

Chapter 1: An Introduction to Current Research Activities on Starch-Polyester Blends

1 Abstract

North-American biodegradable plastic market in 2005 is estimated to be around 60 million lbs. Starch-based polymer blends is expected to account for 30 million lbs with significantly lower growth rates than other biodegradable polymers like polyesters. The main hurdle in the growth of starch-based products is the thermodynamic immiscibility of starch with other polymers with serious mechanical property deterioration at >25-30wt% starch. Higher amounts of starch in the blends entails adding suitable functional groups on starch and other polymers in the blend and make them more compatible. The primary challenge is to develop fast reaction chemistries that can be transformed into viable processes and integrated into existing process lines with economically viable formulations. This chapter will give an overview of current bioplastic market as well as challenges that need to be overcome to develop new technologies that would expand the scope of current market.

1.2 Significance and Applications

1.2.1 North American Biodegradable Plastic Market

The biodegradable polymer market for North America is expected to grow to 60 million lbs in 2005 from 25 million lbs in 2000. (1). However the starch-based polymer consumption is expected to only increase from 20 to 30 million lbs during this time. Most of the future growth is expected to be in the area of synthetic biodegradable polyesters (1). Major volume consumption of starch (either by itself or blends with other polymers) are in the following application areas:

a) Loose-fill Packaging: Out of 25 million lbs starch market in 2000, loose-fill packaging accounted for 20 million lbs (1). These products consisted of >90% starch by weight. Different kinds of starch were used- corn, wheat, hydroxypropylated high amylose corn- with a small amount of additives like polyvinyl alcohol, glycerol, polyethylene glycol or silicon dioxide (2). These products have acceptable properties sufficient for protective packaging applications. The main non-biodegradable competitor to starch-based loose-fills is expanded polystyrene (EPS) foams. EPS foams are made by a multi-step process. Partly expanded polystyrene beads are made by incorporating blowing agents into styrene before polymerization or extrusion compounded into polystyrene after polymerization. These foam beads were subsequently expanded into loose-fill with steam and quenched below glass transition temperature (T_g) for a day to allow air to diffuse into cells. To achieve desired foam densities, expansion and quenching processes were repeated 2 or 3 times (2). Starch-based loose-fill is usually manufactured in a one-step process, via an extrusion cooking process. Granular starch and water are fed into an extruder, usually a twin-screw where heat and shear caused the starch to gelatinize. Water, released as steam at the die of the extruder, was the primary blowing agent. Complete expansion or density reduction took place immediately after the product exits the extruder (2). Compared to EPS, starch loose-fills had two main disadvantages:

- i) Cost: Starch-based loose-fills cost approximately \$21 per cubic meter delivered which is about 30% higher than the price of EPS-based loose-fill. A recent comparative study by Minnesota Office of Waste Management (MOWM) claimed that starch-based loose-fill is a reasonable alternative to EPS loose-fills if composting infrastructures exist and EPS recycling is impractical (2).
- ii) Properties: EPS loose-fills provided better protection with less material than starch-based loose-fills. This was because of lower values for several property parameters.

These include foam density, cell structure, compressive stress and resiliency. The differences in properties are illustrated in Table 1.1.

b) Starch-Polymer Blends: Starch is blended with other biodegradable polymers and could be used in applications like compost and garbage bags, disposable tableware, baby napkins, agricultural mulches, vegetable wrappings, fresh food thermoformed trays and miscellaneous items. This segment of the market accounted for 5 million lbs of the 25 million lb starch-based biodegradable market (1). Polymers that have been

Table 1.1: Property differences between EPS and starch loose-fills (2)

| Loose-Fill Type | Foam Density, g/cc | Cell Structure | Compressive Stress, MPa | Resiliency |
|------------------------|---------------------------|-----------------------|--------------------------------|-----------------------|
| EPS | 0.0079 | Closed | 0.041 | Higher |
| Starch | 0.0167- 0.0226 | Open | 0.0565-0.1051 | 10% lower than EPS |

blended with starch could be divided into two classes- polyesters and non-polyesters. Biodegradable synthetic polyesters that have been blended with starch included polycaprolactone (PCL) (3-8), polylactic acid (PLA) (4,9), polybutylene succinate (PBS) (3), polytetramethylene adipate-co-terephthalate (PAT) (3) and polyhydroxy butyrate (PHB) (9,10). The chemical structures of the repeating units of these polyesters are illustrated in Figure 1.1. All polyesters are characterized by the presence of ester (-COO) group. All synthetic polymers-polyesters and non-polyesters- are expensive with their costs ranging from \$2.50/lb to \$8/lb. There are fewer

biodegradable non-polyesters than polyesters and subsequent paragraphs will focus more on starch-polyester blends.

