

# CHAPTER I

## INTRODUCTION

Expanding industrial activities create a continuous demand for improved materials that satisfy increasingly stringent property requirements such as higher strength, modulus, thermal and/or electrical conductivity, heat distortion temperature, lower thermal expansion coefficient, higher degradability, and reduced cost. The development of polymeric blends whose constituents may act synergistically to produce enchanted properties have attracted much research and development over the last few decades.

Fillers have always played an important role in the plastics industry. In fact, the early growth of the phenolic plastics industry would not have been possible without the enhancement of properties by the use of fillers. The commodity resins, i.e. polyvinyl chloride, polystyrene, polyethylene, and polypropylene, have properties that meet the requirements of high-volume end uses, and thus they have been sold and used essentially as pure resins. In the past decade, however, price escalations, combined with the possibility of future shortages of resins and petroleum feedstocks, have established an urgent need for the widespread utilization of fillers.

### **1.1 Fillers**

Fillers are finely divided solids added to polymer systems to modify the properties of the polymer and reduce costs. These properties include mechanical, thermal, electrical, and degradability. Fillers can constitute either a major or a minor part of a polymer composite material. The structure

of filler particles ranges from precise geometrical forms, such as spheres, hexagonal plates, or short fibers, to irregular masses. A wide variety of fillers, from low cost materials possessing modest performance-enhancing properties to high-priced functional fillers or engineered materials designed to achieve very specific results, are available. They can generally be classified into five categories [Katz *et al.*, (1974)]:

- 1.) Mineral fillers
- 2.) Metallic, conductive, and magnetic fillers
- 3.) Organic fillers
- 4.) Spherical fillers
- 5.) Synthetic inorganic fillers

The properties of the filler generally exert a significant influence on the performance and processing characteristics of the compositions in which they are part. These properties include particle shape, size, and distribution, surface chemistry, and purity. Filler particle size distribution and shape affect the rheology and loading limits of the filled compositions. Particles with fibrous, needle-like, or other irregular shapes yield compositions more resistant to flow, as compared to compositions filled with spheres or other fillers with more regular morphologies. Thus, fillers with regular shapes can be used in compositions at higher loadings than fillers with irregular shapes, assuming that all other properties remain the same.

The filler to be used depends on what properties are desired. There is not an ideal filler, since each of the infinite end uses will call for a particular set of characteristics, including mechanical, chemical, and electrical properties, cost constraints, and processing needs. If there were an ideal filler, its characteristics would include the following:

- 1.) Low cost
- 2.) Availability
- 3.) Low oil absorption

- 4.) Good surface wetting and bonding
- 5.) Good chemical resistance
- 6.) High strength

In addition, if complete manufacturing control were possible, the following properties would be desirable: color, shape, density, modulus, size (and its distribution), thermal expansion, and electrical and thermal properties. Since no one filler possesses all of these desirable properties or controllable aspects, users must make an optimum compromise for the application.

Although different fillers exert different properties to the blends, they all rely on their effectiveness as a filler by being completely and uniformly dispersed throughout the polymer matrix. Therefore, the process of mixing is of utmost importance to achieve both good distribution and dispersion for obtaining a satisfactory product.

Many fillers used in plastics are colloidal in nature and exist in the form of aggregates composed of primary particles permanently fused together. In turn, aggregates can cluster together under the influence of surface forces in collections of aggregates, referred to as agglomerates. Dispersive mixing usually involves a physical change in the components and requires high shear forces to bring about the change.

The state of dispersion is strongly affected by the methods and conditions of mixing. Physical dispersion or the uniform mechanical distribution of filler particles in the polymer matrix is often difficult to achieve. However, all phases of the dispersion process are time-dependent and the dispersion and distribution of fillers almost always improves with mixing time. To understand the correlation between the mixing process and compound properties, it is important to characterize the phase morphology. Many procedures have been used through the years to characterize the level of dispersion of fillers. These include optical microscopy, electron microscopy, surface roughness, electrical conductivity, and small-angle light scattering.

