

## CHAPTER I

### INTRODUCTION

The ever-growing production and use of synthetic polymers have led to a deterioration of the waste disposal problem after their use, since most of them are not degraded when exposed to the environment. So there has been a growing interest in developing new materials based on renewable and degradable polymers. These materials could be used as substitutes of products made of non-renewable synthetic polymers.

Starch is an attractive and cheap alternative in developing degradable materials. In the early 1970s, Griffin proposed the idea of using starch as a filler in polyethylene in order to increase the degradability of the resulting material. Most of starch applications in the field of polymer blends, however, are focused on polyethylene because it is widely used as packaging material and as film in agricultural applications.

Starch has been considered as a candidate in certain thermoplastic applications because of its known degradability, availability, and low cost. The polyethylene/starch blends were proposed for applications such as agricultural uses and disposable packaging, where deterioration of physical properties occurs as starch degrades (Otey and Mark, 1976). Consumption of accessible starch by microorganisms when polyethylene/ starch blends are placed in a suitable environment can occur. Removal of starch presumably leaves a porous structure of residual components that are normally non-biodegradable. The increasing of surface area of polyethylene residue may speed its degradation by environmental factors (Bastioli *et al.*, 1991).

Since Griffin has reported the use of starch as a filler to facilitate the decomposition of polyethylene in 1973, many researchers have continuously studied on blending of starch with synthetic polymers. Most studies

investigated on mechanical properties of the blends of starch and polyethylene. It was found that addition of starch to the polyethylene film resulted in decreasing of mechanical properties in the blend film (Willett, 1994). Moreover, increasing the amount of starch, in order to increase degradability of the blends, causes a decrease in mechanical properties. The reason for this is incompatibility and poor adhesion between starch and polyethylene due to the different polar character of these two components. Starch has hydrophilic nature while polyethylene has hydrophobic nature.

A way that can increase compatibility of polyethylene/starch blends is the use of a compatibilizer containing functional groups that are miscible with both polyethylene and starch. Otey *et al.* (1979) discovered that compounds of ethylene-acrylic acid copolymer (EAA) and starch could be formed into films that were flexible, water-resistant, heat stable and biodegradable. Then they developed a process for incorporating starch into a copolymer of ethylene and acrylic acid (EAA) or a combination of EAA and polyethylene. Either casting, simple extruding, or milling the starch-EAA composites were used to produce films. The processes were relatively slow and expensive in comparison with the more conventional extrusion blowing technique. Films produced by this technology yielded a uniform distribution of starch particles throughout the polymer matrix. These films typically contained 30-60% starch by weight. The degree of transparency, resistance to UV radiation, flexibility and tensile strength all decreased with an increase in the proportion of starch used. Shogren *et al.* (1992) studied on compatibility of starch/EAA/ LDPE blends and found that part of the polar portion of EAA interacted with starch while part of the hydrocarbon portion interacted with LDPE. From this reason, the starch/EAA/LDPE blends had good compatibility. Prinos *et al.* (1998) reported that ethylene-vinyl acetate copolymer could be used as a compatibilizer for LDPE/starch blends. The advantage of using this copolymer was that when it was used in high concentration, the elongation of the blends

was superior even to that of LDPE. This means that higher amounts of starch can be used for blend preparation with satisfactory mechanical properties. Bikiaris *et al.* (1998) found that LDPE/starch blends containing high amount of starch, which still retained high extension in mechanical properties of LDPE, could be prepared by using the polyethylene-graft-maleic anhydride copolymer as a compatibilizer.

Problems of using starch as filler in polyethylene blends are a decrease in mechanical properties and an increase in water absorption of the polymer blends. In addition, from research works in the past, the researchers used different types of starch and processing condition so it is difficult to compare the effectiveness of different types of compatibilizer. In this study, three different compatibilizers, which were poly(ethylene-co-acrylic) (EAA), poly(ethylene-co-vinyl acetate) (EVA), and poly(ethylene-graft-maleic anhydride) (PE-g-MA), were used in HDPE/starch blends in order to compare the effectiveness of these compatibilizers on the improvement of mechanical properties and the reduction of water absorption of the blends by using the same condition of fabrication. The mechanical properties and water absorption of the blends were studied as functions of starch and compatibilizer contents.

