CHAPTER I
INTRODUCTION

Polyolefins and plastics in general have attracted much attention in recent years, mainly due to their widespread use as packaging material, which led to their increased visibility as litter in the environment. Polyolefins are not inherently biodegradable, and considerable efforts have been made to accelerate biodegradation of packaging materials by using natural additives or fillers.

The use of starch as filler in plastic has been of interest for the past 30 years, but only since the mid-1970s were polymer starch blends with acceptable physical properties developed.

A property that makes starch of interest as fillers for formulating biodegradable compounds is that they are subject to biological and oxidative attack. The action of enzymes and oxygen brings about their decomposition when buried in soil. They are inert to water at room temperature but are rapidly digested by the amylase; the porosity thus generated offers the most favorable circumstances for degradative attack.

Work by Griffin (1974) on starch/polyethylene blends stimulated interest in the use of starch as a biodegradable additive for PE resins. Various starch/resin formulations have also been reported, and some of these are commercially available.

1.1 High Density Polyethylene

High density polyethylene (HDPE) is a thermoplastic polyolefin manufactured by ethylene polymerization and has a density of 0.94 g/cm^3 or higher. The first commercial processes for HDPE manufacture were developed in the early 1950s and utilized a variety of transition-metal polymerization catalysts based on molybdenum, chromium, and titanium.

HDPE is one of the largest commodity plastics manufactured worldwide. Dynamics of HDPE production is represented by the following data indicating both the existing and projected demand (tons/year).

Year	1983	1990	1995	2005
Demand , 10^3 tons	6,400	11,440	14,000	20,000-21,000

HDPE is used for many packing applications because it provides excellent moisture barrier properties, good chemical resistance and good stiffness. The growth of HDPE has been attributed to a combination of factors, including a set of physical properties which has resulted in strong market acceptance of molded and extruded products. The characteristics of HDPE which have lead to its widespread use are:

- Low cost
- Easy processability
- Good chemical resistance to most household chemicals
- Good electrical insulation properties
- A sufficiently low water vapor permeability

Blow-molded products are the single largest use of HDPE resins, with packaging applications accounting for the greatest volume. The blow-molding market represents 41% of total HDPE consumption. Among the products manufactured from blow-molding resins are bottles, especially for milk and fruit juice, housewares, toys, pails, drums, and tanks.

Injection-molding products are the second largest application, with approximately 30% of the HDPE market. Specific uses include housewares, toys, food containers, pails, crates, and cases.

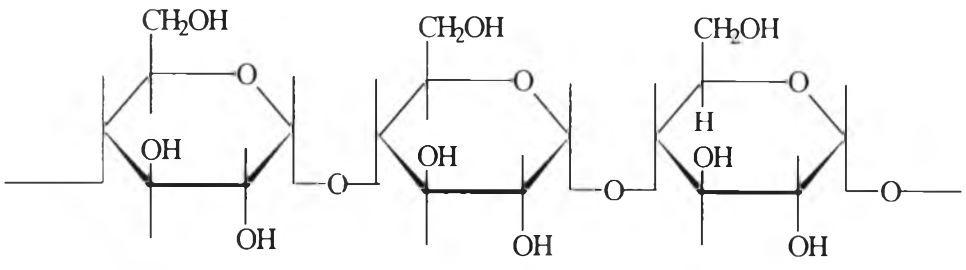
Films are a rapidly growing application for HDPE resins, replacing paper and glass. Polyethylene bags are popular in supermarkets, fast-food outlets, department stores, and for garbage. Films account for about 7% of the total HDPE market.

Pipe and conduit represent another important application area, amounting to about 10% of total HDPE products, and is anticipated to grow 6% per annum. Examples are water and gas pipes, sewer pipes, industrial piping, and other applications where high environmental stress-cracking resistance is important. Other significant applications include wire and cable coating, foam, insulation for coaxial and communication cables, and areas where high resistance to oil and chemicals is desirable.