Most of the studies relating the state of dispersion to the properties of compounds use a microscopy method and determine the average diameters of the agglomerates.

## 1.2 Starch

Starch, an organic filler, is one of the major components of cereal grains. Commercially important starches come from corn, waxy corn, high amylose corn, wheat, rice, potato, tapioca, and pea. The major sources of commercial starch here in Thailand are tapioca and rice. The starches are readily obtained from these plant sources as a fine powder (granular starch) consisting of spherical or ellipsoidal grains ranging in particle size from 3 to 100 $\mu\text{m}$ . Among these, rice starch (3-9 $\mu\text{m}$ ) has among the smallest granule size and potato starch (15-100 $\mu\text{m}$ ) the largest of all starch types [Kirk-Othmer (1997)].

Starch is composed of repeating 1,4- $\alpha$ -D-glucopyranosyl units. It is a mixture of linear (amylose) and branched (amylopectin) units. Amylose is the lower molecular weight polymer, having an average molecular weight of several hundred thousands while at the opposite end, amylopectin has an average molecular weight of several millions [Ramkumar *et al.* (1996)]. Most starches consist of about 25% amylose and 75% amylopectin molecules, though high amylose starches, having up to 100% amylose content, can be found. These are termed waxy starches because of the vitreous sheen of waxy corn grain when cut.

The abundant hydroxyl groups on starch molecules impart the characteristic hydrophilic property inherent in starches. The molecules attract water and themselves through hydrogen bonding. Starch granules are insoluble in cold water but swell slightly due to the absorption of water. With continued uptake of water at ambient temperature, the granule diameter

increases 9.1% for corn and 22.7% for waxy corn. Starches absorb water until they become saturated. Different starches absorb moisture to different extents depending of the ambient percent relative humidity (%RH). For example, at 10%RH corn starch has an equilibrium water content of 7% whereas at 90%RH the equilibrium water content increases to 20%. In hot water a larger irreversible swelling occurs producing gelatinization, which takes place over a discrete temperature range that depends on the starch type [Kirk-Othmer (1997)],

Starch type	Irreversible swelling temperature range (°C)
Potato	59-68
Tapioca	58.5-70
Corn	62-72
Waxy corn	63-72
Wheat	58-64

Gelatinization is the formation of an amylose and amylopectin network upon melting of starch crystallites. The starch gelatinization temperature range begins with the onset of granule swelling and ends at the point where nearly 100% of the granules are gelatinized. At a specific temperature during heating (the lower limit of gelatinization temperature), the kinetic energy of the molecules is sufficient to overcome intermolecular hydrogen bonding in the interior of the starch granule. The amorphous regions of the granule are initially solvated and the granule swells rapidly. During swelling, some of the linear amylose molecules leach out of the granule into the surrounding solution. When the material is cooled, the dispersion thickens and, if

sufficiently concentrated, may form a gel. In order to utilize starch in its granular form, the starch must be kept dry to avoid gel formation.

Starches are used primarily as a food ingredient, in sizing of paper and textile, and in the adhesive industry. Their uses can be dated back to 3500-4000 BC when the Egyptians used wheat starch modified by boiling in vinegar to produce a smooth surface of papyrus documents [Kirk-Othmer (1997)]. What makes them an attractive filler for thermoplastics are:

- 1.) low cost
- 2.) readily available
- 3.) renewable resource
- 4.) confer partial biodegradability to the plastic

Starch is thermally processable when a plasticizer, such as water, is added to lower the glass transition temperature ( $T_g$ ) and melt temperature ( $T_m$ ) below the decomposition temperature [Mayer and Kaplan, (1994)]. The melting point depression of starch by water has been studied by several authors [Biliaderisi *et al.*, (1986); Paton, (1987); Donovan, (1979) and has been successfully fitted by the equation of Flory with an interaction parameter  $\chi_1$  of approximately 0.5 [Lelievre, (1973)]. The  $T_g$  depression of starch by water has been reported by Shogren *et al.*, (1992).

