CHAPTER I

INTRODUCTION

1.1 Plastics

During recent decades there has been a continuous increase in the use of commodity plastics for packaging applications and this has led to an increase in the amount of plastic waste. The low density plastic waste has affected the overall composition of municipal solid waste and caused an undesirable increase in the volume/weight ratio of garbage. Furthermore plastic waste may represent an undesired pollutant in many ecosystems (i.e. to soil, freshwaters and marine habitats) because they are generally inherently inert to attack by microorganisms or by chemicals in the environment. Conventional garbage disposal methods such as incineration, landfill and recycling have serious limitations, as follows:

1.1.1 Incineration

Incineration of high calorific waste materials requires high capital cost to operate and maintain. Equipment must be able to resist the corrosion caused by HCl produced from the burning of polyvinyl chloride articles, and also perform the scrubbing of exhaust gases to meet atmospheric purity standards (Huffman, 1973). Because of the high capital costs, the emission of corrosive and toxic gases and the need for high temperatures, this method of waste disposal is rarely used today.

1.1.2 <u>Landfill</u>

Landfill is the most common method of municipal solid waste disposal practiced today. There are two main techniques for landfilling: open dumping and sanitary landfill.

1.1.2.1 Open Dumping. Open dumping was the original method of waste disposal. In this method refuse is deposited in an open area and allowed to decompose. Its sole advantage, relatively low disposal costs, is far out-weighed by the disadvantages, namely odor, the scattering of lightweight waste materials by the wind, and the presence of rats and mice. Open dumping is still being practiced, but its importance is diminishing.

1.1.2.2 Sanitary Landfill. Sanitary landfill is a modern method of landfilling. It is a method of disposing of refuse on land without creating nuisances or hazards to public health or safety. The method utilizes the principles of engineering to confine the refuse to the smallest practicable land area, to reduce it to the smallest practicable volume and to cover it with a layer of earth at the conclusion of each day's operation or at more frequent intervals as may be necessary (Pavoni, 1975). Sanitary landfill is a low-cost method of disposal, but under certain conditions the burial of solid waste has the potential for chemical and/or bacteriological pollution of ground and surface water. The method of disposal must be designed to enable methane and other gases in sanitary landfills to escape into the atmosphere. If the escape of gas is prevented, it might find its way into sewers serving homes in the area, thus causing potential explosions. A drawback of this method is that it results in a reduction in available landfill space.

1.1.3 <u>Recycling</u>

Recycling is, at present, only viable for high cost, low volume specialty plastics. Some polymers used for packaging, notably polymethylmethacrylate and polystyrene, can be readily depolymerised by

heating, leading to the recovery of a substantial proportion of the original monomers. However, these polymer types form only a minor part of the polymer waste stream. The major generic polymer types, notably polyethylene, polypropylene and poly(vinyl chloride), do not yield monomer but low molecular weight fragments which have little value other than as fuel. In addition, PVC presents its own particular problem, both in pyrolysis and on combustion, due to the formation of highly-corrosive HCl gas which rapidly corrodes the recycling plant. There are two serious technical problems involved in the reprocessing of plastic waste. The first is the adverse effects of incompatible impurities (other polymer types, paper, metal foil, etc.) on the mechanical properties of recycled products. The second is the degradation that occurs to the polymers due to the additional heating involved in the recycling of the plastic. This may lead not only to inferior initial properties, but the long-term performance of recycled products may be inadequate for their new use.

For the above reasons, conventional methods of waste disposal are not so attractive. Therefore, there has been increasing interest in environmentally degradable plastics. A degradable plastic is defined as *a plastic which is designed to undergo a significant change in its chemical structure under specific environment conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the polymer and the application in a period of time that determines its classification* [American Society for Testing and Materials (ASTM 1991)]. Various approaches have been considered to render synthetic plastics degradable. Photodegradable polymers are produced by introducing chromophores by copolymerization (e.g. ethylene and carbon monoxide) or by mixing photosensitive additives (ketone based compounds) with the polymer. Aliphatic polyesters and their derivatives have been synthesized to obtain new biodegradable polymers. These new synthetic materials are often too expensive for nonmedical use and,

so, for nonmedical applications, the modification of traditional synthetic polymers is usually adopted. Natural polymers containing hydrolysable groups have been mixed with polyolefins to introduce biodegradability (Omichi, 1992).