## Theoretical Background

### 1.1 High Density Polyethylene

High density polyethylene (HDPE) is a thermoplastic polyolefin produced either by Ziegler-Natta catalyst or by metal oxide catalyst, usually referred to as Phillips catalyst. As the name implies, the polymer chains in HDPE can easily pack tightly and crystalline structures are formed, thus increasing the density. HDPE has a density of 0.935 - 0.960 g/cm<sup>3</sup>.

HDPE is one of the largest commodity plastics. The characters of HDPE resulting in strong market acceptance of molded and extruded products are:

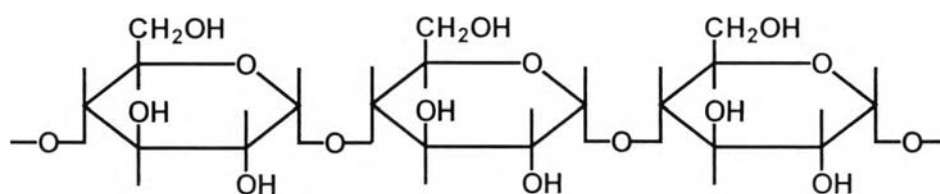
- Low cost
- Easy processability
- Good mechanical properties
- Good chemical resistance
- Good electrical insulation properties
- Good moisture barrier properties

In the field of application, HDPE can be produced into blow molding, injection molding, film, sheet, pipe, etc. The products manufactured from blow molding, which is the largest application are bottles (especially for milk, fruit juice, and household chemical), toys, cans, drums, containers, and fuel tanks. The second largest application, injection molding products are housewares, toys, food containers, pails, crates, and cases. Film products being a rapidly growing application are grocery bag films, shrink films, agricultural films, and packaging films. Pipe and conduit represent another important application. Examples are water pipes, gas pipes sewer pipes, and industrial pipes.

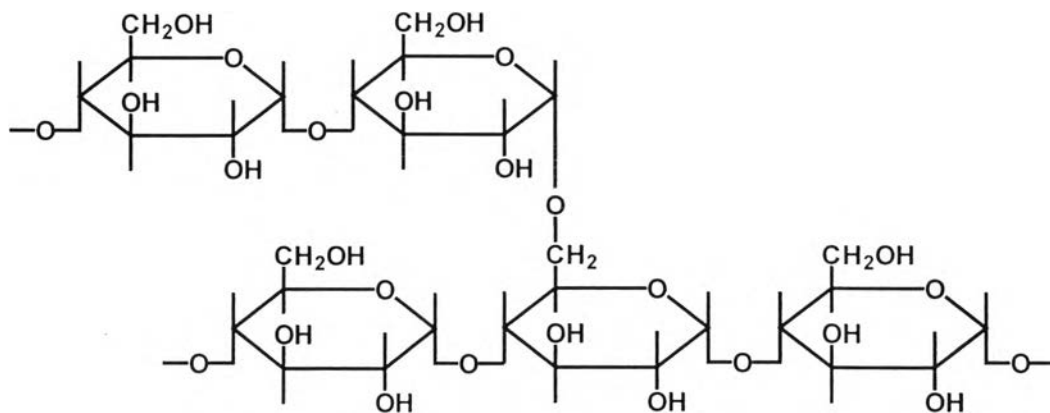
A significant part of used HDPE is collected from consumers for recycling. It is due primarily to its ability to be reprocessed readily with minimal decreasing of its properties. Uncollected HDPE can be disposed of by incineration and landfill. When HDPE products are incinerated in municipal facilities, HDPE produces a large amount of heat and toxic chemicals leading to public concern over these hazard emissions. In landfill, it is completely inert, degraded very slowly, and does cause the solid waste problems.

## 1.2 Starch

Starch being the major form of carbohydrate storage in green plants, is a form of macromolecules composed of thousands of small glucose molecules. It is composed of amylose (linear structure) and amylopectin (branched structure) units. Amylose is a linear polymer of  $\alpha$ -D-glucopyranosyl units with (1,4) linkage. Amylopectin is a highly branched polymer of  $\alpha$ -D-glucopyranosyl units containing (1,4) linkage and (1,6) linkage at the branch point.