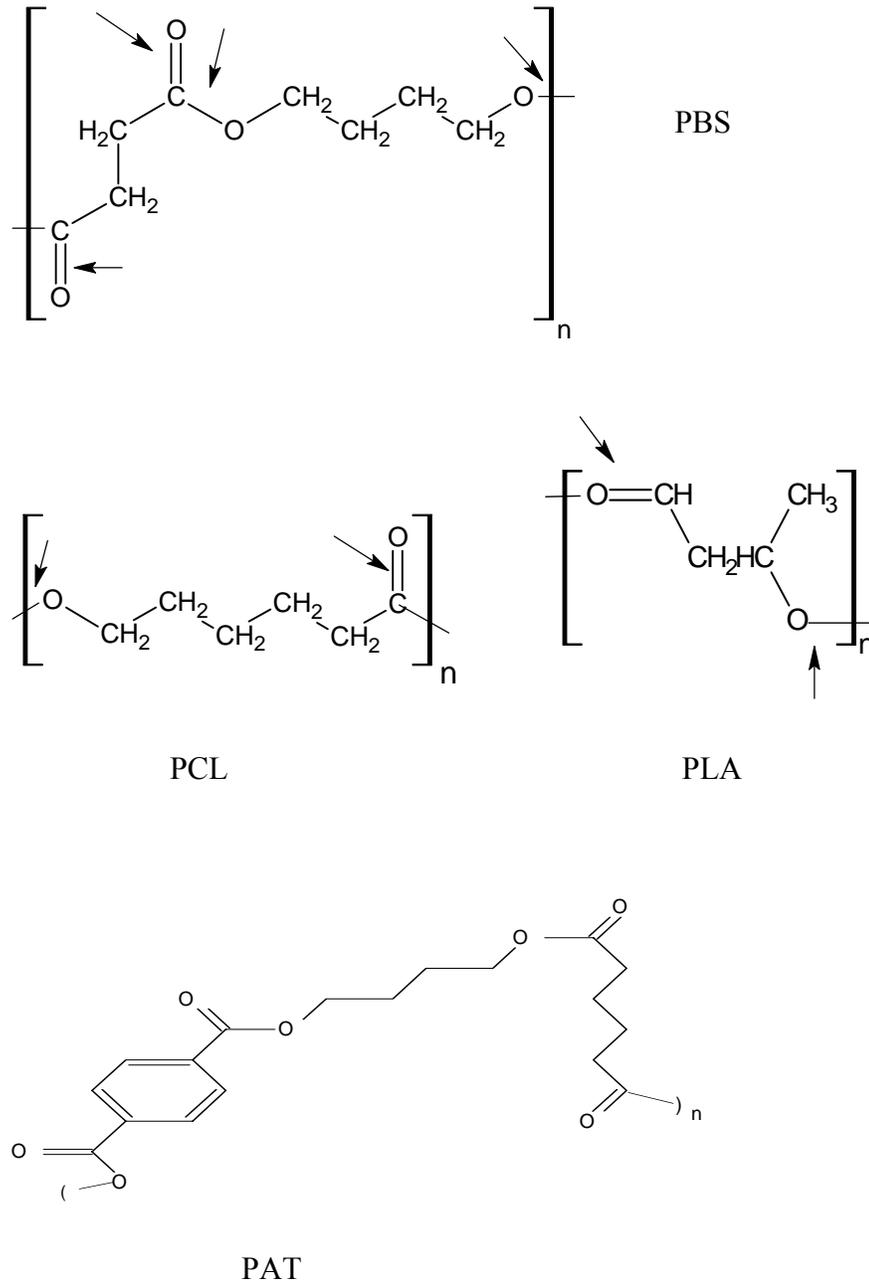


Figure 1.1: Molecular structures of repeating units of various biodegradable synthetic polyesters

