass reactor.

To determine the starch content in the hybrids and polyethylene activity reliably the soap and hexadecane used for the emulsion had to be removed by washing of the latex samples with acetone. It could be shown by comparisons of related IR spectra, as well as TGA diagrams that this method was efficient in removing the surfactant and co-surfactant. The starch content was determined using three methods: TGA, IR spectroscopy and density gradient measurements. In the TGA decomposition of the starch occurs between 250°C and 325°C and the decomposition of the polyethylene between 400°C and 500°C. The correlation of the starch content obtained from TGA with the peak-ratio of starch to polyethylene of 980 cm⁻¹ / 1460 cm⁻¹ is good ($R^2 > 85\%$). The densities of hydroxyethyl starch with 1.457 g/mL and the polyethylene of 0.918 g/mL were sufficiently apart to use the density gradient method, the resulting densities of the hybrids also in
agreements with the starch contents determined by the previous methods. The amount of starch in the hybrids varied between 7.5% and 92.3%.

The DSC diagrams of the hybrids of both the CF$_3$–nickel enolate catalysts and the salicylaldiminate based catalysts showed as expected melting peaks characteristic of polyethylene. Interestingly, the DSC of the biodegraded samples showed an increase in the crystallinity of the polyethylene.

SEM images of the dried samples indicated that the polyethylene and starch are uniformly distributed in the samples with the starch appearing as brighter material. However, the presence of the hybrid caused that the surface of pressed and cut films to have some texture compared to pure polyethylene. TEM images showed the characteristic lentil-type shape of the polyethylene formed in the emulsion polymerizations with the average diameter size of the polyethylene particle size being about 200 nm. As expected based on their water solubility the two types of starches did not appear as solids in the TEM images of the latex samples. The potato starch samples appeared to indicate some swelling of the particles due to incorporated water.

The direct biodegradability tests of the solid hybrids observed after the exposure to fungi over three weeks proved quite effective. These tests were done with briefly dried, solid samples containing soap and residual hexadecane because they did not prove to be of hindrance. Upon degradation holes in the matrix can be observed due to the metabolism of the starch by the fungi. The IR spectra of the biodegraded samples indicated some of the starch had been depleted and all
of the soap had been removed. TGAs and DSCs also indicated that not only the starch but also the soap diminished. The hybrids disintegrated, though there was no substantial decrease in the polyethylene peaks, however, as is expected when the molecular weight is higher than 600 g/mol. Aspergillus turned out to be the most active type among the three fungi applied. Hydroxyethyl starch led to more rapid degradation than the potato starch.

In summary, it could be shown in this work that using a sustainable polymerization process with water as solvent uniform and highly biodegradable hybrids of polyethylene and starch could be produced.
OUTLOOK AND FUTURE WORK

In future runs it would be useful to apply higher ethylene pressures during the polymerization, so that also polymer/biomass hybrids with the salicylaldiminate or similar catalysts can be obtained. The basic laws of polymerization kinetics let us predict that upon a significant increase of the monomer concentration the activity should increase, while at the same time also the molecular weight of the polymers can be increased. The latter was particularly an issue when polymerizations had to be run at 60°C with the CF$_3$-bearing nickel enolate, because it is not active below 55°C.

At the higher monomer pressure also less surfactant and co-surfactant has to be used, which would result in products that would resemble the pure polymer more. However, to apply the higher pressure a steel autoclave is required. The selection of other water resistant single-site catalysts could significantly increase the activity.

To monitor the potential degradation of the polymer itself some internal standard may be used that can be used as reference. The biodegradability tests could be more quantified by weighing samples before and after degradation tests or measuring the carbon dioxide developed in the process. It would be interesting also to apply composting field tests with these samples. The samples with higher molecular weights could be also tested for a variety of mechanical properties.
REFERENCES


http://www.cheng.cam.ac.uk/research/groups/polymer/RMP/nitin/Starchstructure.html.


APPENDIX
Figure 1: IR spectrum of potato starch

Figure 2: IR spectrum of Run #1
Figure 3: IR spectrum of Run #1 (acetone washed)

Figure 4: IR spectrum of Run #3
Figure 5: IR spectrum of Run #4

Figure 6: IR spectrum of Run #5
Figure 7: IR spectrum of Run #5 (acetone washed)

Figure 8: IR spectrum of Run #6
Figure 9: IR spectrum of Run #6 (acetone washed)

Figure 10: IR spectrum of Run #7
Figure 11: IR spectrum of Run #9

Figure 12: IR spectrum of Run #10
Figure 13: IR spectrum of Run #10 (acetone washed)

Figure 14: IR spectrum of Run #11
Figure 15: IR spectrum of Run #11 (acetone washed)

Figure 16: IR spectrum of Run #12
Figure 17: IR spectrum of Run #13

Figure 18: IR spectrum of Run #14
Figure 1: Thermograph of Sodium dodecyl sulfate (SDS)

Figure 2: Thermograph of Hydroxyethyl starch
Figure 3: Thermograph of Run #1

Figure 4: Thermograph of Run #1 (acetone washed)
Figure 5: Thermograph of Run #3

Figure 6: Thermograph of Run #4
Figure 7: Thermograph of Run #5 (before biodegradation test)

Figure 8: Thermograph of Run #5 (after biodegradation test)
Figure 9: Thermograph of Run #5 (acetone washed)

Figure 10: Thermograph of Run #8 (before biodegradation test)
Figure 11: Thermograph of Run #8 (after biodegradation test)

Figure 12: Thermograph of Run #9
Figure 13: Thermograph of Run # 10

Figure 14: Thermograph of Run #12
Figure 1: Thermograph of Run #1

Figure 2: Thermograph of Run #2
Figure 3: Thermograph of Run #3

Figure 4: Thermograph of Run #5 (before biodegradation)
Figure 5: Thermograph of Run #5 (after biodegradation)

Figure 6: Thermograph of Run #7
Figure 7: Thermograph of Run #10

Figure 8: Thermograph of Run #12
Figure 9: Thermograph of Run #14
Figure 1: SEM image of Run #1

Figure 2: SEM image of Run #4
Figure 3: SEM image of Run #7

Figure 4: SEM image of Run #7
Figure 5: SEM image of Run #8

Figure 6: SEM image of Run #9
Figure 7: SEM image of Run # 9
Figure 1: TEM image of Run #4

Figure 2: TEM image of Run #6
Figure 3: TEM image of Run #9