**Figure 1.1** Structure of amylose.



**Figure 1.2** Structure of amylopectin.

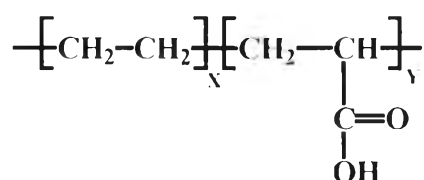
The molecular weights of amylose and amylopectin in the starch are normally in the order of several hundred thousands and several millions, respectively. Starch is found in a granular form, in which amylopectin and possibly amylose molecules are radially arranged towards the granular surface. The starch granules may vary in size from 3 to 50  $\mu\text{m}$ , depending on the source plant. Commercially important starches come from corn, rice, wheat, potato, and tapioca. The major source of commercial starch here in Thailand is tapioca.

### 1.3 Compatibilizer

Compatibilizer is an additive used to improve the compatibility of polymer blends. Compatibilizers used to increase compatibility and adhesion between starch and polyethylene must have two parts in their molecular structures: polar part and hydrocarbon part. Polar part acts as the hydrophilic portion, which can introduce hydrogen bonding between hydroxyl group of

starch and carbonyl group of compatibilizer. Hydrocarbon part acts as the hydrophobic portion, which can have good miscibility with polyethylene

### 1.3.1 Poly(ethylene-co-acrylic acid): EAA

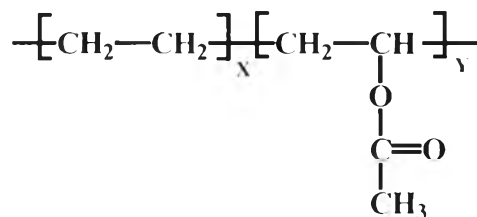


**Figure 1.3** Structure of EAA showing its repeating units.

Acrylic acid is a monomer used in copolymerization with ethylene. Acrylic acid contains a group that is called an organic acid that will easily give a proton to a chemical that can accept the proton. The acid group is pendent off the backbone. The backbone is formed from a carbon-carbon double bond by addition polymerization. The two monomer types (ethylene and acrylic acid) react to give copolymers.

As would be expected from the presence of a polar pendent group, the bondability of EAA is much higher than polyethylene. Crystallinity is lower in EAA than in polyethylene and so film clarity of EAA is higher than that of polyethylene. Acrylic acid increases the adhesiveness of polyethylene when present in ethylene copolymer so EAA is tougher than polyethylene. EAA films are more resistant to oils and greases than polyethylene but are more permeable to water vapor.

### 1.3.2 Poly(ethylene-co-vinyl acetate): EVA



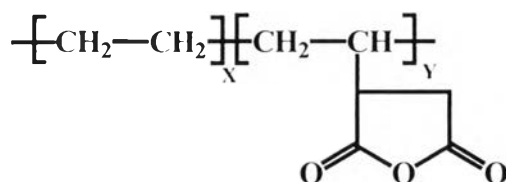
**Figure 1.4** Structure of EVA showing its repeating units.

The vinyl acetate monomer contains a carbon-carbon double bond and a pendent group with several atoms, some of which have significantly different electronegativities so parts of the pendent group are highly polar. The vinyl acetate monomer reduces crystallinity in the copolymer (because of steric interactions with the bulky pendent group) and increases the chemical reactivity of the polymer because of the regions of high polarity. The net result is a very flexible copolymer that bonds well to many other materials. The higher polarity of the copolymer increases the tendency of the material to attract itself and other polar materials. This attractive nature is called cling.

The polarity also changes the permeability of the material. EVA films are much more permeable to water and other polar materials but are better barriers to oils and other nonpolar substances when compared to polyethylene homopolymer. The optical clarity of EVA is better than polyethylene film because of the reduce crystallinity. Commercial concentrations of vinyl acetate groups in the copolymer are 5 to 50 %, with 5 to 20 % being the largest product group. At these concentrations, the costs are still low, bonding properties are excellent, and flexibility is good but the material is not to soft.



### 1.3.3 Poly(ethylene-graft- maleic anhydride): PE-g-MA



**Figure 1.5** Structure of PE-g-MA showing its repeating units.

Anhydride functionality can be incorporated into a polymer by copolymerization or grafting of anhydrides like maleic anhydride. Maleic anhydride can be grafted with relative ease onto many polymers at normal melt processing temperatures. Maleic anhydride is a high polarity pendent group of this copolymer.

## 1.4 Mechanical Properties

The mechanical properties are important properties for plastic applications because plastic materials are used according to their desirable mechanical properties. Investigation of mechanical properties readily brings out characteristics of elasticity, plasticity, and strength.

