CHAPTER 2

EXPERIMENTAL METHODS AND CHARACTERIZATION

2.1 Chemicals, Apparatus and Instruments

2.1.1 Chemicals

The various chemicals used in this research project were shown in Table 2.1.

Table 2.1 Chemicals used in this research project.

Chemicals	**Designation**	**Usage**	**Physical Appearance**	**Supplier**
Poly(butylene succinate)	PBS	Polymer	White solid	Mitsubishi chemical
Cellulose acetate butyrate	CAB	Polymer	White powder	Eastman Chemical Company
Poly(ester adipate)	Paraplex G40	Plasticizer	Viscous liquid	HallStar
Chloroform	$CHCl_3$	Solvent	Liquid	Lab-Scan

2.1.2 Apparatus and Instruments

The main apparatus and instruments used were as listed in Table 2.2.

Table 2.2 Apparatus and instruments used this research project.

Apparatus and Instruments	Company	Model
Internal Mixer	HAAKE Polylab	Rheomex 252p
Compression Molding	LabTech Engineering	LP-S-20
Universal Mechanical Testing Machine	Lloyd Instruments	LRX
Universal Tensile Testing Machine	Instron	55R4502
Dynamic Mechanical Analyzer	Mettle Toledo	SDTA861
400 MHz ^{1}H-NMR Spectrometer	Bruker	Avace 400
Differential Scanning Calorimeter	Mettle Toledo	DSC 822^e
Thermogravimetric Analyzer	Perkin-Elmer	TGA7
Scanning Electron Microscope	Jeol	JSM 5910-LV
Ubbelohde Viscometers	Schott-Geräte	532 03 0c, 0o
Melt Flow Indexer	Lloyd Instruments	MFI-10

2.2 Characterization of starting materials

2.2.1 Materials

Poly(butylene succinate) (PBS-grade AZ 91TN cot ND13Y9) used in this research was a commercial product produced by Mitsubishi chemical in the form white crystalline solid. Cellulose acetate butyrate (CAB type 500-5) was obtained in power form by Eastman Chemical Company (Kingsport, Tennessee), with butyryl content 51%, acetyl content 4%, and hydroxyl content 1% and number average molecular weight was 57,000. The polymers were vacuum dried at 60 °C for 24 h prior to use. The choice of these plasticizers was based on requisites such as non-toxicity and biocompatibility. Polyester adipate (Paraplex G 40) was supplied by HallStar, with molecular weight of 6,000. Furthermore, the analytical reagent grade of chloroform was used for preparation of solution blend films.

2.2.2 Proton Nuclear Magnetic Resonance Spectroscopy (^{1}H-NMR)

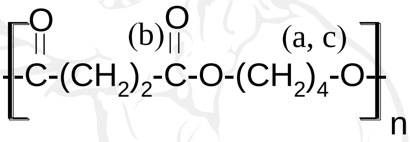
Nuclear magnetic resonance (NMR) spectroscopy is an important method for materials characterization, especially polymers, arising in part because the signals can be assigned to specific atoms along the polymer’ s backbone and side chains. The properties of NMR signals depend on the magnetic environment of the NMR-active nuclei and local fields that they experience. Since the NMR spectrum is determined by local forces, this method provides valuable and unique information about polymers on an atomic-length scale. The timescale involved in NMR measurements makes it possible to study certain tie-dependent processes, including chemical reaction rates. Other applications include the study of isomerism, internal relaxation, conformation analysis, and tautomerism [Hunt, & James, 1993]. In this research project, polymer structures were characterized by a combination of 400 MHz ^{1}H-NMR spectrometer using a Bruker Avace Spectrometer Avace 400. The samples were dissolved in deuterated chloroform ($CDCl_3$, AR grade, Aldrich). The spectra were obtained from Mestre-C data processing software.

The proton nuclear magnetic resonance (^{1}H-NMR) spectra of the commercial starting materials (such as PBS, CAB and Paraplex G40) are shown in Figures 2.1-2.6, respectively.

The data in Table 2.3 for PBS sample commercial in this work, there is seen to be close agreement in the chemical shifts of the various protons. This is strong support of its chemical structure. The observed resonance signals ranged around δ = 1.50-1.75 ppm and ranged around δ = 4.07-4.15 ppm were assigned to methylene protons of the 1,4-butylene glycolic units of PBS (peak a, c), whereas the signal arising ranged around δ = 2.55-2.67 ppm was attributed to the methylene protons of the succinic acid units of PBS (peak b). These ^{1}H -NMR spectra were obtained using deuterated chloroform as solvent at 21 ºC (Figure 2.1).

