

CHAPTER II

LITERATURE SURVEY

Polymers, or macromolecules, are very large molecules formed by linkages of many smaller molecules, which are referred to as constitutional units or monomers. Plastics are polymeric materials which, at some point in their manufacture, can be shaped by heat, pressure, or both. There are many polymers, such as cellulose, which are not plastics. On the other hand, all plastics are polymers.

Plastics used in packaging can be divided into two broad groups on the basis of the structure and the bonding mechanism between the macromolecules (Figure 2.1). First, plastics whose macromolecules have linear or branched chains are called thermoplastic. The individual molecular chains are held together exclusively by secondary bonding forces. They, once formed, can be melted and formed again. Besides the group of thermoplastic, there are another group of plastics in which the individual molecules are bonded to one another by cross-link. Plastics based on highly cross-linked molecular chain are called thermoset. Once formed, the thermosetting plastic can not be melted or reshaped by using heat and pressure.

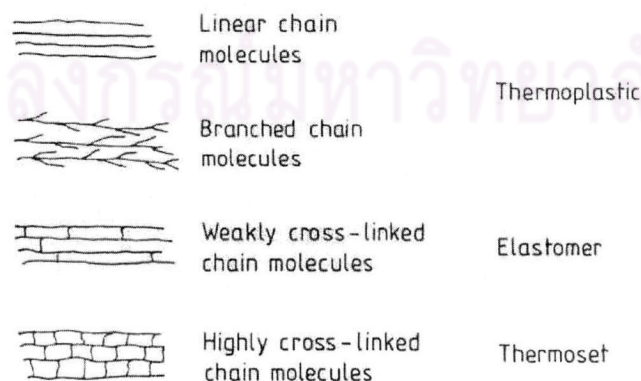


Figure 2.1 Illustration of the arrangement of chain molecules in plastic [8]

Packaging is a major market for the plastic industry. Almost all plastics used in packaging are thermoplastic, e.g., polyethylene, polypropylene, polystyrene, polyvinyl chloride, polyethylene terephthalate, nylon and polycarbonate. As seen in Figure 2.2, about 60% of all plastics used in packaging in the U.S. is polyethylene. Similarly, polyethylene is widely used in Thailand as well. This is mainly because of its low cost and excellent properties for many applications.

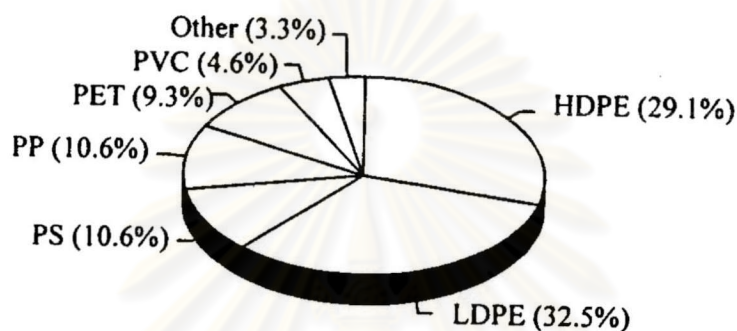


Figure 2.2 Proportion of different plastics used in packaging [9]

2.1 Low Density Polyethylene (LDPE)

Polyethylene was first produced in the laboratories of Imperial Chemical Industries, Ltd. (ICI), England [10]. The first commercial ethylene polymer was branch polyethylene commonly designated as low-density polyethylene (LDPE).

Polyethylene has the simplest structure of any plastics. It consists of an essentially linear molecule with repeating units. For LDPE, it has a branched structure, as shown in Figure 2.3.

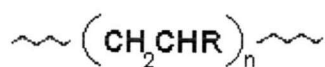


Figure 2.3 Low-density polyethylene structure

where R may be -H, $-(\text{CH}_2)_m\text{CH}_3$ or more complex structure with sub-branching

LDPE is a partially (50-60%) crystalline solid melting at about 115°C, with density in the range 0.910-0.925 g/cm³ [11].

The mechanical properties of LDPE are between those of rigid materials like polystyrene and limp plasticized polymer like the vinyls. LDPE has a good toughness. At room temperature, LDPE is fairly soft and flexible material. It can maintain this flexibility well under cold condition, so is applicable in frozen food packaging. However, at moderately elevated temperature, e.g., 100°C, it becomes too soft for many uses.

The electrical properties of LDPE are outstanding. In thick sections it is translucent because of its crystallinity, but high transparency is obtained in thin films. It is very inert chemically. It does not dissolve in any solvent at room temperature, but it is slightly swelled by liquids such as benzene and carbon tetrachloride which are solvents at high temperatures. It has good resistance to acids and alkaline, so, it is often used in containers for acids. Its non-polar nature makes it a relative good barrier against water vapor. Properties of LDPE are shown in Table 2.1.

Table 2.1: Typical Properties of Low-density Polyethylene [9,11-12]

Properties	Value
Glass transition temperature (°C)	-120
Melting temperature (°C)	105 - 115
Decomposition temperature (°C)	340 - 440
Density (g/cm ³)	0.912 - 0.925
Tensile strength (MPa)	8.2 - 31.4
Tensile modulus (MPa)	55.1 - 172
Elongation at break (%)	100 - 965
Tear strength (g/25µm)	200 - 300
Impact strength, Izod (ft/lb/in notch)	> 16
Water absorption (%)	< 0.01
Flammability	Burn with blue flame

LDPE is the most widely used packaging polymer, accounting for about one-third of all packaging plastics in the U.S. [9]. Because of its lower crystallinity, it is softer and more flexible than HDPE. This property makes LDPE too soft for most bottle applications, but the material of choice for films owing to its low cost. Over three-fourths of the polyethylene film produced goes into packaging application, including bags, pouches and wrapping for product. Other film uses include drapes and tablecloths. It is also used extensively in agriculture (greenhouses, ground cover, tank, pond, and canal liners, etc.) and construction applications. Extrusion coating for packaging material is the second-largest market for LDPE, accounting for almost 10% of the use in the U.S. [10]. The constructions, often laminates of foil, paper and polyethylene, are used in milk-type cartons for a wide variety of food and drinks.

2.2 Polymer Degradation

Regarding to materials composed of synthetic macromolecules, the term polymer degradation is used to denote change in physical properties caused by chemical reactions involving bond scission in the backbone of the macromolecule. In linear polymers, these chemical reactions lead to a reduction in molecular weight.

When considering biopolymers, the definition of polymer degradation is extended to include change of physical properties caused not only by chemical but also by physical reactions, involving the breakdown of higher ordered structure.

In both cases the term polymer degradation involves the deterioration in the functionality of polymeric materials, which in the case of biopolymer usually called denaturation.

It is useful to subdivide this broad field into 5 groups according to its various modes of initiation as follows:

1. Chemical Degradation refers to processes which are induced under the influence of chemical (e.g. acids, bases, solvents, reactive gases, etc) brought into contact with polymers.

2. Thermal Degradation refers to the case where the polymer, at elevated temperature, starts to undergo chemical change without the simultaneous involvement of another compound. Often, it is rather difficult to distinguish between thermal and thermo-chemical degradation because polymeric materials are rarely chemically pure. Impurities or additives present in the material might react with the polymeric matrix, if the temperature is high enough, causing thermo-chemical degradation.