1.3 Challenges in Synthesizing Starch-Polyester Blends

There are several obstacles in synthesizing starch-polyester blends and using them as them as plastic substitutes. These are:

a) Immiscibility of Starch and Polyesters

Starch is a mixture of two polysaccharides-amylose (linear 1,4- α -glucopyranosyl units) and amylopectin (linear 1,4- α -glucopyranosyl units and branched 1,6- α -glucopyranosyl units) (25). The amylose fraction has a degree of polymerization (DP) of 1×10^2 - 4×10^5 and amylopectin has a DP of 1×10^4 - 4×10^7 with branches after every 19-25 linear units. Amylopectin has one of largest molecular weights of all naturally occurring polymers (11). Significant amounts of amylopectin (~72%) are present in native wheat or corn starch, the rest being made up of amylose. The basic repeating unit of starch is the 1,4- α -glucopyranosyl unit and is shown in Figure 1.2. Figure 1.2-a shows the linear chains present in amylose while 1.2-b shows the branching points characteristic of amylopectin. As could be seen from Figures 1.1 and 1.2, there are no functional groups in starch and polyesters that could spontaneously react with each other when mixed. Thus both polymers are immiscible. However in starch-polyester blends at low levels of starch (< 20wt%), it has been observed that mechanical properties were similar to 100% polyester (12). But at >20wt% levels, immiscibility played a role and properties decreased significantly compared to 100% polyester (12). In the former case, applications are quite limited because of high cost of synthetic biodegradable polyesters. The cost of starch varies from \$0.18 to \$0.40/lb depending on type of starch. Thus there is a need to use high levels of starch in starch-polyester blends. In order to overcome miscibility problems, existing functional groups in starch or polyester needed to be modified so that the new functionalities could react with each other. In this way a covalent bond could be formed between starch and polyesters making properties better in blends containing high levels of starch.

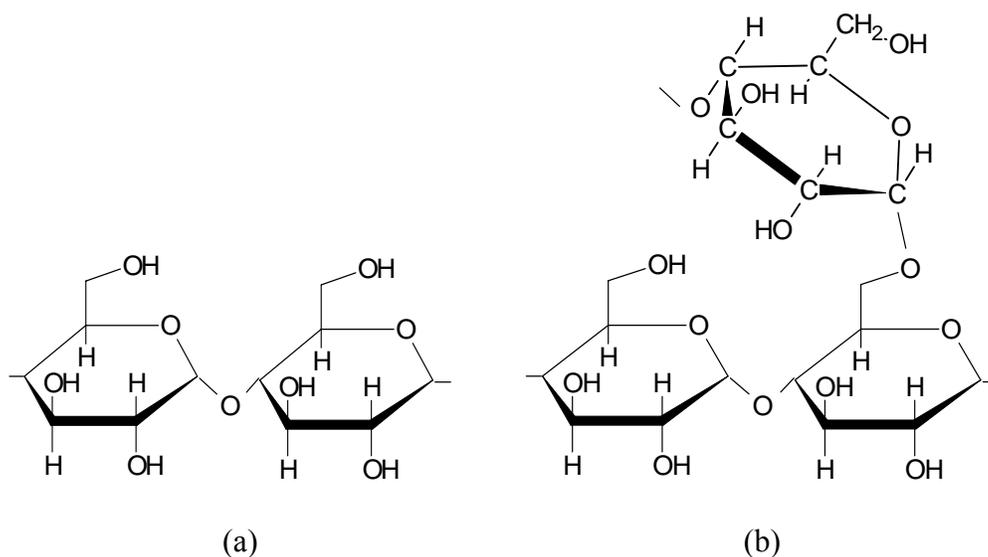


Figure 1.2: a) Two basic linear 1,4- α -glucopyranosyl repeating units of starch (e.g. amylose), b) Two basic linear 1,4- α -glucopyranosyl repeating units with a 1,6-branching (e.g. amylopectin)

b) Processing Challenges Associated with Starch

Native starches are available as granules (2-55 μm) in which both amylose and amylopectin are arranged radially. The granules contained both crystalline and non-crystalline regions in alternating layers (e.g. like layers of onion). Only amylopectin chains contributed to crystallinity. Native corn and wheat starches consisted of 28% amylose and 72% amylopectin (11).

