CHAPTER I
INTRODUCTION

In recent years, a variety of environmental issues related to solid waste disposal has gained attention. The increasing fraction of solid waste attributed to commodity polymers and their generally low degradability upon disposal have been a cause of growing concern (Sagar and Merrill, 1995). New trends in solid waste management and rapid changes in public legislation have led scientists to increase activities on the design of materials that are easily degraded under environmental conditions.

While natural polymers are readily decomposed in the environment, most synthetic polymers have a resistance for degradation by microorganisms in spite of their good mechanical properties. Therefore one of the solutions to achieve the promotion of the degradation of synthetic polymers, such as polyethylene, is the addition of biodegradable fillers (Griffin, 1973). The use of starch and other polysaccharides, which are available in great supply and inexpensive, as biodegradable fillers, has been conducted. It is expected that the polysaccharides portion will be degraded by microorganisms and porosity of the material will be thereby increased. The increasing of surface area will lead the material to be more susceptible to other degradation processes including thermal oxidative degradation. Also, the increasing uses of polysaccharides can reduce our dependence on nonrenewable petrochemicals from which synthetic polymers are derived.

Since Griffin has reported the use of starch as a biopolymer filler to facilitate the decomposition of polyethylene in 1973, many researchers have continuously studied on blending of biopolymers with synthetic polymers. Most studies have been investigated on mechanical properties of blends of starch and polyethylene. Otey *et al.* (1974) improved the mechanical

properties of starch and poly(ethylene-*co*-acrylic acid) blend films by adding urea and polyol. Nikolov *et al.* (1991) improved tensile strength and elongation of starch and LDPE blend films by modification of starch, but the enzyme degradation rate decreased. Bhattacharya *et al.* (1995) reported that the addition of starch to ethylene-propylene-*g*-maleic anhydride reduced in tensile strength and elongation. In previous studies, most of the blends had dealt with starch or modified starch and some of them were unsuitable for most used as the biopolymer fillers because of their hydrophilic nature and low degradability rate. Another potential polysaccharide, which has the similar chemical structure of starch, is chitin.

Chitin is one of the most abundant natural polymers. It is a major structural polymer in shellfish which obtains as a waste from seafood processing industry with an estimated 1.2×10^5 metric tons annually accessible worldwide (Makarios-Laham and Lee, 1995). Due to the plenty of chitin in nature, it is interesting to get benefit from this resource. Moreover, chitin possesses many interesting properties which made chitin be a versatile material (Muzzarelli, 1977; Rathke and Hudson, 1994). Aoi *et al.* (1995, 1997) prepared the blend films from PVA and a chitin derivative having poly (2-methyl-2-oxazoline) side chain which were miscible in the whole range of composition. Lee *et al.* (1996) reported that mechanical properties of blend films of chitin and PVA were improved as compared to those of homopolymers. Arvanitoyannis *et al.* (1997) investigated that percentage elongation of chitosan and PVA blends, plasticized with sugars, increased proportionally to the plasticizer content. Most of studies were based on PVA which have been used in medical area. However, no study has been reported on the chitin and HDPE blend.

It is expected that the addition of chitin into polyethylene may lead to the development of a new material and the effective utilization of chitin. In this study, the mechanical properties, microstructure, and water absorption

property of chitin-filled HDPE blends were studied as a function of chitin content. The properties of HDPE blended with chitin were compared to those of HDPE blended with rice starch which is known as a biopolymer filler for polyethylene.

Theoretical Background

1.1   High-Density Polyethylene

High-density polyethylene (HDPE) is defined as a product of ethylene polymerization with a density of 0.940 g/cm^3 or higher (Kroschwitz, 1997). It is a saturated linear polymer with basis structure of ethylene (Figure 1.1).
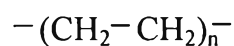

$$-(CH_2-CH_2)_n^-$$

Figure 1.1 Chemical structure of polyethylene.

The first commercial production of HDPE started in 1956 by Phillips Petroleum Company, U.S.A. It is commonly manufactured by either a slurry process or gas phase process. Nearly 90% of commodity-grade resins are produced in the gas phase process (Kroschwitz, 1997). Now HDPE is one of the largest volume commodity plastics produced in the world. World production of HDPE production is represented in Table 1.1.