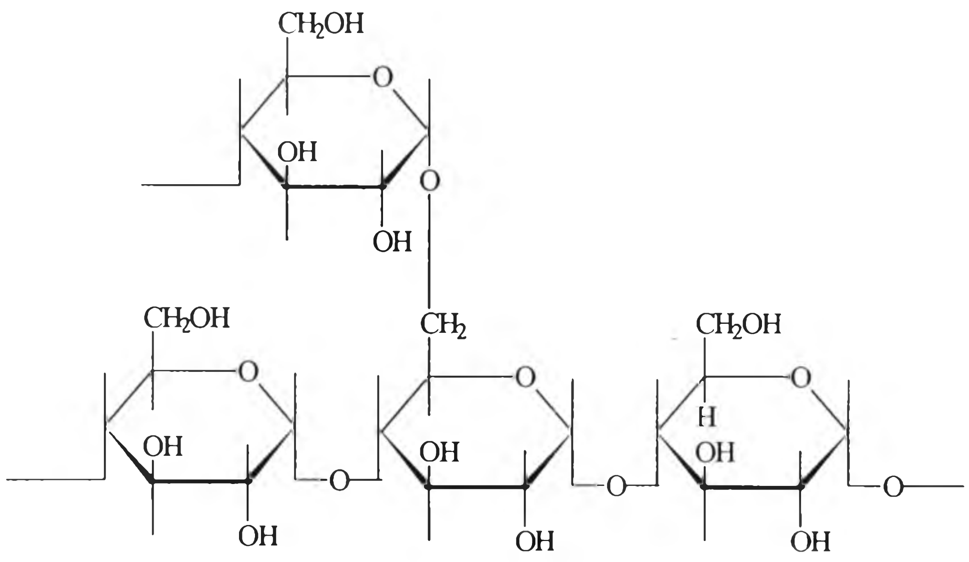
A significant part of HDPE is collected from consumers for recycling; uncollected HDPE can be disposed of by landfill or incineration. In landfills, HDPE is completely inert and therefore degrades very slowly, does not produce gas, and does not leach any pollutants into groundwater. When incinerated in commercial or municipal facilities, HDPE produces a large amount of heat and therefore would constitute less than 10% of the total trash.

1.2 Starch

Starch is a polysaccharide produced by plants as a “storage polymer”. The basic repeating unit involves the linkage of two D-glucose molecules with an α-D-1,4-glycosidic bond. It is a mixture of linear and branched polymer. (Figure 1.1)



Amylose : Linear Polymer



Amylopectin : Branched Polymer

Figure 1.1 The chemical structure of starch components.

Amylose, the linear component, is the lower molecular weight polymer, having an average molecular weight of about 500,000. Amylopectin consists, like amylose, of mostly 1,4-linked α-D-glucopyranosyl units, but with branched chain occurring through α-1,6-linkages at about 1 in every 25 D-glucopyranosyl units. Some measurements show amylopectin to have a molecular weight as high as 10 million.

Starch is stored in plants, as granules or solid particles comprised of molecules of both amylose and amylopectin. The granules may vary in size from 3 to 50 μm, depending on the source plant. In general, starch is insoluble in cold water, alcohol, and ether, and forms a jelly with hot water. Specific gravity is 1.499 to 1.513. Starch granules are thermally stable in an open atmosphere to about 230°C. Above that temperature the starch molecules begin to decompose.

The main problem associated with the use of starch as a filler is its hydrophilic nature and the generally hydrophobic nature of the polymer matrix. The starch particle size limits the amount that can be incorporated into the polymer if the composition is to be blown to a thin film, but this is not such a limitation for sheets or injection-molded articles.

1.3 Mechanical Properties

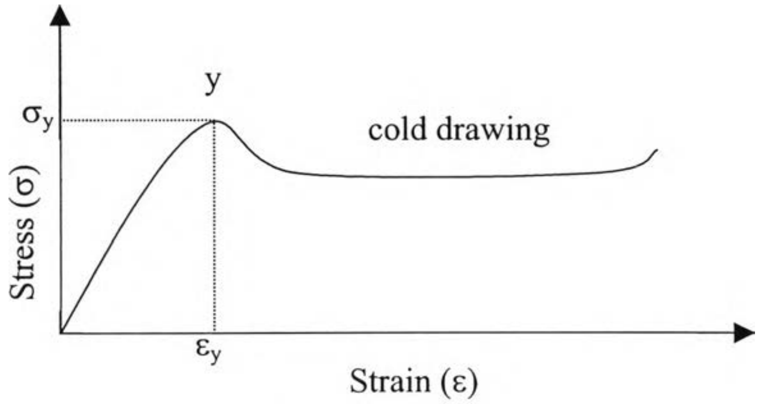
Most plastic materials are used because they have desirable mechanical properties at an economical cost. For this reason, the mechanical properties may be more important than the physical and chemical properties of high polymers for most applications.