While synthesizing starch-polyester blends, starch granules have to be broken up during processing operations so that both amylose and amylopectin are in dispersed form. However the primary challenge during starch processing is to preserve the molecular integrity or molecular weight of starch. Native starch granules showed unique behavior depending on processing conditions and formulation. Starch granules can be broken up in three ways:

i) Melting: The melting point of native starch granules is very high at approximately 170-190⁰C (13). Starch decomposition occurred before melting and thus allowing starch granules to melt resulted in lower molecular weight products also called dextrans. Since mechanical properties are proportional to molecular weights, starch granule melting is not desirable.

ii) Gelatinization: In the presence of low molecular weight plasticizers like water glycerol, starch granules swell. Upon application of shear such as in processing operations, these swollen granules broke up to release the amylose and amylopectin. There were no molecular weight changes during the gelatinization process (13, 14).

iii) Shear Breakdown: Application of shear energy during processing operations (e.g. extrusion, injecting molding) resulted in granule size reduction and release of polymers from granule to the surrounding dispersed polymer matrix. Like melting this process was also accompanied by starch polymer molecular weight reduction. Figure 1.3 illustrates the concept of gelatinization and melting/shear breakdown.

Wang *et al* (13) have reported that when water was present at >60 wt%, starch granules underwent gelatinization at 52-85⁰C (depending on starch type) (11) with no shear breakdown or melting. At lower levels of water, there was gelatinization, shear breakdown as well as melting with gelatinization taking place at higher temperatures. In the absence of any water or plasticizers, there was only melting and shear induced breakdown. Thus synthesis of starch-based bioplastics required processing operations that brought about gelatinization with minimal melting or shear breakdown.

c) Starch Properties

i) Mechanical Properties: Eventhough starch is a high modulus polymer (15) with large stiffness values compared to many synthetic polymers, it is brittle. High T_g's in starch (approximately 140⁰C) (16) contributed to this brittle behavior.

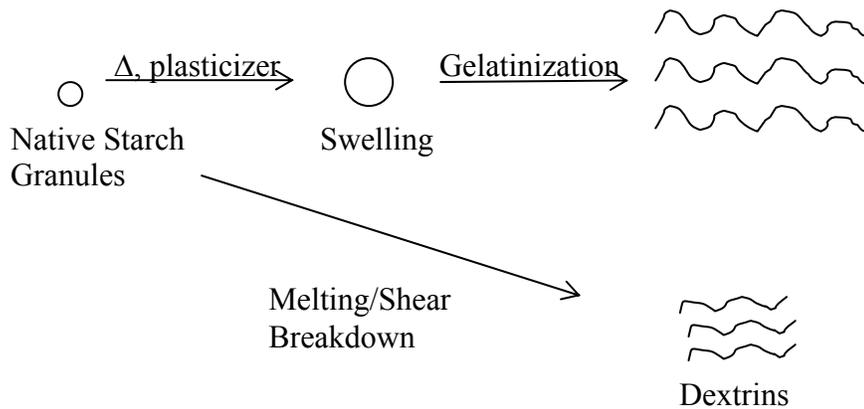


Figure 1.3: Effect of heat and shear on native starch granules inducing gelatinization at high moisture/plasticizer content and melting/shear breakdown at low moisture/plasticizer levels

ii) Barrier Properties: As seen in Figure 1.2, starch is a polyhydroxy polymer. These hydroxyl groups can easily form hydrogen bonds with water thus making starch a hydrophilic polymer.

iii) Property Deterioration with Time: The absorption of water from surrounding environment led to deterioration of mechanical properties because presence of water or any other plasticizer decreased strength and modulus but increased elongation. Also starch is susceptible to fungal attack especially in the presence of water.

