CHAPTER 1

INTRODUCTION

1. 1 Introduction

With biodegradable plastic being popular for most products, the amount of plastic wastes has multiplied, causing problems of landfill disposal as well as posing an impact on the environment. Moreover, almost all plastics today are made from crude oil and natural gas, which are becoming scarce and more expensive. Degradable plastic, therefore, is a wise alternative. Its degradation mechanism varies according to different plastic structures, for example photodegradable, mechanical degradation, or oxidative degradation. These mechanisms could only break a plastic material into small pieces. So, it takes a long time to degrade them into substances that can be reused by plants. Meanwhile, they cannot be dumped in landfills. Degradable plastic differs from Biodegradable Plastic in that the latter can be decomposed by micro-organisms underground and turns into carbon-monoxide and water useful in photosynthesis, as shown in Figure 1.1.

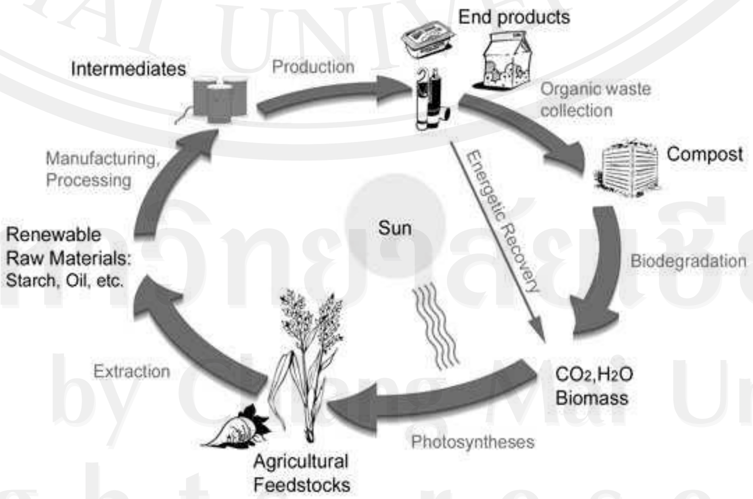


Figure 1.1 Life’s cycle of biodegradable plastic.

Biodegradable plastics can be divided, according to the raw material sources, into 2 types as follows.

1. Biological source: raw materials are from the nature, which can be obtained or renewed (renewable source).
2. Petroleum source: raw materials are obtained from crude oil or natural gas.

1.2 Degradation mechanisms

These definitions of degradation are used throughout the report to describe the degradation processes of the 'biodegradable plastics' currently available or under development. Definitions of these degrade mechanisms for different materials are provided below.

A. Biodegradable

The failure of early 'biodegradable' polymers to properly degrade led to the American Society of Testing and Materials (ASTM) creating definitions on what constitutes 'biodegradability'. The ASTM definition, updated in 1994 (ASTM Standard D-5488-84d), has led to the establishment of labeling terminology for packaging materials. The ASTM defines 'biodegradable' as:

"*capable of undergoing decomposition into carbon dioxide, methane, water, inorganic compounds, or biomass in which the predominant mechanism is the enzymatic action of microorganisms, that can be measured by standardized tests, in a specified period of time, reflecting available disposal condition".*

Biodegradation is degradation caused by biological activity, particularly by enzyme action leading to significant changes in the materials chemical structure. In essence, biodegradable plastics should break down cleanly, in a defined time period, to simple molecules found in the environment such as carbon dioxide and water.

Biodegradation rates are highly dependent on the thickness and geometry of the fabricated articles. While rapid breakdown rates are often quoted these generally apply to thin films. Thick-walled articles such as plates, food trays and cutlery can take up to a year to biologically degrade.

B. Compostable

Compostable biodegradable plastics must be demonstrated to biodegrade and disintegrate in a compost system during the composting process (typically around 12 weeks at temperatures over 50 °C). The compost must meet quality criteria such as heavy metal content, ecotoxicity, and no obvious distinguishable residues caused by the breakdown of the polymers. Compostable plastics are a subset of biodegradable plastics. 'Compostable' is defined by the ASTM as:

"*capable of undergoing biological decomposition in a compost site as part of an available program, such that the plastic is not visually distinguishable and breaks down to carbon dioxide, water, inorganic compounds, and biomass, at a rate constant with known compostable materials (e.g. cellulose)*".

In standards and regulations it is important to clear definitions so that everyone knows what is meant by certain expression. Some of them, used by the CEN working group, are presented in below [CEN, 1997; Pagga, 1997]. It is important to state in a definition that biodegradability is an essential pre-requisite for compostability and that complete biodegradation.