HDPE is a highly crystalline, non-polar thermoplastic material. The appearance of natural HDPE is milky white with some degree of translucence in thin sections. It has excellent chemical resistance to most household and industrial chemicals. It does not absorb moisture and provides good water vapor barrier, which makes it useful in packaging applications. HDPE has good electrical properties, especially dielectric strength, making it well suited for wire and cable applications (Kroschwitz, 1997).

Table 1.1 World production of HDPE, 10^3 ton/year (Kroschwitz, 1997).

Region	1986	1989	1992
North America	3,250	4,090	4,540
Latin America	390	530	650
Western Europe	2,080	2,240	2,575
Eastern Europe	660	710	900
Far East and Australia	1,775	2,230	2,540
Middle East and Africa	420	470	530
Total	8,575	10,270	11,735

HDPE by itself is a safe plastic material on account of its chemical inertness and lack of toxicity. Consequently, film and containers made from HDPE are used on large scale in food and drug packing. Moreover, it has been used in prosthetic devices including hip and knee joint replacements. Nevertheless, HDPE presents health hazards when it burns. Heavy smoke, fumes, or potentially toxic decomposition products can result from incomplete combustion.

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 degradation of its properties and its large use in packaging applications. A typical recycling application includes 25% of recycled material, such as post-consumed recycle, with virgin HDPE, and is processed and used for nonfood contact bottles (Wolfe, 1994). Uncollected HDPE can be disposed of by incineration and landfill. When incinerated in municipal facilities, HDPE produces a large amount of heat and toxic chemicals and therefore public concern over these hazard emissions. In landfill, it is

completely inert, degraded very slowly and does cause the solid waste problems.

1.2   Chitin

Chitin is one of the three most abundant polysaccharides in nature, in addition to cellulose and starch. It ranks second to cellulose as the most plentiful organic compound on earth. It is found naturally in shell of crustaceans, cuticles of insects and in the cell wall of fungi. Typical chitin content in some species is given in Table 1.2.

Chitin,   poly-β-(1,4)-2-acetamido-2-deoxy-D-glucose,   has   the chemical structure shown in Figure 1.2. Some acetamide groups at the C_2 position are deacetylated to amino groups and it is called *deacetylated chitin*. The structures of chitin and deacetylated chitin are shown in Figure 1.2.
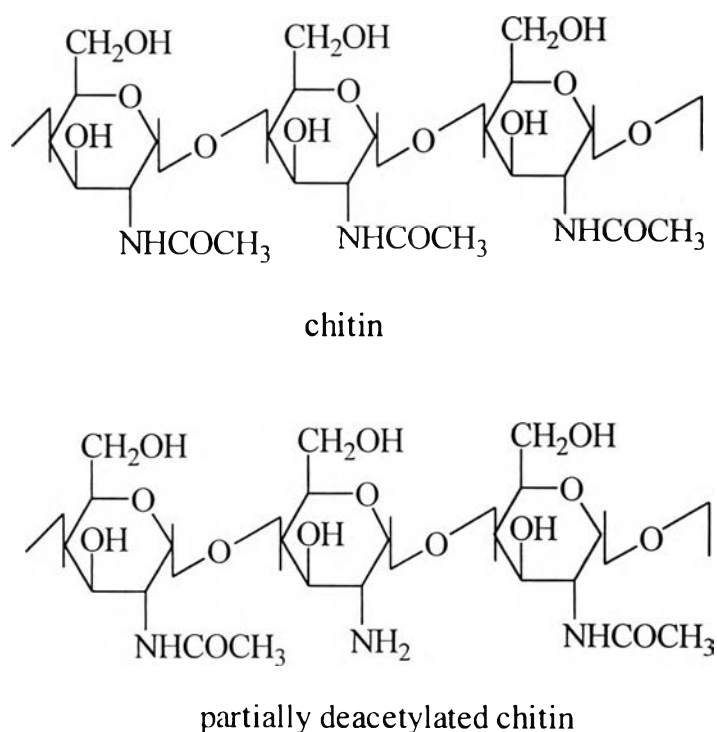
chitin

partially deacetylated chitin

Figure 1.2 Chemical structures of chitin and deacetylated chitin.

Table 1.2   Chitin content of selected crustaceans, insects, molluscan, and fungi (Campbell *et al.*, 1986).