Water content in starch (%)	$T_g$ (°C)
0	230
7	140
11	95
18	53
24	18

Extruding starch and plasticizer alone though, produces a brittle foam. Because of the hydrophilicity of starch, the performance of the materials extruded with starch changes during and after processing as the water content changes. Blending with more hydrophobic polymers produces compounds that are suitable for injection molding and blown film extrusion. Still, the processing of starch-based polymers has its own set of problems. The major one seems to be the difficulty in obtaining a homogeneous dispersion of starch within the polymer matrix. The main problem arises from the fact that starch is highly hygroscopic, and is relatively sensitive to thermomechanical shear. Thus, in order to obtain an effective dispersion of starch in the polymer matrix, the starch must be dried to the lowest moisture content possible and then processed as quickly as possible. Starch has been known to be treated with a silane coupling agent in order to render it hydrophobic and increase its resistance to thermomechanical shear [Huang *et al.* (1990)].

In this study, the processability and mechanical properties of starch-based HDPE blown film are the focus.

### **1.3 Polyethylene film**

Film is defined as flat unsupported sections of a plastic resin whose thickness is very thin - generally regarded as being 0.25 mm or less in thickness.

Polyethylene remains the largest volume film raw material. It is available in a wide range of types, i.e. different copolymers, homopolymer types, molecular weight, and other factors contributing to a long list of resins. Blends of various types may also be used to optimize properties, processability, and economics. Almost two-thirds of the volume of all polyethylene resins are used in film or sheet applications.

Low-density polyethylene (LDPE), the original form of polyethylene, still commands a large market share based on its transparency, tear resistance, impact resistance, and moisture resistance. It has poor resistance to oils and grease, high temperature, and is permeable to odors and gases. It is primarily used in clear packaging of such items as bread, meat, poultry, seafood, frozen foods, and garment bags. It is also used in industrial applications such as liners, stretch wrap, heavy-duty bags, and shrink wrap.

In the late 1980s, linear low-density polyethylene (LLDPE) became a significant factor in the polyethylene film business. This resin has somewhat better strength than LDPE and is cheaper to produce. LLDPE has been most successful in packaging where clarity is not a major priority. It is often used in grocery sacks, stretch wrap, liners, and mulch film. There is a growing market for its use in diapers, both infant and adult.

High-density polyethylene (HDPE) also has a large market share. As molecular weight and density of the polyethylene increases the tensile properties, chemical resistance and barrier properties of the film products increase. Excellent abrasion resistance is also achieved. HDPE film has a large share of the grocery sack business. It is also used for cereal and snack food packaging, where its resistance to moisture penetration is a prime factor. HDPE is manufactured by ethylene polymerization by either the Phillips process or the Ziegler-Natta process.

Polyethylene is expected to continue to be an attractive commodity polymer for many years to come because of its low cost, chemical resistance, and mechanical properties. Especially with the ongoing development of metallocene catalysts, polyethylene can now be manufactured with a precise control of branch content and placement, and thus allows its properties to be tailored.

## 1.4 Mechanical properties

### 1.4.1 Tear resistance

Tear resistance is a measure of the force required to propagate tearing across a film or sheet specimen of a specified length. There are two types of specimens, a rectangular type and one with a constant radius testing length. An Elmendorf-type tearing tester is the most widely used testing machine. In this type of testing machine, a pendulum swings through an arc, acting by gravity, thereby tearing the specimen from a precut slit. The specimen is initially gripped on one half by the pendulum and on the other half by a stationary member. A pointer indicates the loss in energy of the pendulum. The scale indication is a function of the force required to tear the specimen. The average tearing force (ie. the tear resistance) is then calculated using the following formula:

$$\text{Average tearing force, mN} = \frac{\text{average scale reading} \times \text{pendulum constant}}{n}$$

where n = number of plies of film used for each test run

Since there is not a direct linear relationship between tearing force and specimen thickness, data from this test method are reported as tearing force in millinewtons together with specimen thickness. Only sets of data from specimens of similar thickness are comparable.