Degradation	"Degradation is an irreversible process leading to a significant change in the structure of a material, typically characterized by a loss of properties (e.g. integrity, molecular weight or structure, mechanical strength) and/or fragmentation. Degradation is affected by environmental conditions and proceeds over a period of time comprising one or more steps"
Degradable	"A material is called degradable with respect to specific environmental conditions if it undergoes a degradation to a specific extent within a given time measured by specific standard test methods"
Biodegradation	"Biodegradation is a degradation caused by biological activity, especially by enzymatic action, leading to a significant change in the chemical structure of a material"

Inherent biodegradability	"The potential of a material to be biodegraded, established under laboratory conditions"
Ultimate biodegradability	"The breakdown of an organic chemical compound by microorganisms in the presence of oxygen to carbon dioxide, water and mineral salts of any other elements present (mineralization) and new biomass or in the absence of oxygen to carbon dioxide, methane, mineral salts and new biomass"
Compost	"Compost is an organic soil conditioner obtained by biodegradation of a mixture consisting principally of various vegetable residues, occasionally with other organic material and having a limited mineral content"
Compostability	"Compostability is a property of a packaging to be biodegraded in a composting process. To claim compostability it must have been demonstrated that a packaging can be biodegraded in a composting system as can be shown by standard methods. The end-product must meet the relevant compost quality criteria"
Packaging	"Packaging is all products made of any materials of any nature to be used for the containment, protection, handing, delivery and presentation of goods, from raw materials to processed goods, from the producer to the user or the consumer"
Constituents of a packaging material	"All pure chemical materials and substances from which a packaging material is composed"
Packaging materials	"Packaging materials are any materials used for packaging"

C. Hydro-biodegradable and Photo-biodegradable

Hydro-biodegradable and photo-biodegradable polymers are broken down in a two-step process an initial hydrolysis or photo-degradation stage, followed by further biodegradation phase 'water-soluble' and 'photodegradable' polymer also exist.

D. Bio-erodable

Many polymers that are claimed to be 'biodegradable' are in fact 'bio-erodable' and degrade without the action of micro-organism – at least initially. This is also known as abiotic disintegration, and may include processes such as dissolution in water, 'oxidative embrittlement' (heat ageing) or 'photolytic embrittlement' (UV aging).

1.3 Polymer Blend [Knaul *et al*., 1999; Seymour, 1982]

Polymer blends have come to the fore in recent years as the search for new improved materials continues. Their current and potential technological importance is remarkable and their ubiquitous presence in consumer products is testimony to their commercial importance. Furthermore, pursuit of our understanding of the physical and mechanical properties of polymer blends has uncovered new principles, refined earlier fundamental concepts, and revealed further opportunities for research and practical problem solving. In this last respect, polymer blends offer a strong analogy to the previously established role of copolymerization as a means of coming the useful properties of different molecular species, but blends allow this to be done through physical rather than chemical means. The polymer blend may be defined as a combination of two or more polymers resulting from common processing step, e.g., the mixing of two or more polymers in the molten state, or casting from common solvent. These methods of preparation do not usually lead to chemical bonding between the components. The successful implementation of this concept requires different knowledge and techniques than that used to develop new polymers.

Two or more existing polymers may be blended for various reasons. One reason is to achieve a material that has a combination of the properties of the constituents, *e.g.* a blend of two polymers, one of which is chemically resistant and the other tough. Another reason is to save costs by blending a high-performance polymer with a cheaper material. A very important use of blending is the brittleness of the rigid polymer [Bower, 2002]. Ideally two or more polymers may be blended together to form products that show desirable combinations of properties. But this ideality is seldom attained due to some inherent and fundamental problems. Most of the polymer pairs are not thermodynamically miscible and so exist in two different phases in the polymer blend. This breakdown into two phases creates an interfacial tension and poor adhesion between the two phases lead to lower degree of this dispersion and gross separation during later processing or use. Poor adhesion also produces very weak and brittle mechanical properties due to poor stress transfer between phases and hinder the formation of highly structured morphologies. Thus to define the interaction between the polymer pairs at the molecular level, the term "compatibility" has been used in technological literature. Compatibility is not synonymous with miscibility since it is used to characterize the relative ease of fabrication or performance of the two polymers in blend. Blend components which can resist gross phase segregation and/or show desirable blend properties are frequently said to possess some degree of compatibility though they may not be miscible at all from a thermodynamic point of view [Paul, 1978].

1.3.1 Polymer-Polymer Compatibility

Polymer blends can be classified into 3 groups: (1) compatible, (2) incompatible, and (3) partially compatible blends. Compatibility is more the exception than the rule and so blends are usually, at most, only partially compatible and often incompatible.

1.3.1.1 Compatible Blends

Compatible blends can be defined as polymer mixtures that are able to mix at the molecular level in all proportions to give homogeneous products. They are characterized by a glass transition temperature, which is intermediate between the T_gs of the respective homopolymers, as shown in Figure 1.2 (a). To a reasonable approximation, the T_g of a compatible polymer blend can be calculated from the Fox equation [Paul, 1978]:

$$1/T_{g(AB)} = W_A/T_{g(A)} + W_B/T_{g(B)}$$

where:

$T_{g(AB)}$ = T_g (K) of the polymer blend
$T_{g(A)}$, $T_{g(B)}$ = T_gs (K) of the respective homopolymers A and B
W_A, W_B = weight fractions of the homopolymers A and B, respectively.