Organism	Chitin content, wt%
Crustaceans	
Cancer (crab)	72.1^c
Carcinus (crab)	$8.29^b, 64.2^c$
Callinectes (blue crab)	14^a
Crangon (shrimp)	$5.8^b, 69.1^c$
Alaskan shrimp	28^d
Nephrops (lobster)	69.8^c
Insects	
Blattella (cockroach)	$10^b, 18.4^c$
Bombyx (silkworm)	44.2^c
Coleoptera (beetle)	$5\text{-}15^b, 27\text{-}35^c$
Grasshopper	$2\text{-}4^a, 20^c$
Spider	38.2^d
Molluscan (Organs)	
Krill, deproteinized shell	40.2
Squid, skeletalpen	41.0
Oyster shell	3.6
Clamshell	6.1
Fungi	
Aspergillus niger	42.0^e
Penicillium notatum	18.5^e
Saccharomyces cerevisiae (bakers' yeast)	2.9^e

[a]Wet body weight. [b]Dry body weight of cuticle. [c]Organic weight of cuticle.
[d]Total dry weight of cuticle. [e]Dry weight of the cell wall.

Chitin is insoluble in ordinary solvents and highly resistant to hydrolytic cleavage due to its crystalline structure. It is soluble in strong mineral and organic solvents, fluoroalcohols and certain concentrated salt solutions, but most of them degrade chitin (Austin, 1988).

Chitin in crustacean shells is tightly associated with calcium carbonate, proteins and a small amount of pigment and lipid (Figure 1.3). In order to obtain chitin from crustacean shells, the following three steps are required: demineralization, deproteinization and elimination of pigment and lipid, but the method of preparation may be changed with the source of chitin and the level of purity required (Shimahara and Takigushi, 1988; Waiprib, 1991; Kim and Song, 1997).
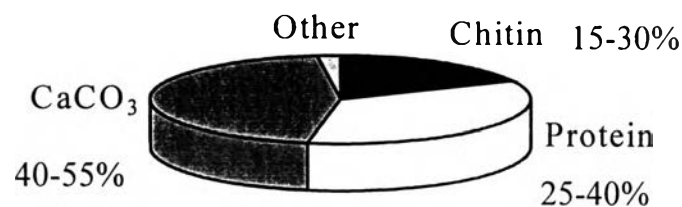

Figure 1.3 Composition of crustacean shells.

The unique properties of chitin such as biocompatibility, non-toxic, non-allergic and antifungal properties make it to be a promising polymer not only in the chemical field but also in medical and industrial areas as summarized in Table 1.3. In developing the industrial applications of polymeric material, chitin and its derivatives were used to blend with synthetic polymers such as PVA and PVC (Aoi *et al.*, 1995, 1997; Lee *et al.*, 1996; Arvanitoyannis *et al.*, 1997). These blends become good candidates as new materials for specific uses or improving the properties of the blends.

Table 1.3 Some applications of chitin-based materials.

Area	Application
Biomedical	Artificial skin (Kim *et al.*, 1995b) Absorbable surgical suture (Brine *et al.*,1992) Drug carrier (Brine *et al.*,1992)
Cosmetics	Skin-care product (Elizabeth, 1993) Hair stiffener (Elizabeth, 1993)
Environmental	Absorbent for waste-water treatment (Yang and Zall, 1984)
Biotechnology	Enzyme immobilization (Muzzarelli, 1980)
Food technology	Food additive (Elizabeth, 1993) Edible film (Elizabeth, 1993) Dietary supplement (Furda and Brine, 1990)
Paper and textile	Paper and fiber sizing (Muzzarelli, 1977) Polymeric dyeing (Muzzarelli, 1977)