The basic characteristics of the mechanical properties of solids are usually determined by the tests resulting in variations deformation-vs-stress dependencies, such as stress-strain diagrams. Examination of such dependencies readily brings out characteristics of elasticity, plasticity, and strength.

1.3.1 Tensile Properties

The tensile test is the experimental stress-strain test method most widely used to characterize the mechanical properties of materials like plastics, metal, and wood. Tensile test involves pulling or stretching a test specimen and measuring the corresponding load applied.

Generally, the data obtained during a tensile test are plotted as a force-extension curve or alternatively a stress-strain curve as shown in Figure 1.2.



where σ_y = Stress at yield
ε_y = Strain at yield
y = Yield point

Figure 1.2 Typical stress-strain curve for a ductile polymer.

Tensile stress is the " load per unit area" of the specimen. Strain is the amount of extension relative to the original length. The tensile modulus is the tensile stress divided by the strain.

The point in the stress-strain curve where the stress (or load) begins to decrease with increasing strain (or extension) is referred to as the *yield point*. After the yield point the specimen exhibits non-recoverable, plastic deformation. Thus, for molded products this point would normally represent the limit of it usefulness.

At the yield point there is a sudden decrease in the cross sectional dimension (width and thickness) of the specimen. This is termed 'necking'.

After the yield point, polymer chains are able to slip past each other at the same rate as the specimen is being elongated - at constant load. This process is called 'cold drawing'. After all the possible polymer chains have been cold drawn, the load (or stress) of the specimen will begin to increase with increasing extension until the specimen breaks. During the cold drawing process the polymer chains become oriented, which is the cause of the eventual increase in strength observed on the stress-strain graph. The phenomenon of cold drawing is illustrated in Figure 1.3.

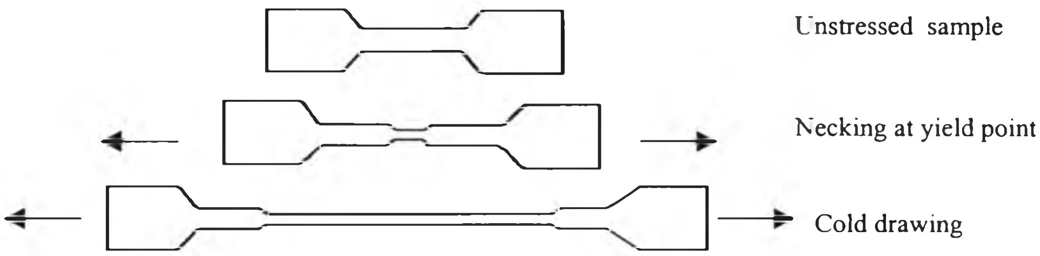


Figure 1.3 Stages in cold drawing of a test specimen.

The maximum tensile stress sustained by a specimen during a tension test is its *tensile strength*. When the maximum stress occurs at the yield point, this stress is designated *tensile strength at yield*. The percent elongation at yield is the extension at yield divided by the original gage length of the specimen multiplied by 100.

1.3.2 Flexural Properties

Flexural stress-strain testing determines the load necessary to generate a given level of strain in a specimen under bending conditions. Basically, the test consists of bending a relatively long, flat specimen of rectangular cross-section, using either 3-point or 4-point bending conditions as shown in Figure 1.4.

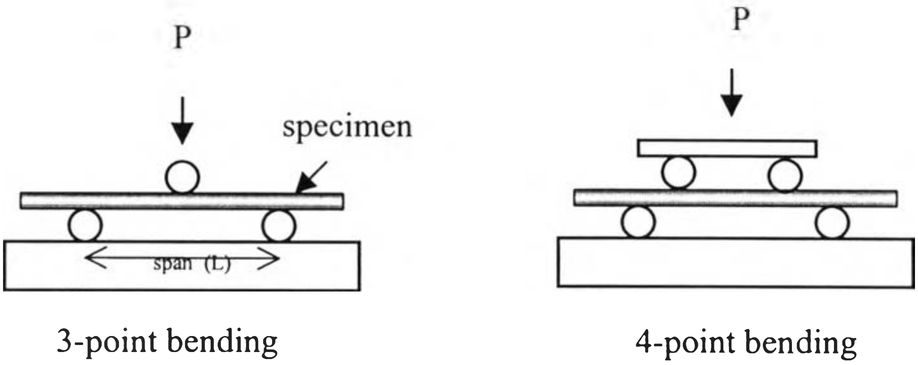


Figure 1.4 Types of flexural testing.