3. Biodegradation is strongly related to chemical degradation as far as microbial attack is concerned. Microorganisms produce a great variety of enzymes which are capable of reacting with natural and synthetic polymers. The enzymatic attack of the polymer is a chemical process which is induced by microorganisms in order to obtain food (the polymer serves as a carbon source). The microbial attack of polymer occurs over a rather wide ranges of temperatures.

4. Mechanical Degradation generally refers to macroscopic effects brought about under the influence of shear force.

5. Photodegradation (or Light-induced degradation) concerns the physical and chemical change caused by irradiation of polymers with ultraviolet or visible light. The importance of photodegradation of polymer derives from the fact that the ultraviolet portion of the sunlight spectrum can be absorbed by various polymeric materials. The resulting chemical process may lead to severe property deterioration.

The strong inter-relationship between the various modes of polymer degradation should be emphasized. Frequently, circumstances permit the simultaneous occurrence of the various modes of degradation. Typical examples are: (a) environmental processes, which involve the simultaneous action of UV light, oxygen and harmful

atmospheric emission or (b) oxidative deterioration of thermoplastic of polymers during processing, which is based on the simultaneous action of heat, mechanical force and oxygen.

2.3 Biodegradation

The general mechanism of degradation of polymers into the small molecules employed by nature is a chemical one. Living organisms are capable of producing enzymes which can attack biopolymers. The attack is usually specific with respect to both the enzyme/biopolymer couple and the site of attack at the polymer. Thus, the formation of the specific decomposition products is guaranteed.

2.3.1 Mode of Biological Degradation

Generally, natural and synthetic polymers can be attacked by living organisms either chemically or mechanically.

The chemical mode relates to the decomposition of polymers in the digestive tracts of highly organized living species, humans, for example, or to the attack of microorganisms. Commonly, enzymes are involved in the chemical mode of polymer degradation. Although a great number of microorganisms can produce a variety of enzymes, microorganisms usually specialize on the attack of only a single substrate and are, therefore, producing only one or a few enzymes. If the substrate is changed, the microorganisms start, after a few weeks or months, the production of new enzymes capable of attacking the new substrate. The capability of microorganisms to adapt to new substrate is, of course, of great importance to the problem of the biodegradability of synthetic polymers. It is now generally accepted that a great number of microorganisms are capable of attacking synthetic polymers. At this point it must be emphasized that generally synthetic polymers are biodegradable. The reason we are not usually

confronted with problems caused by microbial attack of synthetic polymer is simply because this class of material is in principle brand new to nature. Thus, it can be anticipated that the situation will become different after the realm of microorganisms has adapted more generally to man-made polymers.

The mechanical mode of biodegradation of polymers relates to the attack by certain mammals (e.g. rodents) and insects. Regarding materials composed of natural polymers, wood and wool, for instance, the attack by animals is a serious problem. In a number of cases the reasons for attacking the polymer include also the nutritional needs of the attacking mammal or insect (e.g. death-watch beetles and termites digest wood or moths eat wool). Synthetic polymers (e.g. polyethylene or polystyrene), on the other hand, are not attacked for reasons of nutrition. The attacking animal bites or chews articles made of synthetic polymers because the physical properties of the polymeric material are compatible with the natural needs of the animal. A typical example is the need of rodents for biting, which can cause serious problems, e.g. for plastic insulation of electrical cables placed in the ground.

2.3.2 Methods of Testing Biodegradability

There are four main groups of procedures for studying biological decomposition of plastic material.

(1) Soil Burial Method

Standard samples of the material are buried in various soils, in outdoor location or under laboratory condition. From time to time, samples are withdrawn and analyzed for signs and quantitative characteristics of decomposition, such as weight loss, mechanical properties or a microscopic (SEM) examination. This method lacks reproducibility because of soil of various origin (from garden soil to sewage sludge) and the difficulties in controlling climatic factors (temperature and humidity).

(2) Culture of Fungi or Bacteria

More reproducible results can be obtained by using cultured fungi or bacteria. Commonly, the microbial degradability of synthetic polymers is studied by growth tests on solid agar media. Nutrient-salt agar is poured onto the sterile dishes and after the agar solidified, the medium is inoculated by spreading the fungus or bacteria spore suspension throughout the surface of the agar. The polymer material (the latter in the form of films, granules, plaques or powder) is deposited on the inoculated agar surface. The agar media contain all nutrients necessary for microbial growth except a carbon source. Typical microorganism employed for these tests are listed in Table 2.2. The test is run over a definite time (usually 3 weeks).

Table 2.2: Typical microorganism employed for biodegradability tests of synthetic polymer [13]

Microorganisms	Species
Fungi	<i>Aspergillus niger</i> , <i>Aspergillus flavus</i> , <i>Chaetomicum globosum</i> , <i>Penicillium funiculosum</i> , <i>Pullularia pullulans</i>
Bacteria	<i>Pseudomonas aeruginosa</i> , <i>Bacillus cereus</i> , <i>Coryneformes</i>
Actinomycetes	bacterium, <i>Bacillus</i> sp.

The growth rate of inoculated fungi or bacteria is measured after incubation for a convenient period of time. According to ASTM G21-96, growth rates are classified according to the fraction of the gel-surface covered with colonies into 5 classes as follow:

0 = no visible growth

1 = less than 10% covered

2 = 10-30% covered

3 = 30-60% covered

4 = 60-100% covered.

After microbial treatment, weight changes and other physical or chemical alterations are checked.

(3) Enzymatic Degradation

Biodegradation proceeds in many cases via chemical reaction catalyzed by enzymes which are synthesized by microorganisms and have very specific action. Testing of biodegradation can be accelerated by using isolated and purified enzymes instead of the microbes themselves. Thus the study of the detail of degradation is possible, and reaction condition such as temperature, pH, pressure and irradiation may be easily varied. A compilation of several typical enzymes together with their substrate polymer is presented in Table 2.3.

Table 2.3: Enzyme capable of rupturing main chains in natural polymers [13]

	Enzyme	Polymer	Occurrence
Carbohydrases	amylase	amylose	bacteria, malt, pancreas
	phosphorylase	amylose, amylopectin, cellulose	bacteria, yeast, animal, plants
	cellulase	polysaccharides in cell wall	bacteria, fungi
	lysozyme		bodily secretions, whites of eggs
Proteases	pepsin	proteins	gastric mucosa
	trypsin	proteins	pancreas
	carboxypeptidase	proteins	bacteria, pancreas
Esterases	ribonucleases	ribonucleic acid (RNA)	bacteria, plants, spleen, pancreas
	deoxyribonucleases	deoxyribonucleic acid (DNA)	bacteria, pancreas

(4) Activated Sludge Waste Water Treatment

This method is the simulation studies ranging from laboratory designed equipment, which replicates aerobic sewage treatment and anaerobic sludge digestion, through the exposure trials where material is submerged in activated sludge environment. Exposure trials require that the sample be securely held on some form of racking for aqueous environments. The racks, normally made of stainless steel, are submerged into the test situation and samples are periodically removed. This test method is designed to be applicable for all plastic materials that are not inhibitory to the bacterial presented in the activated sludge.