1.4. Reactive Extrusion as a Tool for Synthesizing Starch-Polyester Reactive Blends (RB's)

As mentioned before suitable functional groups needed to be introduced on starch and/or polyester to compatibilize the two otherwise immiscible polymers. One of the most commonly processing operation to carry out these reactions is by extrusion. Extruders are widely used in normal plastic processing operations; thus a reactive

extrusion process could be easily integrated into existing processing lines. There are two main challenges in using an extruder for reactive processes. These are:

a) Reaction Time: The residence time of polymer melts inside extruders could be varied from seconds to minutes. Thus reaction kinetics should be fast enough to achieve 100% reactant consumption within the extruder.

b) Undesirable Side Reactions: Since it was necessary to increase reaction kinetics, most of the reactions were initiated by organic peroxides. Free radicals are generated at the beginning of reactions and unless process conditions in the extruder are optimized, undesirable side reactions could occur. One of the common undesirable reactions in peroxide initiated processes is the polymer degradation (backbone chain scission) and undesirable intra-polymer cross-linking rather than inter-polymer cross-linking (17-19).

1.4.1 Studies on Reactive Extrusion of Starch-Polyester Blends

Three technologies on starch-polyester reactive extrusion developed recently will be reviewed here. One of the products is already in market used as compost bags. A brief comparison between our work and others has been discussed.

1.4.1.1 Maleic Anhydride (MA) Functionalized Biodegradable Polyester-Starch Blends

Maleated polyesters have been synthesized from high molecular weight PCL (17), PBS (18), PAT (18) and PLA (19) by adding MA to polyesters. In the first reactive extrusion step, maleated polyesters were prepared from reactive extrusion in the presence of organic peroxide initiators like benzoyl peroxide (BPO), dicumyl peroxide (DCP) and dimethyl dibutylperoxy hexane (17-19). Grafted MA % ranged from 0.4 to 1.6% in the polyesters. In the second reactive extrusion step, maleated polyesters (at

5wt% level) were used as compatibilizers in corresponding starch-polyester blends (20,21). A schematic of the process (20) is given in Figure 1.4 for starch-PCL blends with maleated PCL as compatibilizer. The final product consisted of starch, modified and unmodified polyester and MA-crosslinked starch-polyester polymer. Extrusion parameters like temperature, initiator and MA concentration and residence time were optimized to avoid crosslinking and scission side-reactions during extrusion. DMA studies showed a decrease in glass transition of starch from 74 to 65⁰ C in compatibilized starch-PBS blends and it was related to better miscibility between starch and PBS in the presence of maleated PBS (20).