With 3-point bending, the maximum stress occurs in the specimen where the center support is. This is not the best condition. In 4-point bending test the stress is evenly spread over the region between two center support. Nevertheless, 3-point bending tests are the most common type of flexure tests performed. The effect of the load on the test bar in 3-point bending is shown in Figure 1.5.

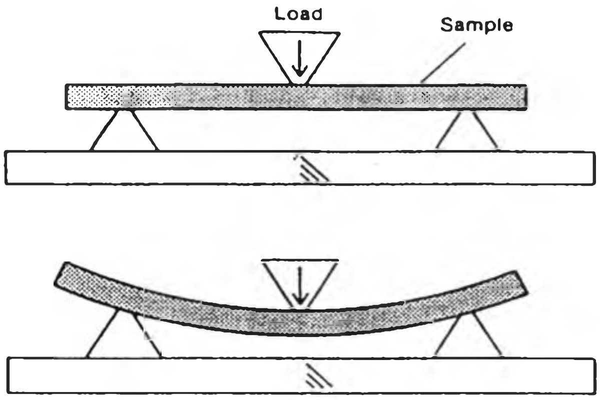


Figure 1.5 Effect of load on test bar in 3-point bending.

Consider the stresses present in a test specimen during a 3-point flexural test (Figure 1.6). There will be a *tensile stress* on the outer surface and a compressive stress on the inner surface. Somewhere between these two surfaces there will be a neutral region where the specimen will experience neither tensile nor compressive stresses, this is called the neural surface or 'neutral axis'

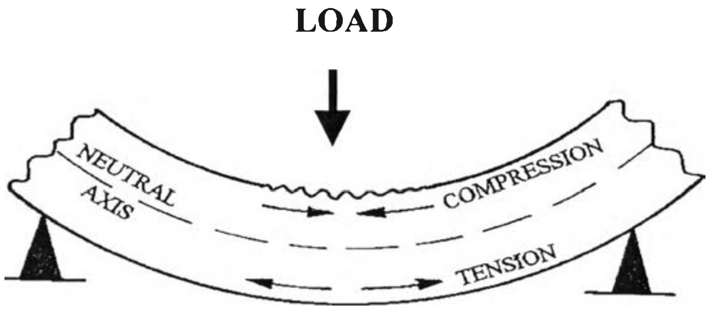


Figure 1.6 The stresses present in a test specimen during a 3-point bending test.

Flexural strength is the maximum stress developed when a bar-shaped test piece, acting as a simple beam, is subjected to a bending force perpendicular to the bar.

The load should be applied at a specified crosshead speed. For 3-point bending, the flexural strength (S) is calculated from the following expression, in which P is the load at a given point on the deflection curve, L is the support span, b is the width of the bar, and d is the depth of the beam:

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

The following expression, in which D is the deflection under load P (see Figure 1.7), can be used to obtain the maximum strain (r) of the specimen under test:

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

Data for 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.

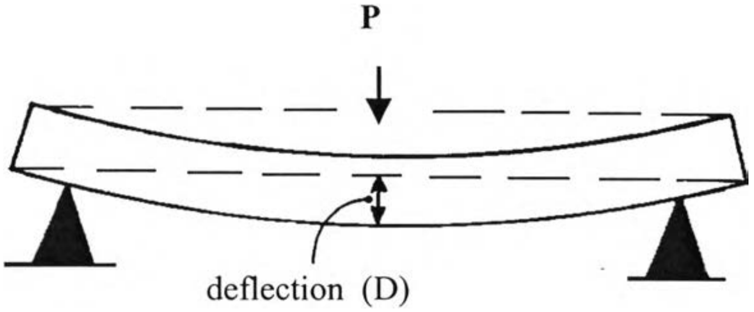


Figure 1.7 The deflection (D) of the test specimen under load P.

1.3.3 Impact Strength

Impact tests are high-speed fracture tests that measure the energy to break a specimen. In general, there are two types of impact test. First, tests in which a pendulum of known energy strike (impacts) a specimen. Example of this type of impact test are Izod impact and Charpy impact. Second, tests where weight are allowed to fall from known heights onto the specimen. Example of this type are falling ball impact and falling dart impact.