### 1.4.2 Tensile properties

Tensile properties are determined by pulling a test specimen at a constant rate. The resulting stress (or load applied) is measured and recorded as a function of strain (or elongation). The stress and strain are defined mathematically by:

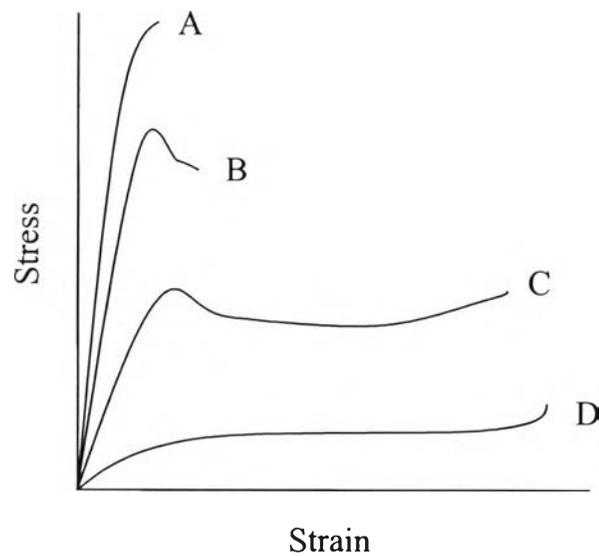
$$\text{Stress} = \frac{\text{Load applied on specimen}}{\text{Cross - sectional area of specimen}}$$

$$\text{Strain} = \frac{\text{Increase in length of specimen}}{\text{original length of specimen}}$$

Tensile strength is the maximum tensile stress which a material is capable of supporting. It is calculated from the maximum load carried during the tensile test and the original cross-sectional area of the specimen. 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 test provides insight into the stress-strain behavior of a material under uniaxial tensile loading and makes it possible to distinguish between brittle and ductile materials under a given set of test conditions. Tensile values are strongly influenced by temperature, loading rate, moisture level, and fabrication conditions [Ward, (1990)]. Figure 1.1 shows stress-strain curves for a polymer at four different temperatures.

At a temperature well below the glass transition temperature (curve A), brittle fracture occurs. The stress rises linearly to the breaking point with increasing strain, and rupture occurs at a low strain. At a high temperature (curve D), the polymer is rubber-like and stress rises to the breaking point with a sigmoidal relationship to the strain. Rupture occurs at a very high strain.



**Figure 1.1** Stress-strain curves for a polymer at different temperatures. Curve A, brittle fracture; curve B, ductile failure; curve C, cold drawing; curve D, rubber-like behavior [Ward, (1990)].

In an intermediate temperature range below the glass transition (curve B), the stress-strain relationship resembles that of a ductile metal, showing a stress maximum, i.e. a yield point before rupture occurs. At a slightly higher temperature but still below the glass transition (curve C), the remarkable phenomenon of necking and cold drawing is observed. The curve again shows yield point and a subsequent decrease in the stress. However, with a further increase in the applied strain, the stress falls to a constant level at which a neck forms. Eventually the stress begins to rise again and rupture occurs.

## 1.5 Literature Review

Potts *et al.* (1973) studied the influence of molecular weight of polyethylene on its susceptibility to biodegradation. They found that polyethylene was biodegraded if the molecular weight was less than 500 Da. This size presumably represents a threshold for transport into a microbial cell for metabolism by  $\beta$ -oxidation or other catabolic mechanisms. However, at this molecular weight, polyethylene will not produce materials with useful performance properties.

Griffin (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 the LDPE film in a compost environment was accelerated by the absorption of unsaturated lipids. 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.