2.4 Biodegradable Polymer

Degradable plastics, especially polyolefins, which are widely used in disposable packaging materials, have been of interest for many years due to environmental pollution. In response to this concern, the development of the new biodegradable polymeric material has focused mainly on the following four areas since the beginning of 1970s:

1. Synthesis of new biodegradable polymer such as poly- β -hydroxybutyrate (PHB), polyhydroxyvalarate (PHV).
2. Modification of natural polymers.
3. Modification of synthetic polymers such as polylactide (PL), polyglycolide (PG) and polycaprolactone (PCL).
4. Biodegradable polymer composite. (Starch-Filled Plastics)

Biodegradable Polymer Composite (Starch-Filled Plastics)

Starch can be used as a natural filler in synthetic polymers and particularly in polyolefins to speed degradation. When the starch based films are exposed to

during the first 40 days, whereas lower percentage starch blends (< 30wt%) exhibited a slower and probably incomplete removal of starch.

Later, in 1992, Strantz et al. [16] studied the stability of corn starch-containing polyethylene films to starch-degrading enzyme. Processes have been developed to incorporate corn starch into plastics with the intent of increasing the rate of plastic biodegradation. The effect of starch-degrading enzyme on food-grade PE film that contained 6% corn starch (CSPE) was examined. Controlled PE film with no added starch, CSPE and laboratory grade soluble starch were treated with α -amylase. Samples were removed periodically for determination of reducing sugar content. Treatment with α -amylase released over 30% of soluble starch as glucose, while less than 1% of starch in CSPE was released. These results indicated that breakdown of CSPE by starch degrading enzymes was limited.

In 1998, Ioannis et al. [17] studied the mechanical properties, gas/water permeability and biodegradability of LDPE and rice or potato starch blends before and after storage in bioreactor. They reported that high starch content (> 30wt%) promoted brittleness and resulted in lower tensile strength and modulus. Gas permeability and water vapor transmission rate increased proportionally to starch content. Degradability of samples tested by immersion in bioreactor and burial in soil showed a substantial decrease in mechanical strength, tensile and flexural modulus, and percentage elongation.

A few years later, in 2000, Nita and co-workers [18] examined the biodegradability of blend films based on LDPE and various natural polymers, namely, non-modified wood flour (NWF), modified wood flour (MWF), starch (S), lignin (L) and dextrin (D) by soil burial test over periods of 6, 12 and 24 months. The mechanical properties, weight loss, water absorption, as well as thermal behavior of samples exposed to soil were evaluated. They found that incorporation of NWF, MWF, S, L and D into LDPE decreased the LDPE mechanical characteristics. The weight loss of LDPE/natural polymer blends increased with duration of sample exposure in soil and

depended also on both the type and concentration of the natural polymer used. The samples most susceptible to biodegradation were the blends of LDPE with dextrin and lignin. The increase in natural polymer concentration in blends led to an increase in weight loss. The water absorption increased with both the increase in natural polymer content in blends and with the duration of exposure in soil.

In the same year, the structure and properties of degradable LDPE-plasticized starch blends were studied by Zuchowska et al. [19]. Potato starch was plasticized by glycerol and blended with LDPE. They concluded that in the initial stage of degradation with microorganism the most important factor is the continuity of starch phase. An increase in starch content improved the accessibility of the polymer matrix. A susceptibility to degradation during soil or fungus aging not only of the starch phase but also the polymer phase was observed.

2.5 Starch

In nature, starch represents a link with the energy of the sun, which is partially captured during photosynthesis. Starch serves as a food reserve for plants and provides a mechanism by which non-photosynthesizing organism, such as man, can utilize the energy supplied by sun. Starch, the second most abundant polysaccharide, is a reserve carbohydrate which is stored as microscopic granules (2 to 150 μm in diameter) in various parts of plants such as seeds, roots, tubers, and stems.

Starch is composed of carbon, hydrogen and oxygen in the ratio of 6:10:5 as an empirical formula of $\text{C}_6\text{H}_{10}\text{O}_5$. It is a condensation polymer of glucose. The glucose units in the starch are presented as anhydroglucose, the linkage between the glucose units being formed as a molecule of water is removed during a step polymerization. The linkage of the one glucose to another through the C-1 oxygen is normally known as a glucosidic bond. Generally, starch consists of two major components: amylose, a linear polymer, and amylopectin, a highly branched polymer. The ratio of these components

The relative amount of these two fractions is a major factor in determining the properties of starch. Starch granule contains crystalline in amylose component and amorphous in amylopectin component. From their difference in the structure, amylose and amylopectin exhibit different properties. Amylose forms strong flexible films and has value as a coating agent. The branched component, amylopectin, forms film with poor properties but finds wide usage as a thickening agent, especially in food and paper applications. Starch is thermally stable in an open atmosphere to about 230°C. Above that temperature the starch molecules start to decompose. Native starch is presented in semicrystalline granular form with density of 1.5 g/cm³ [20]. Granular starch can be solvated to disperse an amorphous molecule by heating with plasticizers (mainly water) or by treating it with organic solvents, aqueous alkaline and salt solution. The conversion from crystalline granular starch to the dispersed and amorphous state is known as gelatinization.

Starch is used for the production of various biodegradable materials. It can be used as fillers or can be transformed into thermoplastic starch which can be processed alone or in combination with specific or synthetic polymers. Its structure can be easily altered in various ways. When processing at high temperature and pressures in the presence of high amount of water, a totally amorphous material can be produced and can be molded in various forms, even in film. This material, however, becomes brittle when the water content is less than 5 wt%. Thus, usually water is replaced by plasticizers and glycerine. The plasticized starch has a higher elongation (~170%) but its tensile strength is relatively low (0.7MPa) [21].

2.6 Banana Starch

Banana is a common name for any of a genus of tropical, tree-like herbaceous plants and also for their fruit. Species of the genus are native to South East Asia but are now grown extensively in all tropical countries. Banana is a large, herbaceous perennial with a plant rhizome (underground stem), from which the plant is perpetuated by

sprouts. In the tropics the stems are annual that is, they die after the fruit ripens, and new stems are developed from buds on the rhizome. These buds are the common means of propagating and making new plantations, and the growth is so rapid that the fruit is usually ripe within ten months after the offsets are planted. When fully grown the stem reaches a height of 3 to 12 meters. The fruits vary in length from about 10 to 30 centimeter. The average weight of a bunch is about 11 kilogram.

Banana is considered as the fourth on the list of developing world's most important food crops, after rice, wheat and maize. However, bananas have won an entry in the Guinness Book of World Record as the most consumed fruit in the world. There are more than 20 varieties of bananas in Thailand. Banana is probably the most familiar to Thais, for whom it was an essential of nourishment in their childhood. It is high in vitamins and good for the intestinal and digestive system. All parts of the plant can be utilized. The Thai people eat the fruit and cook it as a sweetmeat, in assorted ways. It can also be an ingredient in or accompany Thai dishes. It is grown in all regions of the country. Scientific discoveries have not passed over the field of food and nutrition. Modern improvements in food preservation and processing can also be seen in the handling of bananas in Thailand.