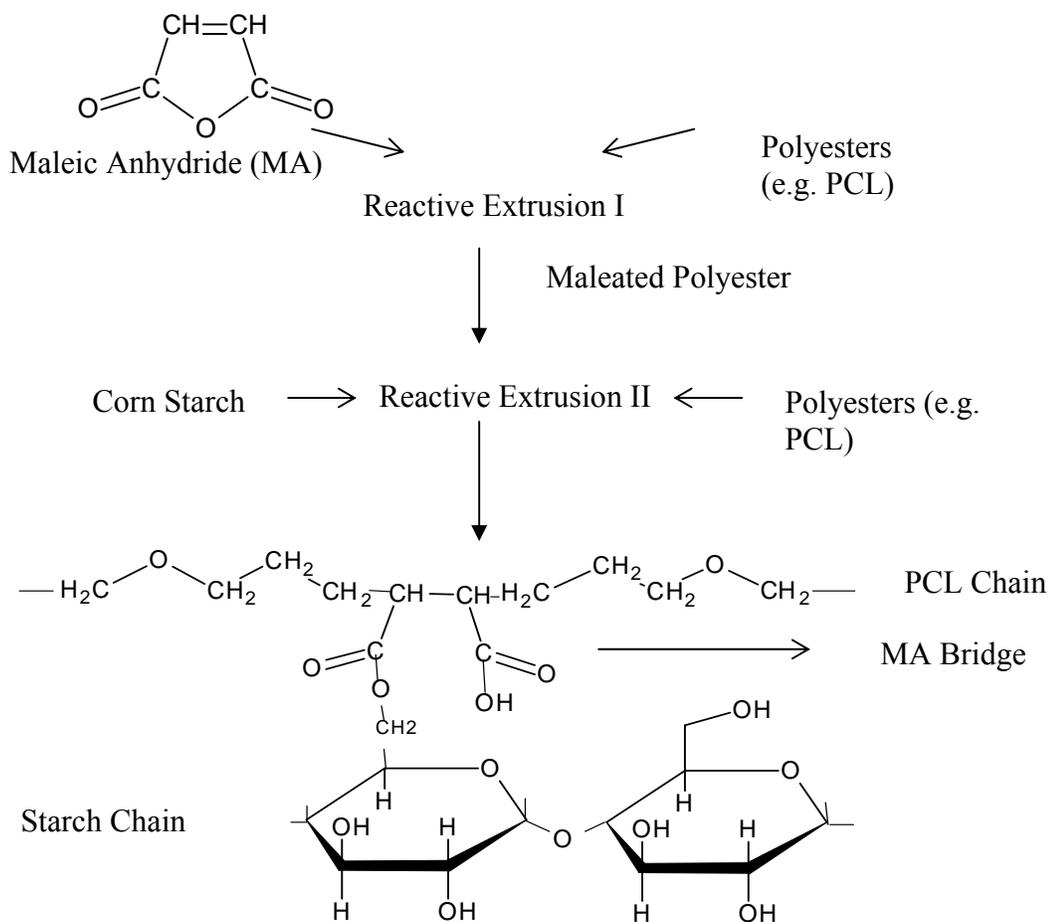


Figure 1.4: Compatibilization of starch and polyesters (PCL) using maleic anhydride

1.4.1.2 ϵ -Caprolactone Grafting and Polymerization on Starch

Narayan *et al* (22-25) synthesized starch-PCL blends by polymerizing ϵ -caprolactone monomer in the presence of starch in the presence of aluminum or titanium alkoxides as catalysts. In batch preparation methods (22), a low monomer (caprolactone) conversion of 30% was achieved in the presence of starch and aluminum alkoxides. However use of titanium alkoxides led to 98.5% conversion. High conversions were achieved during the reactive extrusion process (23-25) with PCL molecular weights (M_n) ranging from 25,000 to 400,000 at residence times of 1-3 minutes. Relevant patents (23-25) mentioned a temperature of 180⁰ C during the extrusion process and discussed effects of screw configuration, residence time and acid value of the monomer on molecular weight. However the patent indicated that the starch-PCL blends were synthesized in 3 extrusion steps- i) Homopolymerization of ϵ -caprolactone to PCL in the presence of aluminium alkoxides, ii) Extrusion of starch-plasticizer pellets and iii) Reactive extrusion blending of materials from i & ii. These films are currently marketed by the name of Envar and used as compost bags. Figure 1.5 shows the schematic of the reaction extrusion processes.

1.4.1.3 Current Studies by our Group

Our research group has recently developed a novel reactive extrusion process in which high amounts of plasticized starch (approximately 60wt%) could be blended with a biodegradable polyester (polycaprolactone) in the presence of nanoclay resulting in tough nanocomposite blends with elongational properties approaching that of 100% PCL (12,26). Starch, PCL, plasticizer, modified montmorillonite (MMT) organoclay and Fenton's reagent (H_2O_2 and Fe^{2+}) were extruded in a conical co-rotating twin-screw micro-extruder at 120⁰C and injection molded at 150⁰C. A simple schematic of the process is illustrated in Figure 1.6. Native starch was partially oxidized by the