An extensive search of potential biodegradable fillers for thermoplastics led to the discovery of starch as a cost effective additive. Starch satisfies the requirements of adequate thermal stability, minimum interference with melt properties and disturbance of product quality. Starch is a native agricultural product, thus the replacement of wholly petroleum-based plastics with starch-filled plastics should help conserve petroleum for other uses.
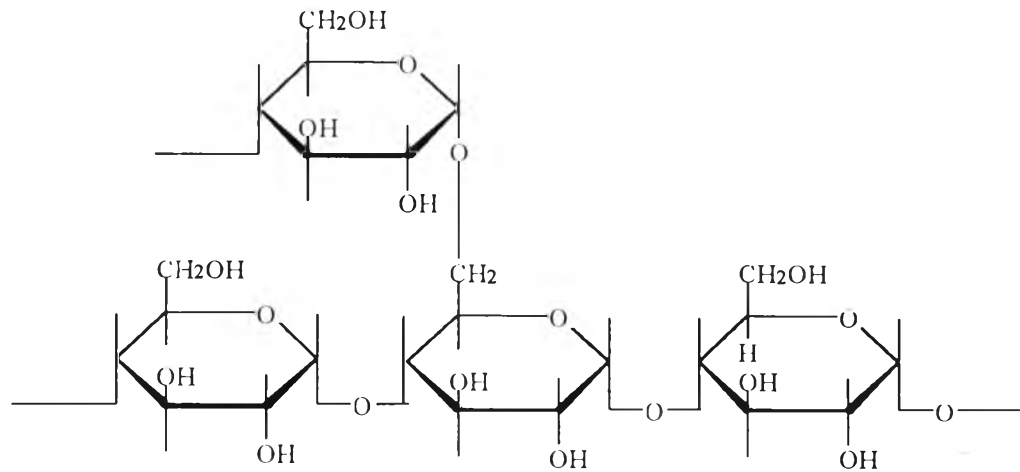
1.2   Starch

Starch is a complex mixture of glucans, which may be envisioned as condensation polymers of glucose molecules connected by acetal linkages. Its two major components are a mostly linear α-(1-4)-D-glucan termed amylose and a highly branched α-(1-4)-D-glucan termed amylopectin, which has α-(1-6) linkages at the branch points (Fig. 1.1). The linear amylose molecules of starch have molecular weights between 0.2 - 2 million, while the branched amylopectin molecules have molecular weights as high as 100 - 400 million (Otey, 1984).

Starch granules are hydrophilic since each starch monomer unit contains three free hydroxyl groups. Consequently, starch exhibits different moisture levels as the relative humidity changes. Cornstarch granules retain about 6% moisture at 0% relative humidity (RH) but about 20% moisture when in equilibrium at 80% RH.

CH2OH structure
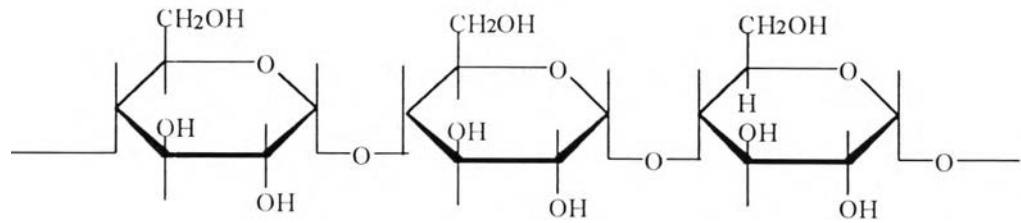
AMYLOSE - Linear Polymer

AMYLOPECTIN - Branched Polymer

Figure 1.1 Chemical structure of the components of starch.