1.3 Rice Starch

Rice starch is a major form of carbohydrate storage in green plants and is considered to be the third most abundant polysaccharide, next to cellulose and chitin, produced on earth. It contains two distinct types of D-glucopyranose polymer which are mainly amylose and amylopectin (Figure1.4). Amylose is a linear polymer of α-D-glucopyranosyl units with $1\rightarrow 4$ linkage. It consists of about 350 D-glucopyranosyl units and has a molecular weight range of 1.6-7.0×10^5. Amylopectin, having molecular weight range of 4-5×10^8, is a highly branched polymer of α-D-glucopyranosyl units containing $1\rightarrow 4$ links with $1\rightarrow 6$ linked branches. Each branch in amylopectin consists of about 25 D-glucopyranosyl units.
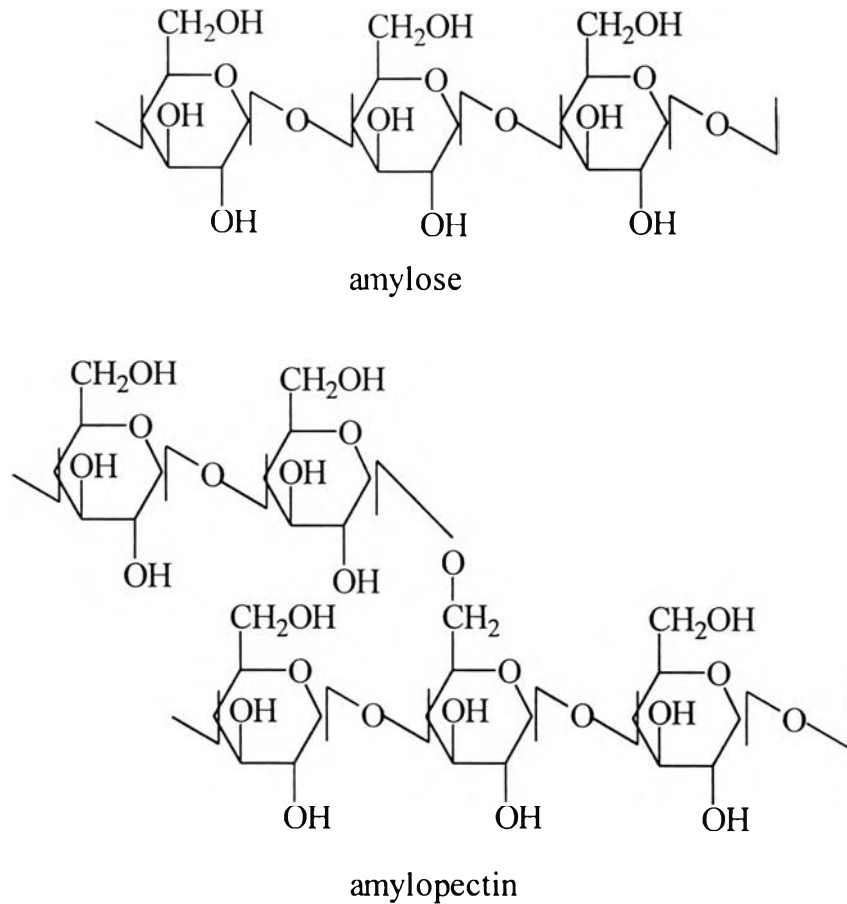
Figure 1.4 Structures of amylose and amylopectin.

Commercial starches are obtained from seeds, particularly corn, wheat and rice, and from roots particularly potato and tapioca (cassava). The size of starch granules varies in diameter from 1-150 μm. Among commercial starches, the granular size of rice starch (3-9 μm) is the smallest while that of potato starch (15-100 μm) is the largest. In general, starch is insoluble in cold water but it swells in hot water, so-called gelatinization (Kroschwitz, 1997).

Starch is an important raw material for industrial applications. A particular interest is the use of starch as a biopolymer filler in traditional plastics for manufacturing of degradable polymers (Narayan, 1991). For examples, high-amylose starch produces strong film and is suitable for making

biodegradable plastics, and small granule starch is used as an appropriate PE film filler (Albertsson and Huong, 1995).

1.4   Mechanical Properties

The mechanical properties, among all the properties of plastic materials, are often the most important properties because of virtually all service conditions and the majority of end-use applications. The material selection for a variety of applications is quite often based on mechanical properties such as tensile strength, modulus, elongation, and impact strength.

1.4.1   Tensile Property

Tensile test is a measurement of the ability of a material to withstand forces that tend to pull it apart and to determine to what extent the material stretches before breaking.