1.3.1.2 Incompatible Blends

Incompatible blends are formed when two or more polymers are combined together and separate completely into multiphase structures. Incompatible polymer blends will exhibit the two T_g characteristic of the components of the mixture, provide that the two T_g are far enough apart to be resolvable by the measuring technique employed for their detection.

1.3.1.3 Partially Compatible Blends

Most polymer blends fall somewhere between the 2 limits of complete compatibility and complete incompatibility. The extent to which two or more polymer are compatible depends on various factors of which the strength of the polymer-polymer intermolecular interactions is usually the most influential. The PBS/CAB and PBS/CAB/plasticizer blends studied in this research are expected to fall into this category of partial compatibility.

1.3.2 Prepared of Polymer Blends

Since it is polymer blends with which this research is concerned, they are now described here in more detail. The two methods that are most widely used to prepare polymer blends are solution blending and melt mixing.

1.3.2.1 Solution Blending [Sasisil, 2004]

This method involves choosing a suitable solvent which can dissolve both polymers to give a stable polymer blend solution. The solid polymer blend is then recovered either by evaporating off the solvent or by precipitating it into a non-solvent. In both cases, the blend is dried to constant weight in a vacuum oven. This method has the advantage that the need to use high temperatures is avoided, thereby reducing the risk of thermal degradation. However, there are the disadvantages that the polymer blend may contain some solvent impurity, as well as the inconvenience and expense of having to use relatively large amounts of solvent and non-solvent.

1.3.2.2 Melt Mixing [Sasisil, 2004]

In this method, two or more polymers are melted together and then mixed at the molecular level. The main advantage of this approach is that it is directly applicable to conventional melt processing operations such as extrusion and compression-molding. The main advantage is that requires high temperatures which may cause thermal degradation to occur in the less stable component.

1.4 Experimental Determination of Blend Compatibility

1.4.1 Direct Methods

Amongst the most commonly used direct experimental methods of determining polymer-polymer compatibility are those based on measurements of the following bulk properties: [Paul, 1978; Sasisil, 2004]

1.4.1.1 Glass Transition Temperature, T_g

The glass transition temperature (T_g), of a polymer blend can be determined via measurements of such properties as shown in Table 1.1.

Table 1.1 Properties and techniques used for measurement of the T_g.

Polymer Properties	Techniques
Specific volume	Dilatometry
Heat capacity	Differential scanning calorimetry (DSC)
Refractive index	Refractometry
Dielectric constant	Dielectric measurements
Dynamic modulus	Dynamic mechanical analysis (DMA)

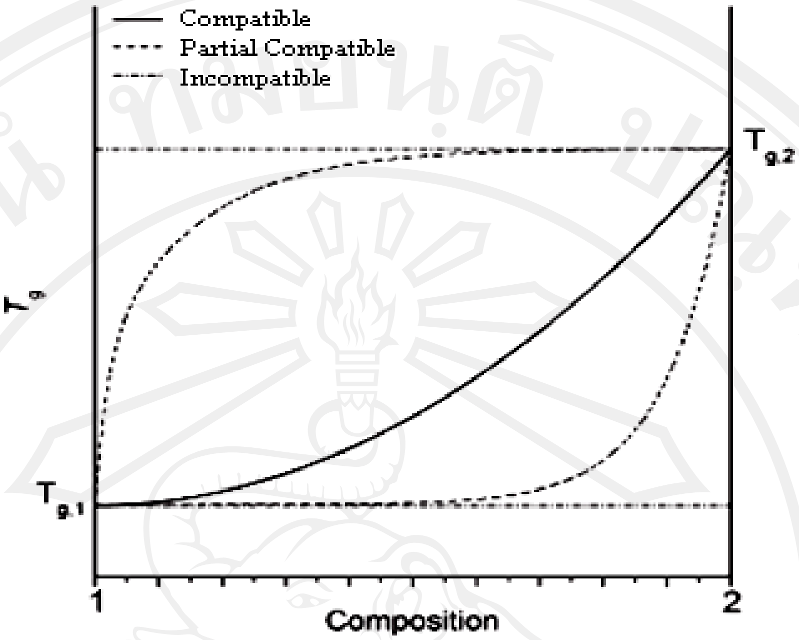


Figure 1.2 A schematic representation of the dependence of T_g on composition in binary polymer blends: — compatible system; - - - partial compatible; -·-· incompatible system [Brostow *et al*., 2008].