### 1.4.1 Tensile properties

Testing of tensile properties is probably the most widely used short-term mechanical test of all. This is because it is relatively easy to perform, gives reasonably reproducible results and yields a great deal of information. From this test one can obtain not only tensile strength, but also elongation and modulus.

Tensile properties are determined by stretching a test specimen at a constant rate and measuring the corresponding load applied. The resulting

stress (or load applied) is measured and recorded as a function of strain (or elongation). The stress, strain, and modulus are defined mathematically by:

$$\text{Stress} = \frac{\text{Load applied on specimen}}{\text{Cross - section area of specimen}}$$

$$\text{Strain} = \frac{\text{Increase in length of specimen after stretching}}{\text{Original length of specimen}}$$

$$\text{Modulus} = \frac{\text{Stress}}{\text{Strain}}$$

Tensile strength is the maximum tensile stress, which a material is capable of supporting. If the tensile strength occurs at the sample's yield point, this stress is designated as the tensile strength at yield. If it occurs at the sample's break point, it is then designated the tensile strength at break. The tensile strength at yield of a ductile material, which corresponds to the onset of significant permanent deformation, is often the limiting stress for applications, rather than the tensile strength at break which corresponds to the actual rupture of the test specimen.

The percentage of elongation at break is the ratio, expressed in percentage, of the extension (change in gauge length) at break point to the original gauge length multiplied by 100.

#### 1.4.2 Flexural Properties

Flexural properties are usually measured in order to obtain a measure of stiffness or rigidity. Often measured by applying a stress at the center of a rectangular bar, which is supported at two other points: that is, three-point loading is applied in a bending test. During the test, the force applied and the

deflection, which results is measured and the test is easily performed on a universal testing machine. From this measurement, flexural strength and modulus are determined.

Flexural strength is the maximum stress developed when a rectangular bar test piece is subjected to a bending force perpendicular to the bar. The flexural strength (  $S$  ) is calculated from the following expression:

$$S = \frac{3PL}{2bd^2} \quad (1.1)$$

where  $P$  is the load at a given point (N)

$L$  is the length of support span (mm)

$b$  is the width of the bar (mm)

$d$  is the depth of the bar (mm)

The following expression can be used to obtain the maximum strain (  $r$  ) of the specimen under test:

$$r = \frac{6Dd}{L^2} \quad (1.2)$$

where  $D$  is the deflection under load  $P$  (mm)

Flexural modulus, which is a measure of bending stiffness, can be obtained by plotting flexural stress (  $S$  ) versus flexural strain (  $r$  ) during the test and measuring the slope of the curve obtained.

### 1.4.3 Impact Resistance

A traditional measure of the fracture behavior of a material is the impact test. This is commonly used to assess the impact resistance of the

material. The impact property of the material is directly related to the overall toughness that indicates the ability of the material to absorb applied energy. The specimen used in the test is usually notched to provide a stress concentration area that promotes a brittle rather than a ductile failure. Usually a molded, notched bar is used and this supported bar is struck by a swinging pendulum: the energy absorbed in breaking the bar is measured. In general, there are two types of impact test; Izod impact and Charpy impact.

The Izod impact test is the most widely used impact resistance test for plastic. The Izod test bar is held vertically by gripping one end in a vice. The other free end is then struck on the same side as the notch, at a specified height and speed, with a swinging pendulum. The results are often reported in  $\text{kJ/m}^2$  and in this system the energy to break the specimen is divided by the area fractured: if a notched sample is used the fracture area is obtained by multiplying the width of the specimen by the depth behind the notch.

Some plastics are "notch sensitive". This means that the recorded impact resistance is very dependent on the notch tip radius. The notch dimension varies from one standard to another so it is essential that the standard employed is quoted.

### **1.5 Microstructure**

Microstructure of materials must be understood in order to develop relationships between the structure and properties of materials. The morphology of polymer blends is determined by a wide range of electron microscope techniques. In polymer blends system, the micrographs can illustrate the dispersion of dispersed phase and the adhesion between dispersed phase and continuous phase.

## **1.6 Water absorption**

Water absorption characteristics of plastics depend largely upon the basis type and final composition of a material. For example, materials containing only hydrogen and carbon atoms such as polyethylene are extremely water-resistance. This property can be altered by the addition of additives such as fillers. Starch is the filler that shows a greater affinity to water so it can affect the water absorption property of the polymer blends. Consequently, the water absorption of the polymer blends should be investigated for the application of a finished product.