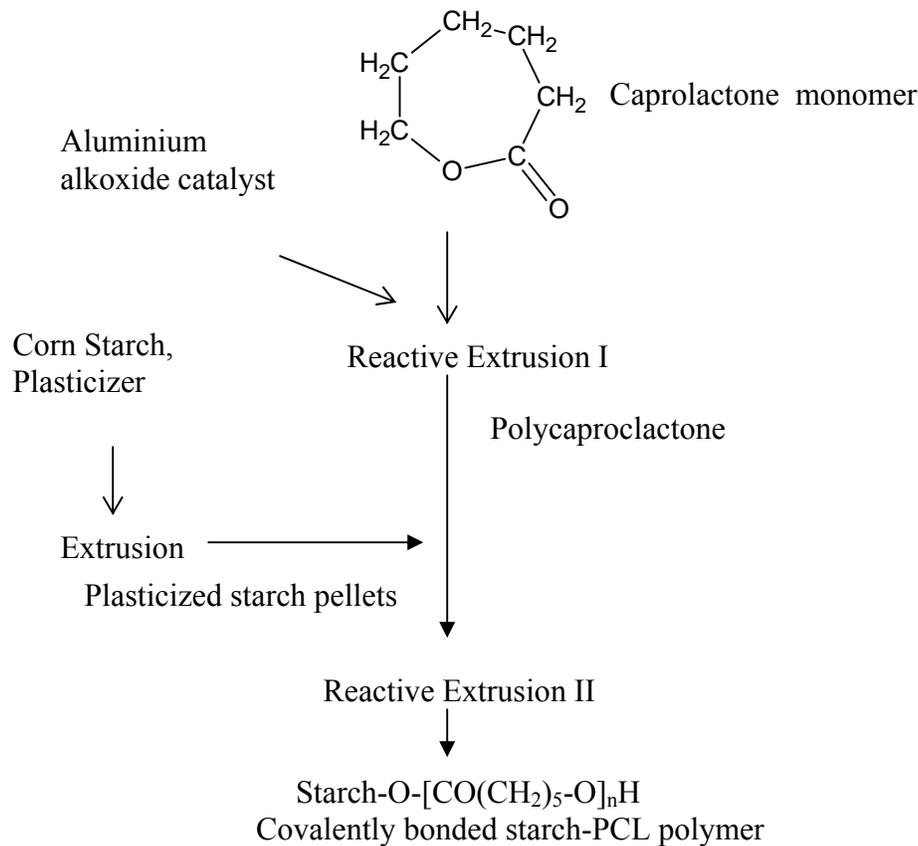


Figure 1.5: Polymerization of caprolactone monomer and addition of PCL to starch by reactive extrusion

peroxide and ester groups in PCL could subsequently cross-link with the carbonyl and/or carboxyl groups in oxidized starch through a peroxide initiated free radical process. This crosslinked starch-PCL fraction acted as a compatibilizer between unmodified starch and PCL. A single extrusion step with a low residence time (~74 seconds) was found to accomplish the above set of reactions. Elongational properties of these reactively extruded starch-PCL nanocomposite blends approached that of 100% PCL at 3 and 6wt% organoclay. Strength remained the same as non-reactive starch-PCL composites prepared from simple physical mixing. Starch-PCL cross-