In the Izod and Charpy impact tests the energy required to break the specimen is determined from the loss in kinetic energy of the pendulum. In the falling ball or falling dart impact tests the amount of energy required to break a sheet or plate of the material is determined from the weight of the ball and the height from which it was dropped.

The Izod impact test is the most widely used impact resistance test for plastic. In the Izod test, a pendulum-type hammer, capable of delivering a blow of 2.7 to 21.7 joules, strikes a notched plastic specimen, which is supported as a cantilever beam. The distance that the pendulum travels after breaking the specimen is inversely related to the energy required to break the test piece.

The Izod impact test is an easy and fast test method. The diagram of the Izod impact test is shown in Figure 1.8. A pendulum of known mass is allowed to fall from a fixed height to strike and break a standard specimen which is clamped at one end (a vertical cantilever) in a vise. At the point of impact, the pendulum travels at a velocity of 3.5 m/s and, for ASTM, delivers an energy of 2.7 joules to the specimen. After impact, the pendulum (together with a moveable pointer) swing up to a height depending on the energy absorbed by the specimen on impact. The pendulum then swings back – and is placed in the upright starting position again – but the pointer remain at the highest point reached. The scale reading opposite the pointer is taken as the impact strength of the material.

Most modern impact testing machines now use the latest electronics instrumentation so that a *digital* value of impact strength is recorded, i.e. a moveable pointer is not used.

Izod tests are normally carried out on 'notched' specimens. There are two types of notch, each having an angle of 45 degree. One notch has a tip radius of 2.5 mm and the other a radius of 1.00 mm. For some materials it is desirable to test specimens without a notch, i.e. 'unnotched'. This is done by reversing a notched specimen in the clamp. Notches must be machined into a specimens, not molded-in (by injection molding or compression molding).

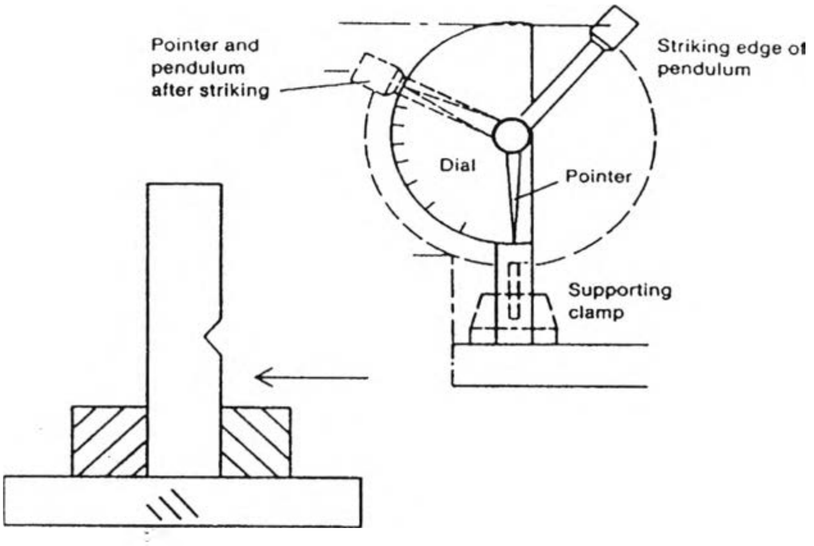


Figure 1.8 Notched Izod impact test (ASTM D256).

Some plastics material are 'notch sensitive'. This means that recorded impact strength are very dependent on the notch tip radius. The effect of the sharpness of the tip of the notch on the impact strength of several polymers is illustrated in Figure 1.9. In this Figure, nylon and poly(vinyl cholide) (PVC) are very notch sensitive compare to an acrylic polymer and a high-impact ABS material.

