

CHAPTER I

INTRODUCTION

1.1 Background

The use of plastics has increased continuously and this has led to an increase in the amount of plastic waste. Disposal of plastic, especially in packaging materials, is becoming a serious problem. Conventional techniques for minimizing disposal problem of plastic waste are recycling, incineration and landfill, but they have serious limitation. Recycling is viable for high cost and low volume specialty plastics. For incineration, not only corrosive and toxic gases are produced but also high energy is required. Due to the low weight-to-volume ratio, plastics tend to occupy more space than other materials in landfill. Moreover, most plastics can not be degraded even after a period of two decades due to its high molecular weight. For this reasons, conventional methods of waste disposal are not so attractive.

In response to this concern, an interest in environmentally degradable plastics has increased. The synthesis of biodegradable polymers, with groups susceptible to hydrolysis attack by microorganisms, such as polycaprolactone (PCL), poly- β -hydroxybutyrate, and polylactic acid, was developed to replace non-biodegradable polymers. However, these polymers are much more expensive than commercial plastics by 4 to 6 times, so they are not widely used. Many research attempts has focused on the use of natural biopolymer such as starch, cellulose, chitin and chitosan, which are fully biodegradation. However, they are unsuitable for most uses in plastics because they are

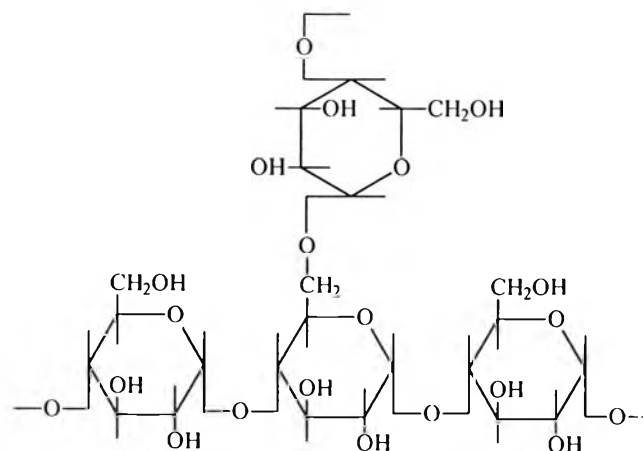
susceptible to water absorption and final products have poor physical properties. To overcome these problems, modification by changing their hydrophilic character to hydrophobic is required. But in most cases, these modified biopolymers retard the biodegradation rates and the cost of modification is high.

Another possible way of increasing susceptibility to environmental degradation of synthetic polymers, at least partly, is the biodegradable filler-filled synthetic polymer. Griffin (1973) was one of the first researchers who proposed idea to increase the degradability of the blends by using starch as a filler in the blends with polyethylene. In the degradation of the blends after this blends are deposited in the environment, various microorganisms consume the starch with leaves many holes on their surface. This results in easier disintegration of the blends into small pieces. It also increases the surface area accessible to oxygen, moisture and microorganisms. Then, the oxidative degradation of polymer matrix and the biodegradation of starch inside are facilitated. The works of Griffin stimulated interest in the use of starch as biodegradable fillers for polyethylene.

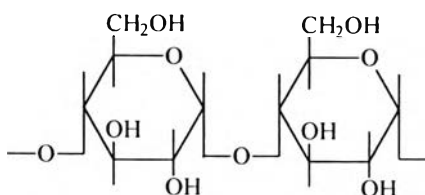
1.2 Starch

Starch is produced by plants and stored in the form of granules. The granules may vary in size from 3 to 50 μm , depending on source of plants. It is fully biodegradable natural raw material that is abundant, inexpensive and renewable.

The basic repeating unit of starch involves the linkage of two D-glucose molecules with acetal linkage. The two major components in starch are amylose and amylopectin which are different in structure.



(a) Amylopectin



(b) Amylose

Figure 1.1 Chemical structure of starch

Amylopectin is the major components, typically ranging from 70-80 %. It is a branch of α -D-(1,4) glucan which has α -D-(1,6) linkage at branch points. Its average molecular weight is about 10 million. The chains of amylopectin are associated as double helices packed in cluster.

Amylose is a linear α -D-(1,4) glucan shaped in the form of a helix and has an average molecular weight about 500,000. The small amount of lipids present in starch are complexed in the cavity of this helix, which is called V-type crystal structure.

Starch granule contains crystalline in amylopectin component and amorphous in amylose component. It is hydrophilic since each starch

monomer unit contains three free hydroxyl groups. Consequently, it changes moisture content as relative humidity changes. By itself, it is unsuitable for most uses as plastic because of its poor mechanical properties and dimension stability.