Starch granules are thermally stable when the granules are heated in an open atmosphere to about 250°C. Above this temperature the starch molecules begin to decompose. Dry starch granules absorb moisture when immersed in water but retain their basic structure due to crystalline and hydrogen-bonded structures within the granules. Native granular starch contains crystalline areas within the amylose (linear) component but the branched amylopectin is largely amorphous and can be mostly extracted in cold water. The granular structure is ruptured by heating in water or treating with aqueous solutions of

reagents that disrupt the crystalline areas and hydrogen bonding within the granules. The constituent molecules become completely soluble in water at 130°C to 150°C and at lower temperatures in alkaline solutions. Starch granules that have been ruptured in aqueous media are said to have been 'gelatinized'. The application of high pressure and shear conditions to starch granules permits disruption of organized structural features at lower water contents than if possible at atmospheric pressure.

1.3   Degradation of Starch-Based Plastics

Starch is an inexpensive material and is readily available from corn and other crops. Starch is totally biodegradable in a wide variety of environments and could permit the development of totally degradable plastic products for specific market demands. Degradation or incineration of starch products would recycle atmospheric CO_2 trapped by starch-producing plants and would not increase potential global warming (Bagley, 1977). All these reasons have caused great interest in starch-based plastics in recent years. Two different technologies for the production of starch-based plastics are currently being studied. The first one uses gelatinized starch mixed with poly(ethylene-co-acrylic acid) (EAA) to produce blends. The second approach utilizes native or modified granular starch as a filler in formulated degradable masterbatch products.

1.3.1   Gelatinized Starch

Starch can be made thermoplastic by plasticization with water at elevated temperatures and pressures and, by this means, starch can be melt processed and melt blended with other thermoplastics. That is, the melt transition of the crystalline component of starch, amylose, can be strongly

depressed with good solvents such as water, and processed at temperatures well below its thermal degradation temperature. Other effective plasticizers for imparting melt processibility include a variety of low molecular weight compounds, such as glycerol and diethylene glycol, and also polymers such as poly(ethylene-co-vinyl alcohol). Gelatinized starch, if dried during processing of the plastic composite, may also serve as a particulate filler in plastics. Alternatively, starch may be plasticized with low levels of water (5-20%) and compatibilized with the other polymers to become a part of the connective matrix of the plastic. This type of thermoplastic starch product is exemplified by the starch-poly(ethylene-co-acrylic acid)(EAA) products extruded by Otey *et al.* (1984).

Otey *et al.* developed a process for incorporating gelatinized starch into either a copolymer of ethylene and acrylic acid (EAA) or a combination of EAA and polyethylene. Addition of ammonia increased the compatibility between the starch and the EAA, resulting in enhanced film tear propagation resistance and reduced aging phenomena due to segmental motions in the amorphous starch. Films were formed by either casting or simple extrusion of the starch-EAA composites. Both of these processing methods are relatively slow and are therefore considerably more expensive than the more conventional extrusion blowing technique. The relatively high processing costs coupled with the high price of EAA, compared to PE, has tended to diminish this composition's potential for achieving large-scale commercial success. Also, at certain starch levels needed to achieve desired mechanical properties, the optimum degrees of biodegradability and ultraviolet (UV) stability are compromised. The sensitivity of the materials to environmental changes, in particular the susceptibility to tear propagation, precludes their use in most packaging applications. Moreover, EAA is entirely non-biodegradable.

Another processing method of gelatinized starch includes premixing film formulations with excess water (maximum 50% solid concentration) at 90 - 100°C in a heavy duty Banbury mixer or Sigma type mixer for 45 min. This method is cheaper than that with aqueous dispersion using EAA pellets. The doughlike product is repeatedly extrusion-processed into strands until the moisture content is less than 5 - 10%, and then blown into film. Addition of an alkali such as ammonium hydroxide is essential for good quality. Here, starch can be added up to 50 - 60%. This premixing of starch and EAA can be avoided by incorporating urea. This reduces the amount of water as well as the time needed to gelatinize the starch. Using this technique, blown film with a lay flat width of 305 mm have been produced.

1.3.2 Granular Starch

The use of a biodegradable filler such as granular starch in an inert polymer can result in the degradation of the starch alone. The behavior of the starch depends largely on the amount incorporated. Wool and co-workers (1991) have calculated a threshold concentration (the percolation threshold) above which continuous biodegradation takes place leaving behind a disintegrated polymer matrix. Below the percolation threshold, microbial invasion is principally limited to surface or near-surface accessible particles. This does not immediately lead to disintegration of the LDPE matrix but it does leave it mechanically weakened. The surface area and oxygen permeability increase and this can improve further degradation of LDPE matrix. Oxygen is usually insoluble in the crystalline regions of polyolefins and oxidation will therefore be confined to the amorphous phases between the crystallites. Oxidation (photo, thermal, chemical etc.) increases biodegradation by breaking bonds, increasing the surface area, causing embrittlement, and increasing hydrophilicity, that are factors which enhance the rate of degradation of the materials.