Many researches have been studied on starch from banana, however, they focus only on composition, physical and chemical properties of banana starch. A little works have been carried out on a banana starch-filled plastics for biodegradable polymer [22].

From the literature, there are 4 methods for extracting starch from banana. In 1981, Kayisu et al. [23] extracted starch from banana by freeze-dried at -18°C for 5 days, and then ground and mixed with distilled deionized water. After mixing, the suspension was allowed to stand for about 15 min. The starch was precipitated and the supernatant was decanted. The precipitated starch was washed several times with distilled water and dried at room temperature for 24-28 hours. The isolated starch has protein content 0.2%, lipid 0.2%, ash 0.02% and moisture 10.8%.

Later on in 1982, Lii and co-workers [3] used sodium hydroxide (NaOH) solution to extract banana starch. Bananas were mixed and ground at low speed for 2 min in one of following four solutions: 0.1N NaOH, 0.05N NaOH, 0.05N NaOH plus 0.02% sodium azide or 0.05N NaOH plus 0.01N HgCl₂. The slurry was filtered and then starch was sedimented from the filtrate. The starch was washed several times with distilled water. They found that addition of sodium azide or mercuric chloride increase amount of impurities and decreased starch recovery. Hence, 0.05N NaOH was used as a solution for starch isolation. They reported that green banana has 61.74% starch, while ripe banana has only 2.58% starch (on a dry weight basis). The starch has a protein content 0.09%, lipid 0.11% and ash 0.057%.

Recently in 2000, Mota et al. [4] extracted starch from eight different varieties of green banana varieties by homogenization of sliced banana with an aqueous solution of 4%w/v sodium chloride, 1%w/v ascorbic acid and 0.185%w/v ethylene-dinitrotetra acitic acid. The homogenate was filtered through cheese cloth. The slurry was centrifuged for 20 min at 2°C and then the precipitate was washed with a cold aqueous solution of 4%w/v sodium chloride. They discovered that the chemical composition of the starch varied according to the variety of green banana. The range obtained were 61-76.5% starch, 2.5-3.3% protein, 4-6% moisture, 0.3-0.8% lipid, 2.6-3.5% ash and 6-15.5% total fiber.

With in the same year, Bello-Perez et al. Isolated starch from banana using a sodium sulfite solution [24]. Bananas were mixed and ground with the solution. The homogenate was sieved through screen and washed with distilled water, and then the homogenate was centrifuged. The white starch was dried at 40°C for 48 hours. This method yielded 43.8% starch.

2.7 Compatibilizer

Because the physical, rheological, or chemical properties required for some applications cannot always be achieved using a single commercially available polymer, polymer are often blended. Most polymer blends tend to be immiscible because of the very low entropy of mixing. The result is the phase separation of the component into discrete domains, which produces inferior mechanical properties due to the lack of penetration of polymer chains from one phase to the other.

Compatibilizers are used to provide compatibility between otherwise immiscible polymers, but they do not produce miscibility on the molecular scale. Their action can be thought of as reducing the interfacial tension between the components by adsorbing at the interface surrounding the domains.

In blending starch with the other synthetic polymers, the hydrophilic character of starch due to the presence of hydroxyl group in starch molecule leads to poor adhesion with synthetic polymer resulting in a reduction of mechanical properties. Therefore, in order to enhance the compatibility between two immiscible polymers, a compatibilizer must be used. Compatibilizers used to increase the 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 the compatibilizer. Hydrocarbon part acts as the hydrophobic portion, which can have good miscibility with polyethylene.

The examples of widely used compatibilizer are ethylene-acrylic acid copolymer (EAA), ethylene-vinyl acetate copolymer (EVA) and polyethylene-g-maleic anhydride copolymer (PE-g-MA). As shown in Figure 2.7 through 2.9, these compatibilizers contain groups capable of forming hydrogen bond with the hydroxyl group of starch, and have the hydrophobic part, that can compatibilize with polymer matrix.

compatibilizer. The prepared blends were studied using mechanical properties measurement and SEM microscopy to determine their morphology. The result showed a much better dispersion of plasticized starch within the LDPE matrix, with a concurrent significant reduction in the phase size, indicating an increased adhesion between the two polymers. This was also reflected in the mechanical properties of the blends which were significantly improved in comparison to the uncompatibilized blends.

Apart from that, Bikiaris and Panayiotou [1] studied LDPE/starch blends compatibilized with two different PE-g-MA copolymers containing 0.4 and 0.8 mol% anhydride groups respectively. The blend could retain satisfactory mechanical properties in comparison with uncompatibilized blends, apparently due to the reaction of anhydride groups with hydroxyl groups of starch. The blends compatibilized with the PE-g-MA copolymer containing 0.8 mol% anhydride group have a higher tensile strength. They were found that as the amount of anhydride groups in the copolymers increase a finer dispersion of starch in the LDPE matrix is achieved. This is reflected in the mechanical properties of the blend and especially in the tensile strength. The biodegradation of the blends followed the exposure to activated sludge. It was found that the compatibilized blends have only a slightly lower degradation rate compared to the uncompatibilized blends.

2.8 Introduction to Photodegradation

Sunlight has been recognized as an important factor in the deteriorative ageing and weathering processes which occur in commercial polymer. Most commercial organic polymers undergo chemical reaction upon (as regular constituents or as impurities) capable of absorbing ultraviolet (UV) light. This fact is important because the spectrum of the sunlight penetrating the earth's atmosphere contains a portion of UV light. Therefore, photoreaction is usually induced when organic polymers are subjected to outdoor exposures.

The wavelength of the radiation from the sun which reaches the earth's surface extends from the infra-red (>700 nm) through the visible spectrum (400-700 nm) into the ultraviolet (UV) (<400 nm). Polymers have different photodegradative sensitivity to UV light of different wavelength. The varying sensitivity results from differences in the chemical structure. As shown in Table 2.4, the maximum sensitivity of several polymers (as determined by the bond dissociation energies) is in the range of 290 and 400 nm. Although the atmosphere of the earth filters out the UV part of solar radiation, the above (so called actinic) range of solar UV radiation is about 6% of the total radiation of the sun which reaches the earth's surface.

Table 2.4: Wavelength of UV radiation (energy of a photon) at which various polymers have maximum sensitivity [6]

Polymer	Wavelength (nm)
Styrene-acrylonitrile copolymer	290 and 325
Polycarbonate	295 and 345
Polyethylene	300
Polystyrene	318
Polyvinyl chloride	320
Polyester	325
Vinyl chloride-vinyl acetate copolymer	327 and 364
Polypropylene	370

2.9 Photooxidation

2.9.1 Autooxidation Process

Plastic is a hydrocarbon polymer. When it is exposed to the radiation energy, chemical bond will break and begin to degrade. Effective degradation happens with the presence of oxygen. The first chemical step in photodegradation is usually a homolytic

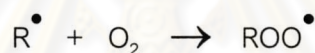
bond scission to form free radicals. These radicals will normally react rapidly with any oxygen present and then form chemical groups, especially hydroperoxide group (ROOH). The hydroperoxide group will then decompose to carbonyl group and hydroxyl group, which is the importance case of plastic degradation. In this way, UV radiation is particularly effective initiator of oxidation.