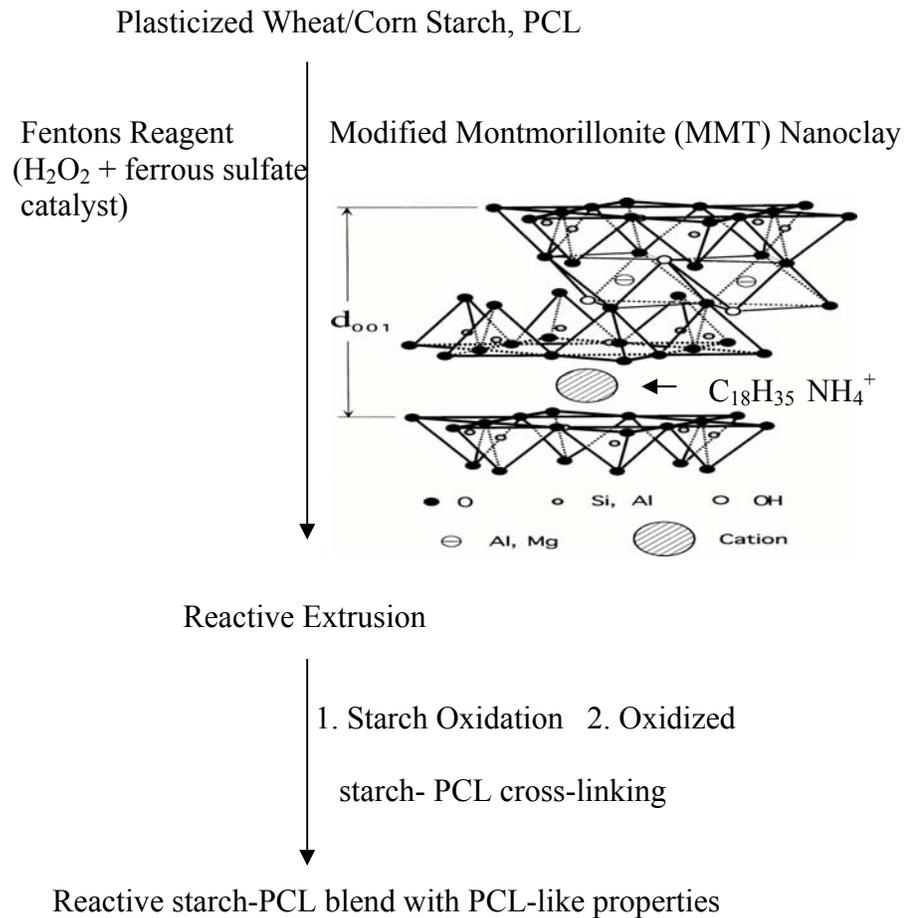


Figure 1.6: Synthesis of starch-PCL reactive blends with PCL-like properties using Fenton's reagent and MMT nanoclay in a single reactive extrusion step.

linking was affected by MMT organoclay and reactive extrusion in the absence of nanoclay resulted in products with mechanical properties lower than the composites. The reactive extrusion concept can be extended to other starch-PCL like polymer blends with polyhydroxy polymers like polyvinyl alcohol and starch on one side and polybutylene succinate, polyhydroxy butyrate-valerate and polylactic acid on the other to create cheap, novel and compatible biodegradable polymer blends with increased toughness.

Subsequent chapters will discuss in detail the synthesis and characterization of starch-PCL nanocomposite blends, their flow behavior and their scale-up from a bench-top to continuous commercial level extruder.

Table 1.2 shows a comparison of mechanical properties and cost from the three different reactive extrusion processes. The raw material cost of maleated blends and Envar were calculated on the basis of formulation given by Bhattacharya *et al* (20) and Narayan *et al* (23-25). Our blends had PCL-like elongation but the strength was lower than observed in other blends. The processing cost of our technology was also expected to be lower because of the requirement of a single extrusion step compared to multiple steps in other technologies.

Table 1.2: A comparison of tensile properties and cost of starch-PCL blends synthesized by different reactive extrusion processes

| Bioplastic | Starch, wt% | Maximum Strength, MPa | Ultimate Elongation, % | Material Cost, \$/lb |
|-------------------|--------------------|------------------------------|-------------------------------|-----------------------------|
| Maleated* Blends | 30 | 18.0 | 10-20 | 2.50 |
| 100% PCL | 0 | 25.0 | 650 | 3.50 |
| Envar | 30 | 16.3 | 257 | 2.53 |
| 100% PCL | 0 | 25.0 | 360 | 3.50 |
| Starch-PCL | 60 | 15.5 | 1045 | 1.68** |
| Reactive Blend | | | | |
| 100% PCL | 0 | 30.8 | 1163 | 3.50 |

* Maleated blends did not have any plasticizers while the other two blends used glycerol as plasticizer

** Starch=\$0.33/lb, PCL=\$3.50/lb, glycerol=\$0.5/lb, clay=\$4/lb (3% level), H₂O₂ (30% solution) = \$0.15/lb, ferrous sulfate = \$0.08/lb

1.5 Conclusion

The market potential of starch-polyester blends is discussed in this chapter. Various challenges in synthesizing these blends are mentioned. A brief review of existing reactive extrusion technologies and comparison with a technology developed by our group has been described. There is a need to improve the economics of biodegradable plastics. This could be done by incorporating higher levels of starch in starch-polyester matrices without compromising mechanical properties. The reactive extrusion process developed by our group can address these challenges thus improving the market potential of starch-based biodegradable plastics.

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