Griffin (1993) invented a system that combines several potential degradation agencies such as photo-oxidation, thermal oxidation and biodegradation. His degradable polymer composition comprises a blend of a normally stable chemically saturated polymer, a less stable chemically unsaturated compound in the form of a polymer or copolymer, an antioxidant that will be active over a limited period and a latent transition metal salt. The presence together of the antioxidant and the prooxidant gives rise to a period of induction before a sharp loss of physical strength occurs, whereby the period of induction can be exploited as the effective working lifetime of the polymer composition. The polymer composition preferably also includes filler particles of a directly biologically sensitive material such as natural granular starch.

The stable polymer is preferably a polyethylene such as low-density polyethylene, linear low-density polyethylene or high-density polyethylene. The associated unsaturated compound may be an elastomer of the type made by the polymerization of a 1,4 diene, or the copolymerization of a 1,4 diene with an ethenoid comonomer. The unsaturated polymer can be natural rubber, e.g. brown or pale crepe Hevea rubber or gutta percha, or a particular styrene butadiene elastomer, e.g. Stereon which not only provides adequate levels of autoxidizable unsaturation but also greatly enhances some of the physical properties of the final product especially the impact strength.

Transition metal salts used are salts formed by combining a transition metal such as cobalt, manganese and copper with an organic acid of sufficiently high molecular weight to give a salt which is soluble in the host polymer blend. The term "transition metal" means an element having greater than 8 and less than 18 electrons in the outer group of electrons. Transition of electrons in the outer shells and the resulting variable valency states render them capable of inducing oxidation reactions. In practice, those transition elements which are highly toxic and radioactive are extremely rare and costly

and therefore are not normally encountered in industrial uses as oxidation catalysts. Typical transition metals whose salts and complexes do feature in such applications and could be considered for use in carrying out the present invention are Ce, Zn, Cu, Ag, Ni, Co, Fe, Mn, Cr, and V. The transition metal would be used in the form of a salt in order to display an adequate level of solubility in the polymer matrix. The organic portions of these salts are typically stearates, palmitates, oleates, behenates, myristates, erucates, linolates, naphthenates, acetonylacetates, 8-hydroxyquinolinates and metalammine salt complexes.

The degradation of a polymer may proceed by one or more mechanisms, including biodegradation, chemical degradation, photo and thermal oxidation, depending on the ambient environment and particular application. The combination of different environmental factors such as sunlight, heat, oxygen, humidity, microorganisms, etc., can produce synergistic effects on the degradation rate of starch-based plastics.

The granular starch present on the surface of a polymer film is attacked by microorganisms such as fungi and bacteria, until most of the starch is assimilated as a carbon source. This weakens the polymer matrix and increases the surface to volume ratio, hydrophilicity and permeability of the film.

Other environmental factors, such as oxygen, sunlight and heat, trigger autoxidation of chemically unstable prooxidants, generating free radicals which attack the molecular structure of the polymer. The molecular weight of the polymer chain is thereby reduced until, ultimately, a level is reached at which consumption by microorganisms can take place at a significant rate.

This research studied the degradation of tapioca starch-based HDPE blends containing natural rubber and zinc stearate as a prooxidant. The degradation of these polymer blends can occur due to the combination of several mechanisms such as thermal oxidative degradation and biodegradation.

An incentive for this research project is the utilization of agricultural products produced in Thailand as fillers in plastics in order to reduce cost and to enhance degradability of plastic products. The agricultural products used for this research are tapioca starch and natural rubber.

1.4   Objectives

- To study the effect of starch and prooxidant additive on the degradation of starch-based HDPE blends.
- To study the degradation of the polymer blends containing different percentages of starch.
- To investigate the changes in morphology, chemical and mechanical properties of the polymer blends after degradation.