The conventional mechanism of autooxidation is as follow :

1. Hydrocarbon molecules break into free radicals.



2. Hydrocarbon radical (R^{\bullet}) reacts with oxygen and form peroxide radicals (ROO^{\bullet}).



3. Peroxy radical accepts H atom from the other hydrocarbon molecule to generate hydroperoxide.



4. Hydroperoxide group are photolytically decomposed into alcoxy radical (RO^{\bullet}).



Frequently, carbonyl groups are major constituents of the end products, being formed in the terminal reaction. The excited carbonyl groups decompose via Norrish reaction of types I, II and III.

The Norrish-I reaction (Figure 2.10) is a radical cleavage of the bond between the carbonyl group and the α -carbon atom, and is usually followed by the formation of carbon monoxide.

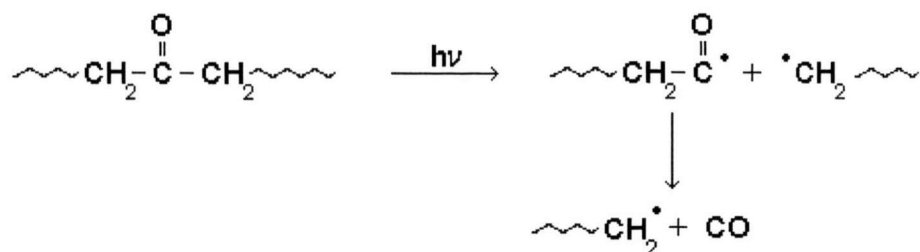


Figure 2.10 Norrish-I reaction

The Norrish-II reaction (Figure 2.11) is a nonradical scission which occurs through the formation of a six-member cyclic intermediate. Abstraction of a hydrogen from the γ -carbon atom results in decomposition by β -scission to an olefin, an alcohol, or ketone. For example, in the case of polyethylene, a terminal double bond and an enol/ketone end groups are formed:

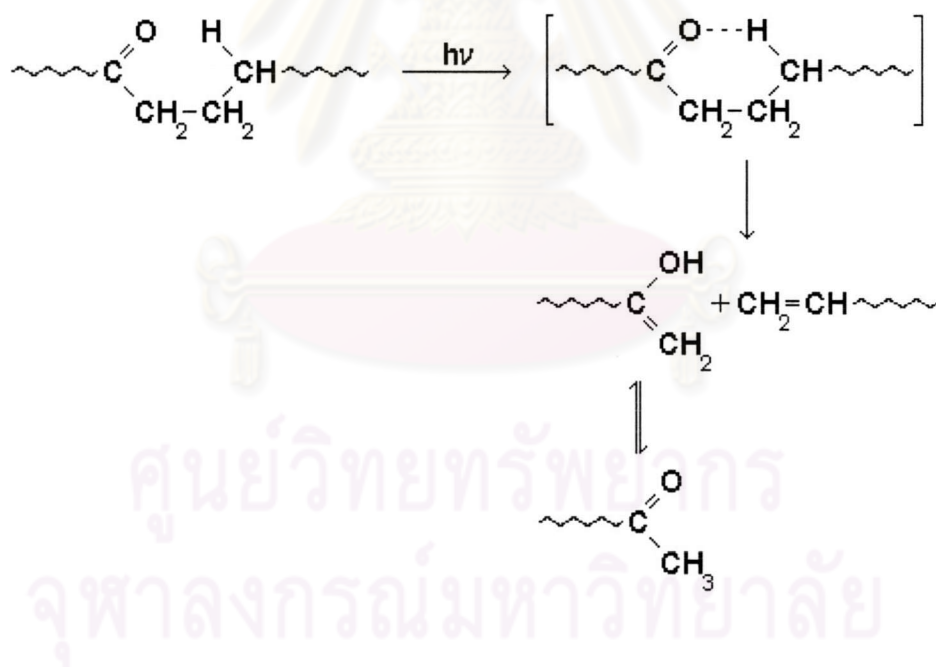


Figure 2.11 Norrish-II reaction

The Norrish-III reaction (Figure 2.12) is also a non-radical chain scission; however, it involves the transfer of a β -hydrogen atom and leads to the formation of an olefin and an aldehyde.

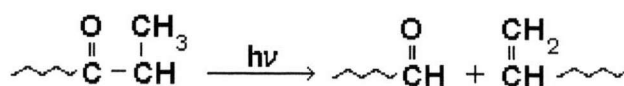


Figure 2.12 Norrish-III reaction

2.9.2 Sensitized and Additive-Initiated Degradation

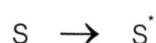
It is clear that the energy of the quanta of UV light is sufficient to break chemical bonds. However, the ever-increasing amount of plastics used for disposable packaging material and their potential for causing permanent pollution of the environment have prompted workers to seek methods of producing polymer with controlled service life. After having finished its useful function, e.g., as a container for milk, the plastic becomes a waste material; it is desirable that this waste can be decomposed with the aid of sunlight, humidity, and bacteria as rapidly as possible.

The photodegradation of plastic can be enhanced by two basic ways. The first one is the introduction of a chromophoric group in the backbone of the polymeric chain during or after the polymerization process in comonomer form. Chromophoric groups are necessary to absorb the incident radiation. In polymer, these are usually unsaturated structures such as carbonyl, ethylenic or aromatic groups. These chromophores can give rise to the initiation of new chain reaction upon prolonged irradiation and thus to rapid deterioration of the polymer. Another way is adding or mixing low-molecular-weight chemical (so called photosensitizer) in the form of additive.

Recently the term sensitization has been used by photochemists to solely denote process involving energy transfer which is subsequently followed by a chemical reaction or a physical process.

The mechanism of photosensitization is as follow :

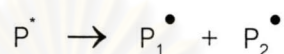
1. An additive absorbs radiation energy and turns into excited state.



2. An excited additive can be transferred absorbing energy to polymer molecule.



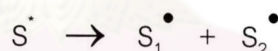
3. Excited polymer molecule will be separated into free radicals.



These free radicals will react with any oxygen presented, leading to the reduction of polymer molecular weight.

Apart from that, an excited additive or photosensitizer can also be changed into free radicals by two routes.

1. Excited initiator molecules dissociating readily into free radicals after excitation or so called "Intermolecular photocleavage"



2. Intermolecular hydrogen abstraction



These free radicals are the beginning of polymer degradation.

2.10 Photosensitizer

Photosensitizer or photoactivator is a compound which has a high absorption coefficient for UV light. The excited compound either decomposes into free radicals and initiates degradation or oxidation of the polymer, or it transfers the excitation energy to polymer (or to oxygen).

Many compounds have been studied for their photo-activity as shown in Table 2.5

Table 2.5: Compounds examined for photoactivity [27]

Aromatic Carbonyl Compounds	Deoxyanision, Flavone, 10-Thioxanthone Dibenzocycloheptadienone 4-Methoxybenzophenone 4,4"-Oxydibenzophenone
Organosulfur Compounds	Benzyl disulfide, Phenyl disulfide 2-Mercaptobenzothiazole
Inorganic Pigments	Titanium dioxide, Zinc Oxide
Quinones	Anthraquinone, 2-Chloroantraquinone 1-Methoxyanthraquinone 2-Ethylanthraquinone, 2-Methylanthraquinone
Organo-metallic Compounds	Ferric octanote (1%), Ferric stearate Manganous stearate
Transition Metal Salts	Copper Carbonate Manganous Chloride Ferrous Ammonium Sulphate
Aromatic Amines	4,4'-Methylenebis (N,N-dimethylanilline) Triphenylamine

A good sensitizer should be easily admixed with the polymer and must not decompose thermally.