Tensile strength, modulus and elongation values are derived from a stress-strain curve. A typical stress-strain diagram is illustrated in Figure 1.5.
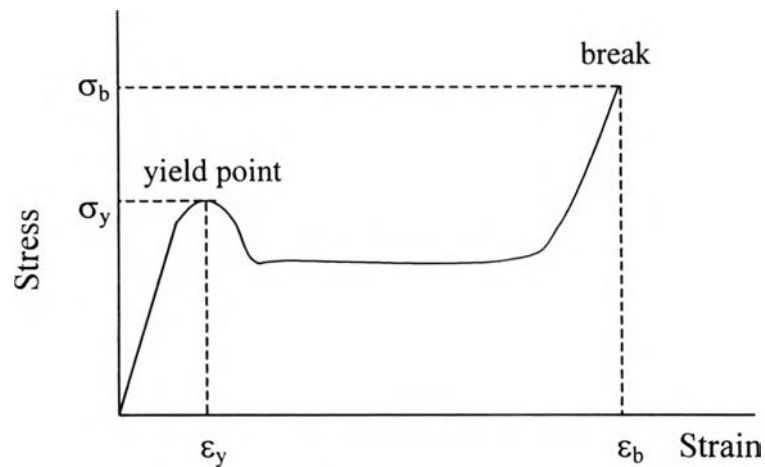
where σ_y = tensile strength at yield

   σ_b = tensile strength at break

   ε_y = elongation at yield

   ε_b = elongation at break

Figure 1.5 Typical stress-strain curve.

Tensile stress (σ) is defined as the force applied to produce deformation in a unit area of a test specimen.   Strain (ε) is the ratio of the elongation to the gauge length of the test specimen or change in length per unit of the original length.   Tensile modulus (E) is the ratio of stress to corresponding strain below the proportional limit of a material.   This is also known as Young's modulus.

The tensile strength at yield (σ_y) 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 (σ_b) which corresponds to the actual rapture of the test specimen.

1.4.2   Flexural Property

Flexural strength is the ability of the material to withstand bending forces applied perpendicular to its longitudinal axis.   It is most

commonly carried out in the three-point bending mode by following ASTM D790 test method, as illustrated in Figure 1.6. When a load is applied at the center of the upper surface of specimen, the upper surface is under compression and the lower surface is in tension.
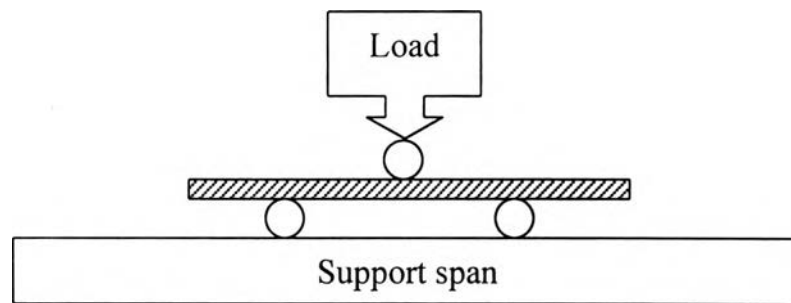

Figure 1.6 Schematic of specimen arrangement for flexural testing.

For three-point bending, the flexural strength (S) is calculated by Equation 1.1.

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

where P = maximum load

L = length of support span

b = width of specimen

d = depth of specimen

The maximum strain (r) of the specimen can be calculated at which the deflection (D) occurs at the midspan by Equation 1.2.

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

The flexural modulus will be obtained by the slope of the initial straight line portion of the flexural stress-strain curve.

1.4.3   Impact Property

The impact property of the polymeric materials is directly related to the overall toughness or the ability of the polymer to absorb applied energy.   The higher the impact strength of the material, the higher the toughness and vice versa.

The objective of the Izod impact test is to measure the relative susceptibility of a specimen to pendulum-type impact load.   The specimen used in the test is usually notched to provide a stress concentration area that promotes a brittle rather than a ductile failure.   It is clamped vertically as a cantilever beam and then struck by a swing of a pendulum released from a fixed distance from the specimen clamp.   The results are expressed in terms of kinetic energy consumed by the pendulum in order to break the specimen.

1.4.4   Hardness

Hardness is defined as the resistance of a material to deformation, particularly permanent deformation, indentation or scratching. The hardness test measures the amount of penetration of an indentor into a specimen. The deeper the penetration, the softer the material.

The Durometer hardness test is mostly used for measuring the relative hardness of soft materials. The test method is based on the penetration of a specified indentor forced into the material under specified conditions. Two types of durometers, type A and type D, are most commonly used. The basic difference between the two types is the shape and dimension of the indentor. Type A durometer is used with relatively soft material while type D durometer is used with slightly harder material.