T_g values are useful indeed for variety purposes. Particularly needed are T_g values as a function of composition for binary polymer blends; they tell us whether the blends are compatible, or partial compatible, or not compatible at all. This situation is illustrated in Figure 1.2. Compatible is characterized by a single glass transition temperature for all the blends. Partial compatible systems have one or two T_g value s which depend on compositions. Incompatible polymers – not an infrequent case – T_g values for pure components do not change with composition. The compatibility (or lack of it) is decisive for all properties [Brostow *et al*., 2008].

1.4.1.2 Transparency

If the film or sheet of the blend, either pressed in bulk or cast film from solution, is transparent, it is a positive indication of compatibility. However, transparency does not, in itself, provide absolute conformation as such.

1.4.1.3 Morphology

Electron microscopy involves the microstructural study of fracture surfaces of bulk samples. Transmission electron microscope (TEM) and scanning electron microscopy (SEM) are the most commonly used forms. Usually, if a blend is incompatible, at least to some extent, evidence of phase heterogeneity can be seen in surface and fracture surface under high magnification.

1.4.2 Indirect Methods

Amongst the various indirect methods which are used to study polymer-polymer compatibility are those listed in Table 1.2.

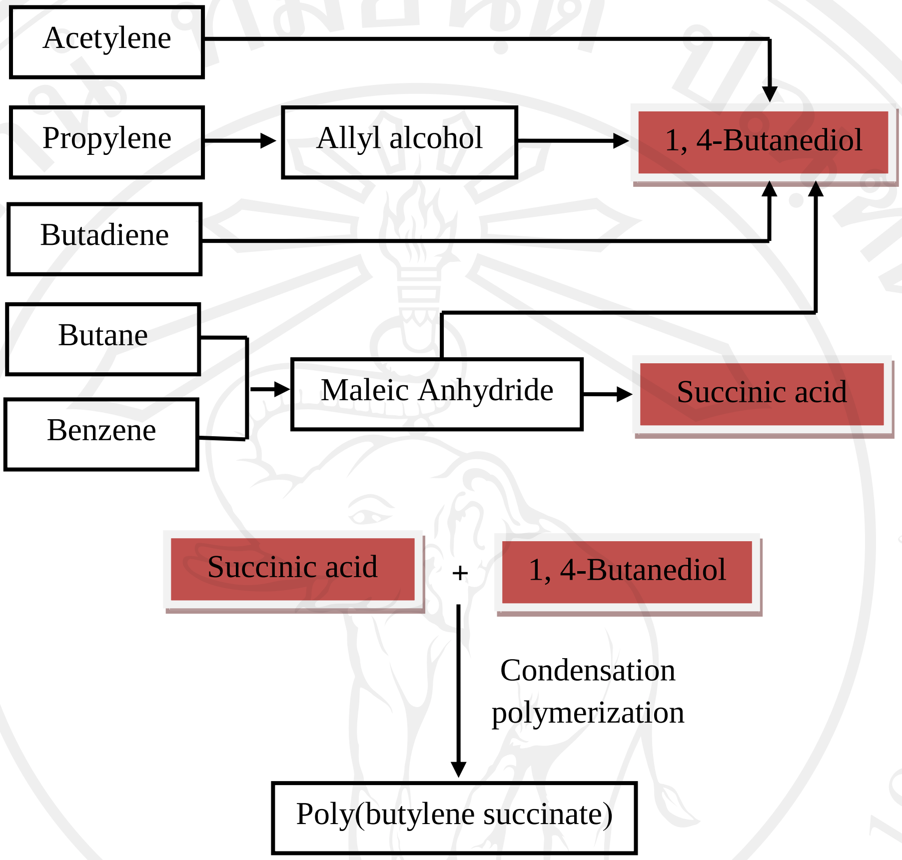
Table 1.2 Indirect methods of polymer compatibility determination.

Polymer Properties	Techniques
Mechanical properties	Tensile strength Elongation at break Impact strength
Thermal/Thermooxidative degradation	Degradation temperature Kinetic/thermodynamic parameters
Density	Bulk density measurements
Viscosity	Melt viscosity (Melt flow index) Solution viscosity

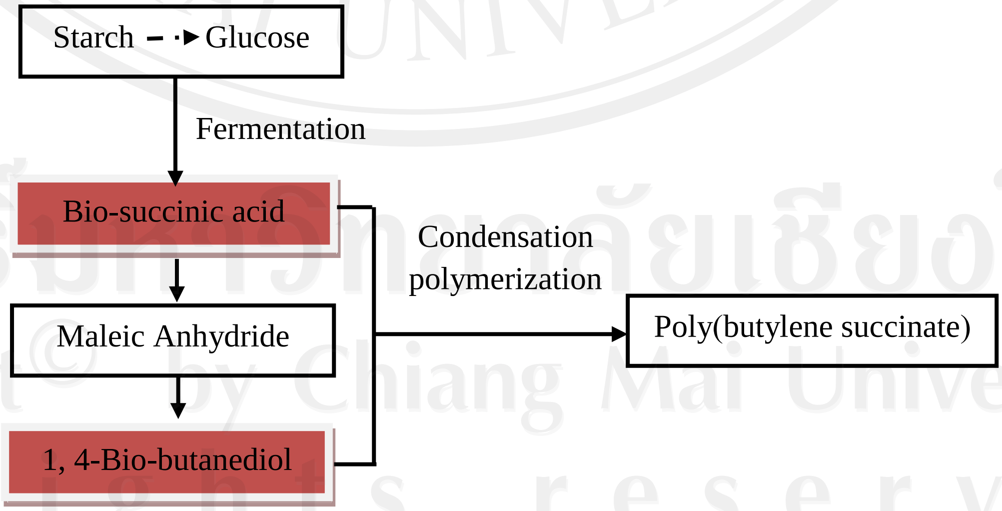
1.5 Poly(butylene succinate) (PBS)