Many studies have been carried out to achieve the promotion of the degradation of synthetic polymer such as PE by addition of photosensitizer. In 1992, Furguson et al. [7] studied the effect of titanium dioxide (TiO_2) and ferric stearate pigments on the polyethylene photodegradability. The amount of TiO_2 was 0.25, 0.50 and 0.75 %wt, and

the amount of ferric stearate were 0.10, 0.25 and 0.40 %wt respectively. The carbonyl index was found to increase in LDPE films containing 0.10 %wt ferric stearate, as well as 0.25 %wt TiO_2 after irradiation.

Later, in 1994, Angulo-Sanchez and co-workers [5] reported the photodegradation of LDPE films formulated with titanium (IV) oxide acetylacetonate (TAc) and titanium dioxide in different proportions. Samples of blow-extruded films were submitted to accelerated UV aging with fluorescent lamps and the polymer degradation was measured. They found that TAc can promote photooxidation and accelerate the film degradation. The carbonyl index, molecular weight and elongation at break decreased proportionally to the exposure time and a faster decrease was observed as the TAc concentration increased.

Afterward, in 1996, Byung Seon Yoon et al.[27] investigated degree of photodegradation and photodegradation after biodegradation of three degradable polymer materials; starch-polyethylene (PE) binary blends, PE containing starch and a photoactivator, and PE containing starch and a photoactivator which was coated with biopolymer. Ferric dithiocarbamate and gelatin were selected as the photoactivator and coating material, respectively. The results showed that the addition of the gelatin-coated ferric salt in PE extended the induction period of degradation and accelerated photodegradation after removal of coating material by biodegradation.

In 1997, the effects of the cerium carboxylate (CeCar_3) with/without aromatic ketones (AK) photosensitizer on the rate of ultraviolet photooxidation of LDPE film and their mechanism in sensitizing photooxidative degradation were studied by Yinchao Lin [28]. Results showed that CeCar_3 can cause the accelerated photooxidative degradation of LDPE films, but CeCar_3 in combination with AK may bring about the accelerated or retarded photooxidative degradation of LDPE films to varying degrees.

Both organic and inorganic metal compounds can sensitize photodegradation. Inorganic metal oxides and salts, e.g., ZnO , TiO_2 , and FeCl_3 accelerate

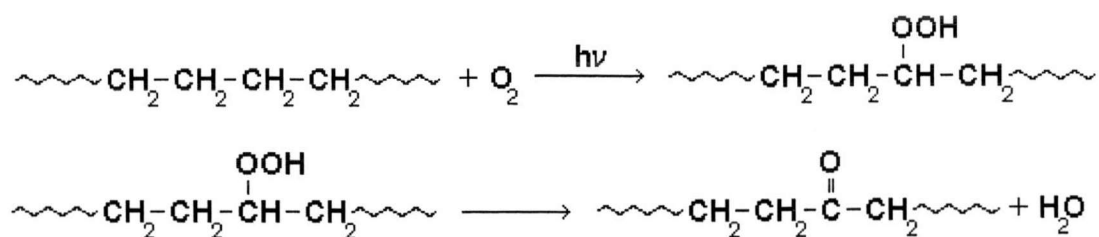
photodegradation. It is assumed that free radicals are formed from these compounds during irradiation [6]. It has been established that ZnO acts both as a PP light-stabilizer [29] and as a light-sensitizer of cross-linked LDPE [30] at the same time.

In 2001, Bircan Dindar and Siddik Icli [31] studied the photodegradation of phenol in presence of TiO₂, Fe₂O₃, and ZnO. Irradiations have been done in photoreactors under sodium lamp, direct sunlight, and concentrated sunlight. They found that the photodegradation of phenol was seen to be faster for all of the oxides irradiated by concentrated sunlight. The photodegradation capacity of TiO₂ is superior to that of ZnO and Fe₂O₃ under a sodium lamp and direct sunlight, but ZnO is found to be as reactive as TiO₂ under concentrated sunlight.

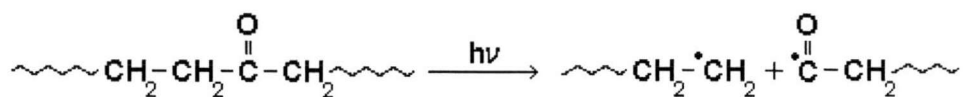
2.11 Photodegradation of Polyethylene

Polyethylene is relatively resistant to UV radiation in the absence of oxygen. However, when it is exposed to both oxygen and UV radiation it becomes brittle because of photooxidation. Hydroperoxide and carbonyl group are generated and then polyethylene molecule that contains carbonyl group will be dissociated by Norrish type I or Norrish type II reactions. These processes result in reduction in polymer molecular weight.

The mechanism of polyethylene photooxidation is shown in Figure 2.13:



Norrish Type I



Norrish Type II

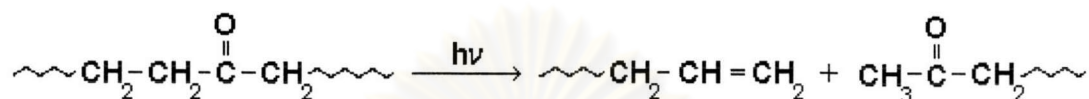
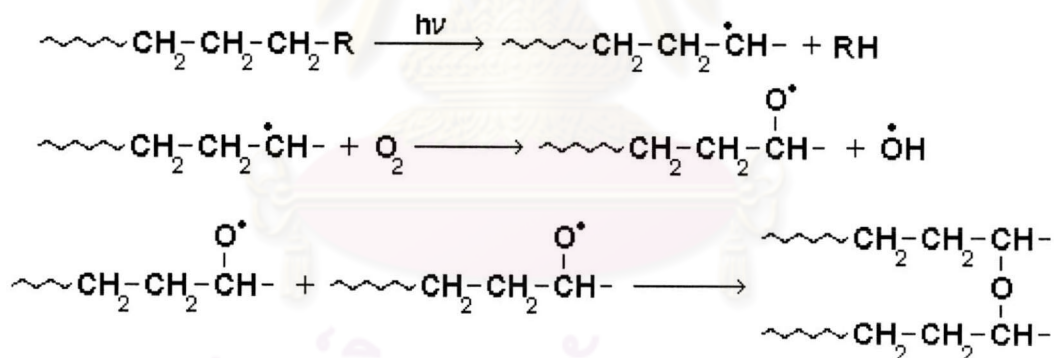


Figure 2.13 The mechanism of polyethylene photooxidation

Furthermore, crosslink reaction between polyethylene molecule can be occurred, as shown in Figure 2.14



or

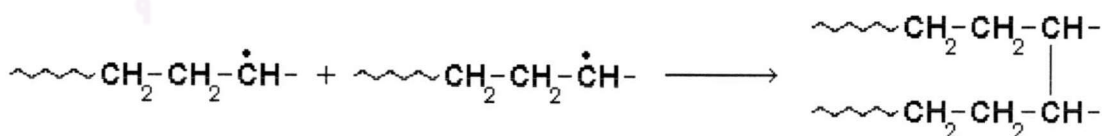


Figure 2.14 Crosslink reaction between polyethylene molecule

2.12 Processing

In this study, there are two procedures for processing LDPE blend films. Twin screw extruder has been used as a mixing device for mixing LDPE, banana starch, and other compositions, whereas chill roll cast film has been used for film production process.