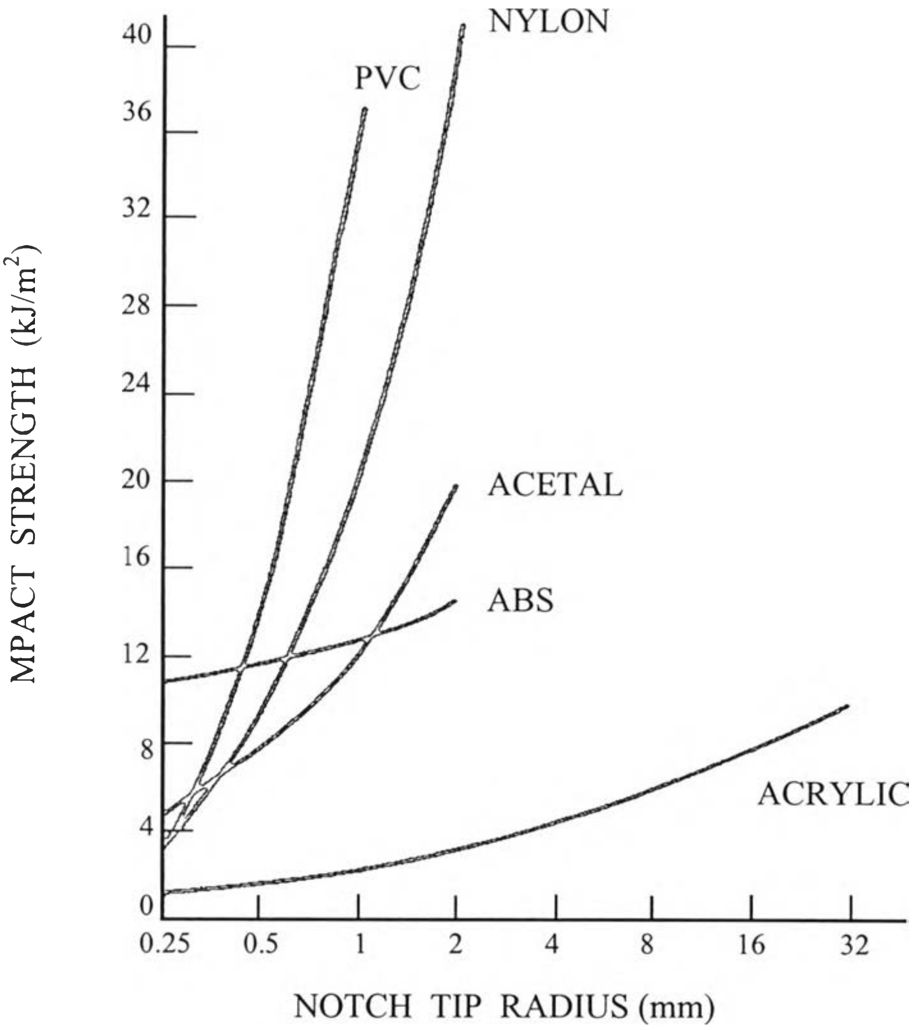


Figure 1.9 Impact strength as a function of the radius of the tip of the notch for the different polymers. (Vincent, 1971).

1.4 Literature Survey

Griffin *et al.* (1973) introduced the idea of increasing biodegradability to otherwise inert polymers by incorporating a cheap biodegradable additive. He mixed granular corn starch in its natural form with LDPE and found that the degradation of PE/starch composite films containing 6-10% of starch in a compost environment was accelerated by the absorption of unsaturated acid. Peroxides were generated and consequently, autoxidation was enhanced. Thus, a purely chemical effect of the biotic surroundings, even with no enzymatic actions, could enhance the degradative autoxidation of the polymers.

Otey *et al.* (1987) prepared composite films incorporating starch in the matrix of PE and found that the content of starch in starch-based films can be increased without affecting the physical properties of films by adding urea and polyol to the starch-poly(ethylene-co-acrylic acid) (EAA) system.

Swanson *et al.* (1988) found that tensile strength and elongation of EAA/LDPE composite films were improved by using the modified starch and introducing hydroxypropyl or acetyl groups in starch.

Griffin (1988) formulated a LDPE material combining several potential degradative effects. LDPE mixed with corn starch, a prooxidant formulation consisting of an unsaturated polymer, a transition metal salt, and a thermal stabilizer, gave a material which could degrade by several mechanisms such as photooxidation and biodegradation. The starch granules were biodegraded while sunlight and oxygen triggered autoxidation of the chemically unstable prooxidant, generating free radicals which could then attack the molecular structure of the LDPE.

Gonsalves *et al.* (1989) conducted research on PE/starch composites blended in a Haake Buchler system 40 torque rheometer at 190°C. A metal catalyst and an autooxidant were added to promote chemical degradation. These blends were then compression molded into sheets and placed in a marine environment for three months. Tests conducted included observation of changes in morphology and thermal properties. The starch/PE samples containing 15% starch showed a 2% increase in weight after exposure to the marine environment. At the same time, the tensile strength decreased by 6%. The molecular weight of the blend was lowered and there was a decrease in M_w/M_n ratio. The surface of the samples revealed a migration of large starch granules onto the surface.