Westhoff *et al.* (1974) evaluated three techniques for incorporating large amounts of starch into PVC plastics. In one method, a starch derivative was coprecipitated with a PVC latex. The precipitate was then filtered off, dried, milled to a fine powder, blended with dioctyl phthalate (DOP), and compression molded in an aluminum cavity. In the second method, starch was gelatinized and mixed with PVC latex, and water removed by heating in an oven. The dry product was milled, mixed with DOP, and molded as before. The third method involved dry-blending starch, PVC, and DOP on a rubber mill and then compression molding the product. Tensile strength and clarity remained good even up to 50% starch loading, but elongation decreased rapidly as the starch content increased.

Huang *et al.* (1975) studied the influence of morphology in polycaprolactone (PCL) on its biodegradability. They demonstrated that morphology influenced the rates of biodegradation, with initial enzyme activity focused on the amorphous regions leaving the crystallites to hydrolyze at a reduced rate.

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. Either casting, simple extruding, or milling the starch-EAA compositions were used to produce films. The processes were relatively slow and expensive in comparison with the more conventional extrusion blowing technique.

Maddever *et al.* (1987) reported work carried out with Ecostar, a starch-based LDPE master batch manufactured by St. Lawrence of Canada. The research findings showed that the effect of starch on starch/polyethylene film properties was similar to that found from the addition of other fillers at similar levels. When starch contents were varied from 0 to 9%, the tear strength increased in the machine direction. The yield strength remained constant within a narrow range while the break strength decreased in both the machine and transverse directions. The ultimate elongation was reduced and the impact strength dropped sharply at 9% loading level.

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. 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 surface of the samples revealed a migration of large starch granules onto the surface.

Yoon *et al.* (1993) studied the effect of native starch on the physical properties of native starch-based polyethylene films. They found that a sharp decline in physical properties of the films occurred at starch loadings of more than 10%.

Vaidya *et al.* (1994-1995) studied the physical properties of compression molded starch/ethylene-propylene maleic anhydride (EPMA) and starch/styrene maleic anhydride (SMA) blends with different starch contents and amylose to amylopectin ratios. It was observed that water absorption increased with increasing starch content and was affected by the amylopectin to amylose ratio of the starch used. When non-functionalized polystyrene or ethylene-propylene rubber was blended in the same concentration, the tensile strength was found to be inferior to those obtained by using maleated polymer in the blend.

Kang *et al.* (1996) studied the mechanical properties of HDPE blown films containing starch or modified starch as fillers. A cholesterol moiety was introduced as a hydrophobic material to modify the starch. The modified starch-based HDPE blown films showed superior tensile strength and elongation over the native starch-based HDPE blown films and also better dispersion and adhesion.

Thiebaud *et al.*(1996) studied the properties of fatty-acid esters of starch and their blends with LDPE. Starch octanoates and dodecanoates were prepared by esterification of native starch with fatty acid chlorides. These starch esters were then mixed with LDPE in various proportions in a Haake Rheomixer. Torque and melt temperature were recorded. 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.

Kim *et al.* (1997) studied the mechanical properties of HDPE blown films on the basis of morphological considerations. They prepared HDPE blown films having a broad range of morphologies under several different processing conditions. The effect of their morphological features on the dart impact resistance, Elmendorf tear resistance, and tensile properties were studied. They reported that the dart impact resistance was highly dependent on the presence of the network structure of lamellar stacks and the level of the intraconnectivity and interconnectivity of lamellar stacks. The coherent orientation of lamellar stacks led to significant anisotropy of tear and tensile properties.

## 1.5 Objectives

The objectives of this study are:

1. To study the effect of starch content on the processability of starch-based HDPE blends
2. To compare the mechanical properties of tapioca starch-based and rice starch-based HDPE blown films
3. To study the water absorption of tapioca starch-based and rice starch-based HDPE blown films and its effect on the mechanical properties of the films