2.12.1 Extrusion

In application for packaging plastics, the first step is to convert the solid plastic, usually in pellet form, into a melt, which can then be shaped using heat and pressure. An example of the equipment used to do this is an extruder for film, sheet, extrusion blow molded bottles and an injection molding machine for injection molded. Extruder and injection molding machines are very similar in concept and structure, differing primarily in how the material leaves the chamber where it is melted.

The purpose of an extruder is to take the solid plastic and, using heat, pressure and shear, transform it into a uniform melt which can then be delivered to the next processing stage. Producing the melt may involve mixing in additive such as color concentrates, blending resins together and incorporating regrind. The final melt must be uniform in concentration. The pressure must be high enough to force the viscous polymer through an opening which imparts a desired shape to the extrudate.

An extruder normally consists of a machine base, a drive (motor, gear box, thrust bearing), a plasticating unit (screw, barrel, temperature control system) and a control cabinet (control device, power supply). A simplified extruder diagram is shown in Figure 2.15.

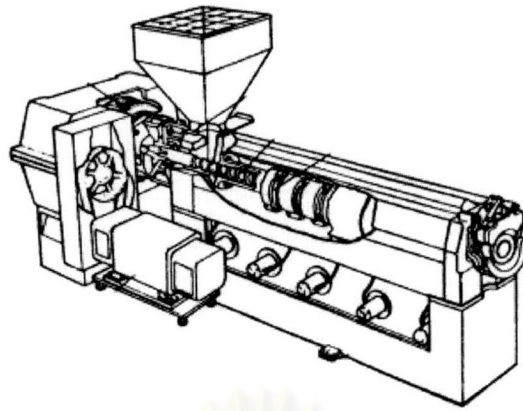


Figure 2.15 Plastic extruder

The extruder accomplishes all this by using a barrel containing a screw with helical channels. The plastic pellets are fed into the barrel through a hopper at one end, and then conveyed by the screw to the other end of the barrel. The depth of the channels in the screw decrease with distance from the hopper, building up pressure on the plastic. External heating as well as internal heating from friction between the plastic and the screw cause the plastic to soften and melt.

Extruder generally contains at least three sections. The first, next to the feed hopper, is the feed section. Its function is to get the plastic into the extruder at a relatively even rate. Commonly, this section is maintained at a relatively cool temperature, to avoid blockage in the feed channel. Next comes the compression section, in which most of the melting occurs and pressure is built up. The transition between the feed section and the compression section can be abrupt or gradual. Finally, next to the extruder outlet, is the metering section. Its purpose is to assure a uniform flow of material out of the extruder. At the end of the barrel, the melted plastic leaves the extruder through a die, which has been designed to impart the desired shape to the stream of melted plastic. This may be the final shape for the plastic, or it simply may be the beginning of further processing.

Different types of extruders are employed depending on the application. The most widely used type is the twin screw extruder.

2.12.2 Twin Screw Extruder

Twin screw extruder is used where superior mixing or conveying is important. They can be divided into co-rotating and counter-rotating types. As the name indicated, the difference is in whether the two screws rotate in the same or in opposite direction.

(1) Co-rotating Twin Screw Extruder (Figure 2.16)

With each revolution, the co-rotating twin screw extruder transfers the melt from the screw channel of one screw to that of the other screw. The conveying mechanism-drag force- is comparable to that found in the single screw extruder. By being transferred from one screw channel to another, however, the melt does follow a longer path and is subjected to higher shear. This types of extruder finds application today primarily in compounding.

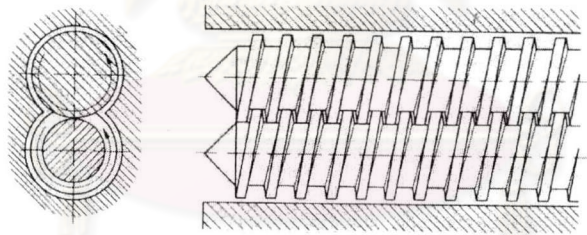


Figure 2.16 Co-rotating twin screw extruder

(2) Counter-rotating Twin Screw Extruder (Figure 2.17)

A fundamentally different conveying mechanism characterizes this extruder. Each screw segment forms a closed chamber that conveys the melted material from the hopper to the end of the screw without any exchange with neighboring chambers. Drag force are not needed for this positive conveying, with the result that little dissipation-induced heating occurs.

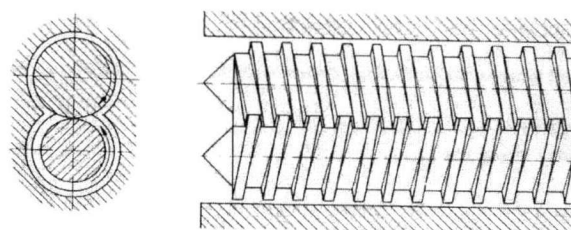


Figure 2.17 Counter-rotating twin screw extruder

2.12.3 Chill Roll Cast Film

Generally, cast film and sheet are produced by extrusion of the melt onto chilled rollers. For production of cast film, the die opening through which the melted plastic exits the extruder is shaped like a slit, producing a rectangular profile in the melt, which the width must be greater than the thickness. The plastic exits the die downwards or at an angle between vertical and horizontal, onto the chilled, highly polished, turning roll where it is quenched from one side, contacting it tangentially. The roll is highly polished to give good surface characteristics to the resulting film. The speed of the roller controls the draw ratio and final film thickness. The film is then sent to a second roller for cooling of the other side. Commonly, the film travels in an S-pattern around at least two chill rolls, before the film is cool enough to wind. In fact, the first roll typically operates at a temperature of at least 40°C (104°F). Finally, the film passes through a system of rollers and is wound onto a roll. A typical film casting process is depicted in Figure 2.18.

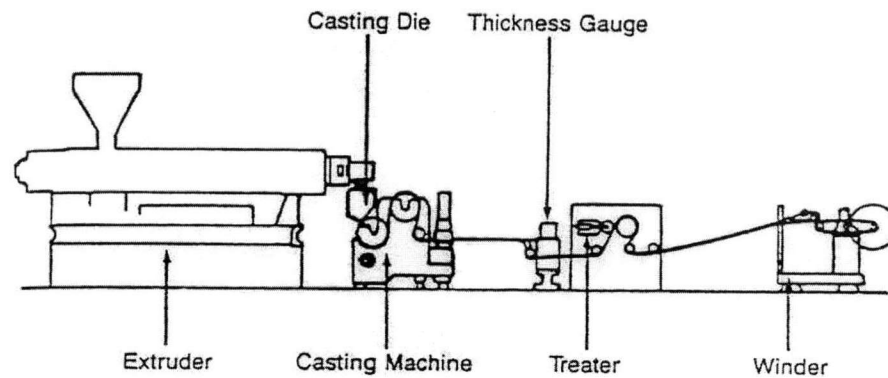


Figure 2.18 Schematic of a film casting operation

In this method, plastic shrinks as it cools, so the film or sheet produced is narrow than the die dimension, and also tends to thicken at the edges, which must be trimmed. Also, any irregularities in the gauge tend to be magnified when the film is rolled up. Cast film variation of $\pm 3\%$ is common, and can produce gauge bands in the roll which can be minimized in two ways. The oldest method is to oscillate the film as it is wound to produce some randomization of the thickness variation. This method has the disadvantage of significantly reducing the width of the web and increasing the amount of scrap generated, which is generally fed back into the extruder in-line. A more modern method is to use sensors to monitor the thickness on-line, and via computer control automatically adjust the die gaps as needed.