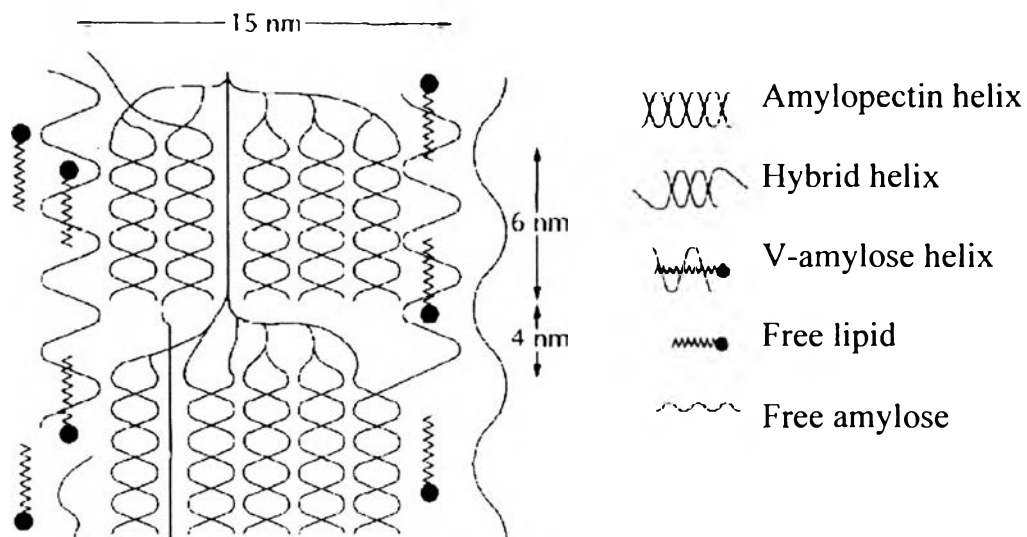


Figure 1.2 Model of starch crystallite

1.3 Polyethylene

Polyethylene is a suitable material for blending since it is widely used as packaging plastics. It is one of the largest commodity plastics, manufactured by ethylene polymerization. The characteristics of polyethylene which lead to its widespread uses are low cost, easy to process, excellent moisture barrier properties, and good chemical resistance. Polyethylene films are a rapidly growing application, replacing paper and glass. Polyethylene bags are popular in fast-food outlets, supermarkets, and department stores. However, its degradability is very low because of its high molecular weight, water resistance and low surface area to volume ratio.

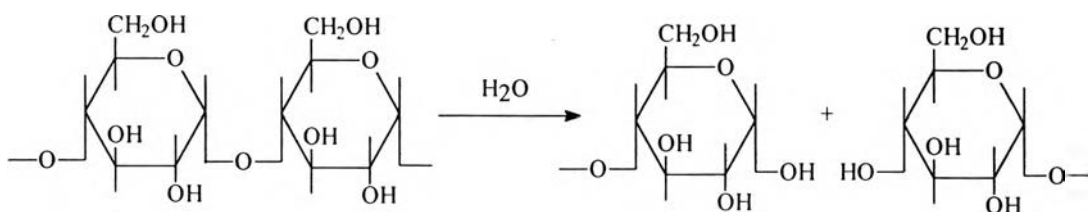
1.4 Polymer Degradation

Polymer degradation is used to denote changes in physical properties caused by chemical reaction (Schnabel, 1981).

1.4.1 Enzymatic Degradation of Starch

Generally, microorganisms produce enzyme involving in the chemical mode of degradation and attack natural polymers. The attack is specific with respect to both the enzyme and biopolymer couple. Thus the formation of specific decomposition products can be predicted.

It is well known that α - and β -amylase are enzymes which active towards starch, one type of polysaccharides. Amylose and amylopectin of starch can be hydrolyzed by the enzymes as in scheme 1.1.



Scheme 1.1 Hydrolysis reaction of starch catalyzed by amylase.

α -Amylases hydrolyze (1-4) linkage and attack starch at random points. The products are dextrans, disaccharide and glucose. β -Amylases also hydrolyze (1-4) linkage but attack specifically only at the end of chain removing successively maltose molecules.

1.4.2 Degradation of Synthetic Polymers

Studies of synthetic polymer degradation in the natural environment have shown that it occurs in 2 stages. In the first stage, heat

and/or ultraviolet light cause oxidative degradation leading to chain scission. After that, in the second stage, microorganisms biodegrade the oligomeric chain formed in the first stage. It means that in order for biodegradation to be possible in synthetic polymer, oxidative degradation must take place to reduce molecular weight to value where microorganism attack can occur (Bikiaris, 1997). Schnabel (1981) reported that microbial degradation was observed with linear paraffins with molecular weight up to 450.

The degradation of the blends in the environment may occur by many mechanisms, including biodegradation, photo and thermal oxidation. The combination of many mechanisms has synergistic effect on the degradation rate (Erlandsson, 1997). In an active compost environment, the temperature reaches up to 70°C for the first few days and falls to about 50°C after 2 months (Bikiaris, 1997). In this conditions, the thermooxidative degradation of polymer matrix is accelerated. This fact leads to the idea of using prooxidant which catalyzed the thermooxidative degradation.

Frequently used prooxidants are a transition metals surfactant such as cobalt stearate and zinc stearate. Autooxidants which contain unsaturated sites are easy to oxidation. The oxidation of double bonds in unsaturated compounds may facilitated the oxidation of polymer matrix. In Griffin's patent (1988,1993), prooxidant system, prooxidant and autooxidant, was added in the starch-filled PE blends to enhance the degradation of PE. The objective of this work is to achieve both biodegradation of starch and thermooxidation of PE.

In this present study, the degradation of tapioca starch-filled PE blends containing prooxidant, autooxidant and compatibilizers was investigated. The degradation procedures performed were both enzymatic degradation and thermooxidative degradation. Three types of compatibilizers, including poly(ethylene-*co*-acrylic acid) (EAA), poly(ethylene-*co*-vinyl acetate) (EVA), and

polyethylene-*graft*-maleic anhydride (PE-*g*-MA), were studied. Zinc stearate was used as a prooxidant and natural rubber was used as an autooxidant. Natural rubber was chosen because it contains unsaturated bonds. It was expected that the combined accelerating effects would produce faster thermooxidation of the blends.

1.5 Objective

- To study the effect of prooxidant on the thermooxidation of PE.
- To study the effect of autooxidant and combination of prooxidant and autooxidant on the thermooxidation of PE.
- To study the starch and volume of starch on the thermooxidation and biodegradation of the blends.
- To investigate the changes in microstructure of PE/starch blends after biodegradation.
- To study the effect of preheat treatment on the percentage of starch hydrolysis.