Poly(butylene succinate), PBS, trade name ‘BIONOLLE’ is biodegradable aliphatic polyester. PBS is a semi-crystalline and flexible and was designed to have the processibility of polyethylene with physical properties similar to those of polyethylene terephthalate. PBS has a number of interesting properties including biodegradability, high flexibility, good thermal stability, excellent impact strength, thermal and chemical resistance, and melt viscosity for further processing [Doi and Fukuda, 1994]. The monomer precursors for making PBS are succinic acid and 1,4-butanediol by the polycondensation reaction [Bhari *et al*., 1998; Doi *et al*., 1996].

Monomer from petrochemical products



Monomer from natural raw materials



Both monomers can be prepared from either petrochemical products (such as acetylene, propylene, butadiene, butane and benzene) or natural raw materials, through the process of fermenting starch and sugar into succinic acid. The acid is used as the reactant for 1,4-butanediol production through preparation of maleic anhydride, as shown in Figure 1.3 [Fujimaki, 1998].

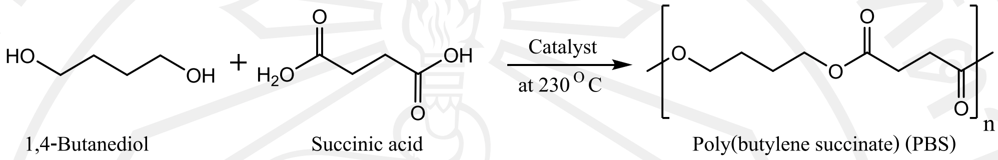


Figure 1.3 Reactant of PBS monomer preparation

Addition of organo-montmorillonite (OMMT) has been reported to increase the strength and modulus of PBS [Chieng *et al*., 2010; Okamoto *et al*., 2003 and Someya *et al*., 2003]. However, the extent of these improvements is rather limited. As the structure of molecular orientation is an important factor in producing polymer materials with outstanding properties, orientating the polymer chains using various methods such as cold rolling should be able to further improve polymer strength and ductility [Lee *et al*., 2010 and Wu *et al*., 2002]. Cold rolling is a process by which a polymer sheet is introduced between two unheated rollers and then compressed and squeezed. It is usually carried out at temperature below the crystallization temperature of the polymer. The technical merits offered by cold rolling process are the controllability, energy saving and better dimensional retention after rolling due to the lower operation temperature. Basically, the rolling conditions, including temperature, time, and final thickness, determine the properties of the rolled product. Understanding the relationship between the deformation characteristics and the induced microstructure is essential to enable prediction on the final properties of the product. Although studies on polymer chain orientation are rather abundant, research on the deformation of polymer nanocomposites is rare. Abu-Zurayk *et al*. [Abu-Zurayk *et al*., 2009] reported that biaxial hot stretching on the nanocomposites has caused the delamination of clay stacks and orientation of clay. However, there is no relevant work has been reported on the uniaxial cold rolling of polymer nanocomposites. It is an interesting field of study in order to further enhance the material properties by using a relatively simple process. During uniaxial cold rolling, the direction of the molecular orientation relative to the applied stress direction is of particular importance [Miller *et al*., 1996]. In this study, uniaxial cold rolling has been carried out on PBS and 2 wt% OMMT filled PBS nanocomposites. Sheets are reduced in thickness by 20–60% which defined by the compression ratio. Uniaxial cold rolling is believed to improve the mechanical properties of nanocomposites. Generally, tensile strength of rigid polymers increases in the direction parallel to the rolling direction, which is known as the machine direction (MD). However, such strength decreases in the direction perpendicular to the rolling direction or known as the transverse direction (TD) [Miller *et al*., 1996 and Vega-Bundrit *et al*., 2003]. Vega-Baudrit *et al.* have previously reported on the dramatic enhancement of strength and modulus of PBS along the MD after uniaxial rolling process. In this research, the mechanical properties of the rolled samples were investigated both in the MD and in the TD. The mechanical properties are greatly influenced by the polymer chain orientation that develops during cold rolling. Birefringence generated by microwave molecular orientation analyzer provides a quantitative study on the molecular orientation of polymers at different. Moreover, it provides the information on the molecular orientation angle (MOA) and molecular orientation ratio (MOR) of polymer chains. Wide angle X-ray diffraction (WAXD) is another common method used to observe the molecular orientation of crystalline phase in PBS. The effects of cold rolling on the degree of crystallinity were studied using WAXD and differential scanning calorimetry (DSC).