Cast film properties can be modified by orientation, or stretching of the film under condition causing some molecular realignment in the direction of the stretch, which persist when the force is removed. Orientation tends to increase crystallinity, barrier properties, and strength in the stretched direction, while decreasing strength in direction perpendicular to the orientation direction.

If the cast film is not stretched significantly in the machine direction (the direction of travel through the production equipment), it is relatively unoriented and has fairly balanced mechanical properties in the machine and cross direction. If the takeoff speed is significantly higher than the rate of extrusion, the plastic is stretched and

uniaxially oriented. The stretching can occur at the initial contact with the chill roll, but is more commonly done after the first chill roll, and usually involves some reheating of the film prior to stretching it. If the plastic is also stretched in the cross machine direction, it is biaxially oriented. Biaxial orientation can be accomplished in either a single step or, as occurs more commonly, in two consecutive steps, as shown in Figure 2.19 and Figure 2.20. The resulting film is “balance” if the orientation is equal in the two directions, or “unbalance” if it is more highly oriented in one direction than the other.

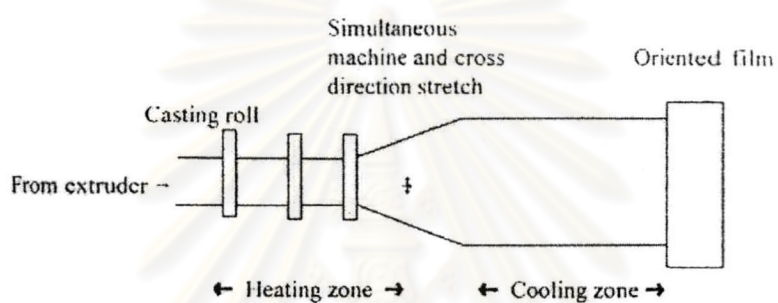


Figure 2.19 One-step orientation of cast film

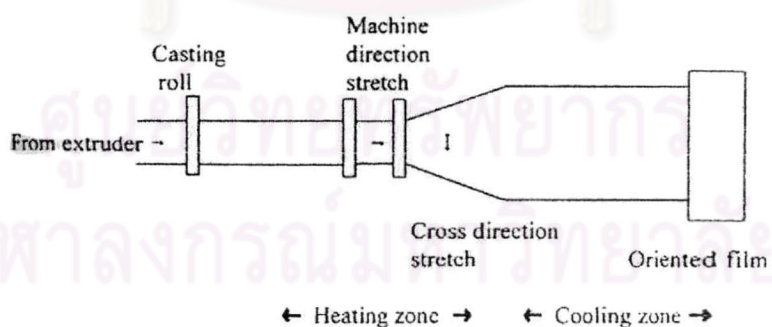


Figure 2.20 Two-step orientation of cast film

2.13 Tensile Properties

Tensile properties are most widely used for defining the quality of production of polymeric materials, their design and engineering behavior. Tensile test, in a broad sense, is a measurement of the ability of a material to withstand force that tends to pull it apart and to determine to what extent the material stretches before breaking. Different types of plastic materials are often compared on the basis of tensile strength, elongation and tensile modulus data.

Tensile stress is the tensile load per unit area of minimum original cross section within the gauge boundaries carried by the test specimen at any given moment. It is expressed in force per unit area. The maximum tensile stress supported by the specimen during a tension test is tensile strength. Elongation is the increase in length produced in the gauge length of the test specimen by a tensile load. It is expressed in unit of length, commonly as a percentage. The ratio of the elongation to gauge length of the test specimen, that is the change in length per unit of original length, is strain. It is expressed as a dimensionless ratio. Modulus of elasticity, an indication of the relative stiffness of a material, is the ratio of stress to corresponding strain below the proportional limit of a material. It can be determined from a stress-strain diagram, as shown in Figure 2.21.

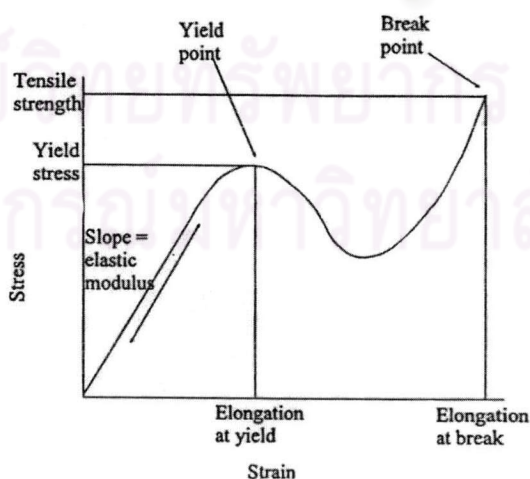


Figure 2.21 Diagram illustrating stress-strain curve

The result of tensile properties are widely different for different polymers and can vary greatly for the same polymer. Such variation in test result is due to the diversity of structure found within the broad range of polymers, strain rate, and environmental conditions such as humidity and temperature. Schematics of tensile curve for different types of polymers can be seen in Figure 2.22.

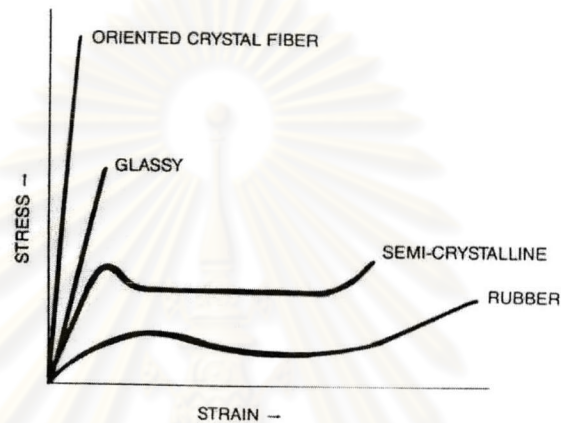


Figure 2.22 Schematic of tensile test result

The four tensile test results given here are typical of polymer in different states that have been tested to failure with a moderate strain rate. The first curve to left shows the extreme case of a crystalline state with the lamella oriented in one direction such as would occur within a fiber. This curve is also characteristic of a highly cross-linked polymer. The next curve shows typical behavior for a polymer in the glassy state. The third curve is that of a semi-crystalline polymer. The last curve is that common to the rubber state which shows no real linear region at the onset of testing.