Nikolov *et al.* (1991) reported that LDPE/modified starch composite films improved the tensile strength and elongation in comparison with the LDPE/native starch composite films, but the enzyme degradation rate of the modified starch-filled cast film was lower than the rate of the native starch-filled film.

Jane *et al.* (1991) reported that the addition of high molecular weight oxidized PE (OPE) improved the tensile strength and elongation of starch/PE composites containing 15% starch. The ratio of OPE/starch ranged from 0.30-0.50 : 1.00. It was suggested that ester formation and hydrogen bonding between carbonyl groups in the OPE and hydroxyl groups on the starch granule surface were responsible for the improvement in properties.

Nikolov *et. al.* (1992) studied on the degradation of two different starch/LLDPE films containing abount 5 wt % corn starch. The major difference between the two films was the presence/absence of a prooxidant additive in the formulation. The accelerated starch biodegradation of the films was investigated by using a buffered Bacillus sp. α-amylase solution whereas oxidatiive degradation of the polyethylene (PE) was hastened by incubating the starch-PE films in a forced-air oven at 70°C. The films without a prooxidant additive did not change significantly during the heat treatment. The films containing a prooxidant lost their physical properties after 20 days of heat treatment. The amount of starch hydrolyzed by α-amylase was directly related to the physical properties of the PE films. The levels of starch degradation ranged between 10 and 50 wt % of initial starch, depending on the extent of the PE degradation.

Willett (1994) studied the mechanical properties of LDPE/granular starch composites and found that the elongation and tensile strength decreased with increasing starch volume fraction (ϕ). The composite modulus increased with increasing ϕ. The addition of a compatibilizer (ethylene-co-acrylic acid copolymer, EAA) did not significantly affect the elongation or tensile strength, but significantly increased the composite tensile modulus.

Mayer *et al.* (1995) prepared blends of cellulose acetate and starch and found that increasing the plasticizer or starch content lowered the tensile strength. Cellulose acetate with a degree of substitution of 2.5 was slowly biodegraded in compost, and the addition of starch and propylene glycol seemed to delay the utilization of the cellulose acetate portion of the blends.

Bhattacharya *et al.* (1995) reported that the addition of starch to ethylene-propylene-g-maleic anhydride copolymer (EPMA) caused a significant reduction in the percent elongation of the blends but little reduction in the tensile strength. For starch/styrene maleic anhydride copolymer (SMA) blends the tensile strength dropped to between 60 and 80% of that of pure SMA. Higher humidity increased the elongation of starch/EPMA blends, but for starch/SMA blends, caused a significant decrease in the tensile strength.

Kang *et al.* (1996) reported that modified starch could be used to improve the mechanical property of starch-filled polyethylene films by introducing a cholesterol moiety as a hydrophobic material. The different starch compositioned HDPE films were prepared with addition of either native starch or modified starch to compare their physical properties. The addition of either native starch or modified starch resulted in decreased crystallinity in all the different composite films containing starch. The modified starch-filled blown films showed higher dispersion and adhesion of filler than native starch-filled films. Accordingly, the tensile strength and elongation at break of modified starch/HDPE compounds were improved in almost all cases.

Thiebaud *et al.* (1997) studied the properties of fatty-acid esters of starch and their blends with LDPE. Starch octanoates and dodecanoates were prepared by esterification of native potato starch with fatty acid chlorides. The ester group was found to act like an internal plasticizer. These starch esters were then mixed with LDPE in various proportions in a Haake Rheomixer. Water and moisture absorption, thermal and mechanical properties were investigated as a function of blend composition. The octanoates/LDPE blends showed better thermal stability and higher elongation, but lower tensile strength and water absorption than the dodecanoates/LDPE blends. It was also found that esterified starch could be used for preparing of blends with LDPE for packaging use and containing up to 15-20 wt % of starch. This amount is higher than the amount of the unmodified starch (6-9wt%) which can be incorporated in industrial LDPE/starch blends with satisfactory mechanical properties. (Nikolov, 1991)

1.5 Objectives

To study the effect of starch content on the mechanical properties of starch-based HDPE blends.

To compare the mechanical properties of tapioca starch-based and rice starch-based HDPE blends.