Synthesis and degradation of PBS has been a subject of several studies [Cho *et al*., 2001 and Okajima *et al*., 2003]. It was shown early that PBS, PBA and many related polymers are enzymatically hydrolyzed by lipases such as *Rhizopus delemar*, *Rhizopus arrhizus* and *Mucor miehei*, *Pseudomonas sp.* and *Aspergillus niger*, *Chromobacterium viscosum*, *Rhizopus orizae*, and *Rhizopus niveus*. Copolymerization affects both the crystallinity and hydrophilicity of polyesters [Hakkarainen, 2002] and the rate of enzymatic hydrolysis is highly influenced by both the chemical structure of the polymer and the degree of crystallinity. Increasing biodegradability as a result of an introduction of groups that are more susceptible to enzymatic attack or due to a reduced crystallinity have been shown in several studies. Copolymerization with a monomer that makes the polyester chain more rigid than the homopolyester, *e.g.* poly(butylene adipate-*co*-butylene terephthalate) compared to poly(butylene adipate) [Gan *et al*., 2004], or an increased molecular orientation in combination with an unfavorable chemical structure reduces biodegradability.

1.6 Cellulose Acetate Butyrate (CAB)

Cellulose is another widely known polysaccharide produced by plants. It is a linear polymer with very long macromolecular chains of one repeating unit, cellobiose [Chandra, & Rustgi, 1998]. Biodegradation of cellulose was proceed by enzymatic oxidation, with peroxidase secreted by fungi. Cellulose can also be degraded by bacteria. As for cellulose degradation products are non-toxic [Klemm, *et al*., 2002]. Cellulose has a degradation temperature (T_d) below its melting temperature and hence cannot be processed in the melt. Moreover, because of its complex morphology of crystalline region and hydrogen bonding, cellulose is difficult to dissolve in common solvents [Sealey *et al*., 1996]. However, cellulose is converted to its organic esters, in the laboratory and commercially. The modified properties of those cellulose derivatives give entry into a range of applications greatly expanded from those available to the parent polysaccharide. It is important to gain a fundamental understanding of how structural changes are effected by cellulose esterification, the ability to predict how those changes will impact properties, and an understanding of how those property changes translate into performance vs. applications, in some cases in cooperation with other materials or ingredients. Cellulose ester plastics have, however, continued to satisfy significant marketplace needs and their properties have continued to attract interest. Representations of the monomer units of the important commercial products, cellulose acetate (CA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB). The mixed esters, CAP and CAB, were introduced in the 1930s and 1940s as tougher versions of CA that could be thermally processes at lower temperatures or with lower amounts of plasticizer. The general characteristics of cellulose organic esters that are valuable in plastics applications include stiffness, moderate heat resistance, high moisture vapor transmission, grease resistance, clarity and appearance, and moderate impact resistance. They are very easy materials to extrude and injection mold, and so are appreciated by end users. Some of the detrimental properties include a relatively narrow window between the polysaccharide backbones at high temperatures (often exacerbated by the presence of residual, neutralized sulfate esters that arise during the manufacturing process). This quality means that in most commercial applications, plasticizers are used in conjunction with cellulose esters [Edgar *et al*., 2001]. Cellulose esters in coating are nearly always used in compatible blends with acrylics, polyesters and the other polymers. This is possible because of their ability to form hydrogen bond through the presence of hydroxyl groups and the carboxyl groups of ester [Edgard *et al*., 2001; Sealey *et al*., 1996]. CA is made from natural resources; some of the three hydroxyl groups in glucose unit of cellulose are substituted for acetyl groups. It is known that the biodegradability of CA depends on the degree of substitution (DS). Biodegradation can be observed in a sample with a DS of less than 2.5 [Sawada, & Fujimaki, 1994]. Since the hydroxyl groups in cellulose acetate are blocked and substituted by acetyl groups in various degrees, the biodegradability of cellulose acetate is less certain. The effects of the degree of substitution in each anhydroglucose unit on microbial attack have been intensively studied. These studies have shown that at least one substituent on every anhydroglucose unit resulted in complete resistance to microbial attack on cellulose due to the chemical blocking of one or more of the hydroxyl groups [Duckett *et al*., 1998]. CA could be dissolved in strong solvent such as acetone, methyl ethyl ketone and ethyl acetate, and they have very low tolerance for hydrocarbons. Cellulose acetate butyrate (CAB) is the most commonly used cellulose organic ester in the coatings industry.

As CAB butyryl content increases, flexibility, solubility, hydrocarbon tolerance, and compatibility increase, while chemical resistance, grease resistance, and hardness decrease. As ester molecular weight increases, compatibility and solubility decrease, toughness and melting point increase, and hardness and density are unaffected. Compatibility, solubility, and maximum nonvolatile content all decrease as ester molecular weight increases. Hydroxyl content impacts moisture resistance and toughness, which both decrease with increased hydroxyl contents [Eastman Chemical Company, 2009].

1.7 Polymeric Plasticizer [Ghosh, 1998]

A plasticizer can be defined as a chemical which reduces the stiffness of an amorphous (glassy) thermoplastic resin [Hammer, 1978]. The fundamental principle associated with plasticizer is to interact with the polymer chains on the molecular level so as to speed up the viscoelastic response of the polymer. Thus it actually increased the molecular mobility of the polymer chains and consequently this decreases the glass transition temperature (T_g) of the polymer. Moreover, a plasticizer may influence the processability of the polymer as well.

The conditions required of a polymeric plasticizer are: [Hammer, 1978]

a) Must be compatible on a molecular scale with the polymer to be plasticized.

b) Must have a sufficiently low T_g so that it will efficiently lower the T_g of the polymer to be plasticized.

c) Have sufficiently high molecular weight to justify the term “polymeric” (versus oligomeric) (approximately $\overline{M}_n \geq 5000$). Also this implies the permanence requirements, which relate to low vapor pressure and low diffusion rate, of the plasticizer within the polymer.

Although these are the required conditions, in this strict sense f the term, the polymer with a lower T_g can be called a polymeric plasticizer for the polymer with a higher T_g in a compatible blend system. If the polymer to be plasticized is semi-crystalline, a plasticizer would subsequently depress the melting temperature and also reduce the degree of crystallinity in most cases (note that cases where the plasticizer acts as a nucleating agent are not considered). The plasticizer forms a compatible additive – one phase being composed of pure crystalline polymer and the other being a compatible amorphous blend. In spite of the fact that the blend system has two separate phases varying in composition, it can be called “compatible” since the molten blend forms a homogeneous mass at temperatures above the crystallinity is well developed, it is difficult to find a plasticizer sufficiently compatible with (soluble in) the polymer to have a significant effect on its properties. The efficiency of a plasticizer can be evaluated by various semi-empirical parameters such as dilution ratio, dilute solution viscosity of the polymer in the plasticizer, depression of the glass transition temperature, melt viscosity of the plasticized polymer, electrical or mechanical properties, or the molecular size or shape of the plasticizer itself [Billmeyer, 1994].

1.8 Literature Reviews

Since the overall properties of PBS are frequently insufficient for various end-use applications, its properties are usually modified by the addition of plasticizers and other polymers [Ray and Dkamota, 2003]. PBS has recently been produced from biorenewable resources to reduce greenhouse gas emission and provide sustainable alternatives to the reliance on limited petroleum-based resources. The Showa High Polymer Co., Ltd. and Mitsubishi Co. Ltd. are now also establishing the production of succinic acid, one of the monomers for producing PBS, from biomass resources and a partially-biobased PBS is being manufactured [Kato *et al*., 2006; Shitani and Kato, 2007].

A large number of studies have been made on biodegradable aliphatic polyester/cellulose ester blends to increase the applicability of biodegradable polymers. Previous work has reported on the influence of molecular structures on the miscibility of the blend system. For example, Nishio *et al.* studied the relation between the ability of cellulose ester derivatives to form a miscible blend with polycaprolactone (PCL) and the influence of the ester structure in terms of the side-chain length and the degree of substitution (DS). They reported that cellulose butyrate, in which the number of carbons in the acyl substitution is four, exhibits the highest miscibility with PCL. They also suggested that the miscibility of cellulose esters is enhanced by an increase in DS [Nishio *et al*., 1997]. Buchanan *et al.* studied the influence of the diol length of an aliphatic polymer on blend miscibility. To probe the relation between the polyester structure and blend miscibility in blends of cellulose acetate propionate (CAP) and an aliphatic polymer, they prepared a series of polyesters from a C5 dicarboxylic acid and a diol which was systematically varied from C2 to C8. They suggested that the polyesters prepared from C2 to C6 diols exhibited miscibility with CAP with that from the C4 diol showing the highest level of miscibility [Buchanan *et al*., 1994].

Tatsushima *et al.* studied the miscibility of PBS/CAB blends prepared by solution casting from chloroform. It was found that CAB inhibited the crystallization of PBS in the blend, and that the PBS was amorphous state when the weight percentage of PBS (Φ_{PBS}) was low, especially over the range of Φ_{PBS} = 0% to 30%. The Young's modulus of the blend films decreased as Φ_{PBS} increased up to Φ_{PBS} = 40% due to the plasticizing effect of PBS. The Young's modulus showed almost the same value as that of pure PBS at $\Phi_{PBS} \geq 40\%$. In PBS blends with poly(ethylene oxide) (PEO) the melting behavior of PBS as studied by DSC was influenced strongly by various experimental conditions such as the blend composition, crystallization temperature and scanning rate. When PBS was blended with poly(butylene adipate) (PBA), it was found that the PBA melt segregated in a different manner depending on the crystallization temperature of PBS while interspherulitic phase segregation of the PBA took place at high temperature [Tatsushima *et al*., 2006].

Cellulose esters are one of the thermoplastics derived from biomass feedstocks. Cellulose acetate butyrate esterified by acetyl and butyryl groups is a brittle and transparent material. Therefore, CAB has been used as a photofilm and coating material. Some researchers have reported that CAB acted as a plasticizer for polyesters, such as poly(hydroxybutyrate) (PHB) [Ray and Dkamota, 2003; Mizukoshi, 2006; Kato *et al*., 2006]. Scandola *et al.* have investigated the miscibility, thermal and viscoelastic properties of blends of PHB with CAB or cellulose acetate propionate (CAP). It has been shown that the system is miscible over the entire composition range. When the CAB or CAP content in the blends was more than 50% by weight, the blends were stable homogeneous amorphous glasses, characterized by single composition-depend glass transition temperature [Scandola *et al*., 1999; Lotti and Scandola, 1992]. PHB crystallized upon room temperature storage and was partially crystalline when the CAB or CAP component was less than 50% by weight.

Plasticizers are an important class of low molecular weight, non-volatile compounds that are widely used in the polymer industry as additives [Sejiduv, 2005]. Their primary role is to improve the flexibility and processability of polymers by lowering the glass transition temperature (T_g). The plasticizer reduces the tension of deformation, hardness, density, viscosity and electrostatic charge of a polymer while, at the same time, increasing the polymer's chain flexibility, resistance to fracture, and dielectric constant [Rosent, 1993]. Other properties are also affected such as degree of crystallinity, optical clarity, and electric conductivity. Over the last half century, legislation and health and safety issues have led to the development of a wide range of currently available commercial plasticizers. They include some fatty acid esters, benzoates, tartrates and chlorinated hydrocarbons, and esters of adipic, azelaic and sebacic acid. Poly(ester adipate) or Paraplex G40, is a high molecular weight permanent plasticizer which offers excellent durability, low volatility, and excellent resistance to extraction by hydrocarbon solvents.

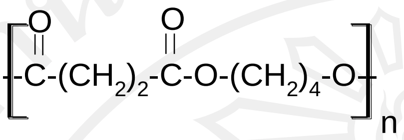
Since the properties of PBS by itself are unsuitable for some applications, it needs to be blended with other biodegradable components which can both modify its properties and lower its unit cost.

1.9 Research Objectives

PBS has several advantages such as flexibility, biodegradability, good thermal stability, good processability and availability from renewable sources for use in packaging films. However, PBS by itself is a rather turbid and low strength material which makes it unsuitable for use in applications where transparency and strength are required. Consequently, PBS tends to be blended with other components to modify its properties and lower its cost. Based on this methodology, a logical starting point for this research is a three-component blend (Figure 1.4) consisting of:

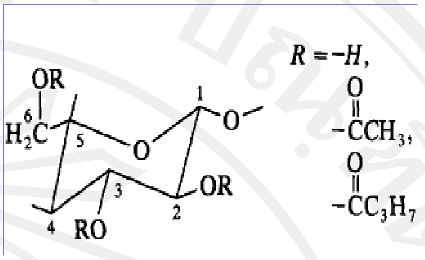
- PBS to provide biodegradability, flexibility and processability
- CAB to provide the high molecular weight component necessary for mechanical strength and to lower the cost of the material

- Paraplex G40 plasticizer to provide the required degree of flexibility for use as, for example, a packaging film

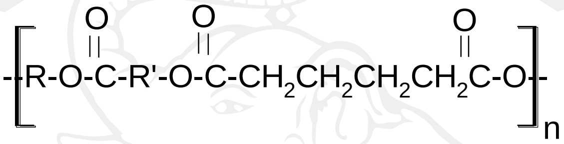


$\left[-\overset{O}{\overset{\|}{C}}-(CH_2)_2-\overset{O}{\overset{\|}{C}}-O-(CH_2)_4-O-\right]_n$

PBS



CAB



$\left[-R-O-\overset{O}{\overset{\|}{C}}-R'-O-\overset{O}{\overset{\|}{C}}-CH_2CH_2CH_2CH_2\overset{O}{\overset{\|}{C}}-O-\right]_n$

Paraplex G40

Figure 1.4 Chemical structures of PBS, CAB and Paraplex G40 for three- component blending.

The scopes of study are to process and test some novel three-component blends based on PBS for use as biodegradable packaging materials. The challenge is to find ways of mixing and processing the three components into films with properties suitable for packaging applications.