Table 2.3 Interpretation of the ^1H -NMR spectra of the commercial PBS.

Proton Assignment	Chemical Shift, δ (ppm)
a	1.50-1.75
b	2.55-2.67
c	4.07-4.15



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

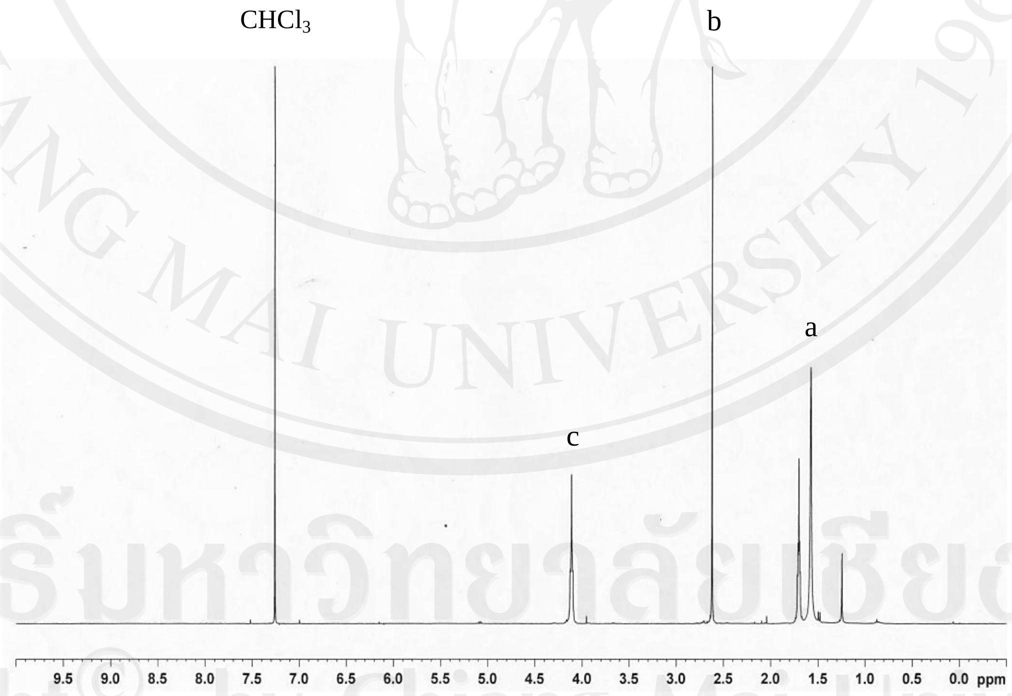


Figure 2.1 400 MHz ^1H-NMR spectrum of PBS commercial in $CDCl_3$ as solvent at 21 °C.

The data in Table 2.4 for CAB sample commercial in this work, there is seen to be close agreement in the chemical shifts of the various protons. This is strong support of its chemical structure. It can be seen that the α-CH_2 protons (peak a) in butyrate group of CAB, ranged around δ = 2.11-2.33 ppm (Figure 2.2). The β-CH_2 protons (peak b) in butyryl group of CAB, centred at δ = 1.54 ppm and methyl CH_3 protons (peak c) centred at δ = 0.90 ppm. The methylene CH_2 protons (peak d) substitute C_6 in cellulose structure of CAB, ranged around δ = 3.33-3.51 ppm. The methyl CH_3 protons (peak e) in acetyl group of CAB, ranged around δ = 1.66-1.67 ppm. The methine C-H protons substitute C_1, C_5 (f) and C_2, C_3 and C_4 (g+h) in cellulose structure of CAB, ranged around δ = 3.63-5.07 ppm and 1.67, 1.90-1.97 ppm, respectively.

Table 2.4 Interpretation of the ^{1}H -NMR spectra of the commercial CAB.

Proton Assignment	Chemical Shift*, δ (ppm)
a	2.11-2.33
b	1.54*
c	0.90*
d	3.33-3.51
e	1.66-1.67
f	3.63-5.07
g+h	1.90*

* given as the peak centre

The data in Table 2.5 for Paraplex G40 sample commercial in this work, there is seen to be close agreement in the chemical shifts of the various protons. This is strong support of its chemical structure. It can be seen that the methylene β-CH_2 protons (peak a) and α-CH_2 protons in adipic group of Paraplex G40, centred at δ = 1.63 and 2.30 ppm. The protons (peak c, d, e and f) in diol group of Paraplex G40, centred at δ = 1.21, 4.00, 4.12 and 5.10 ppm respectively (Figure 2.3).

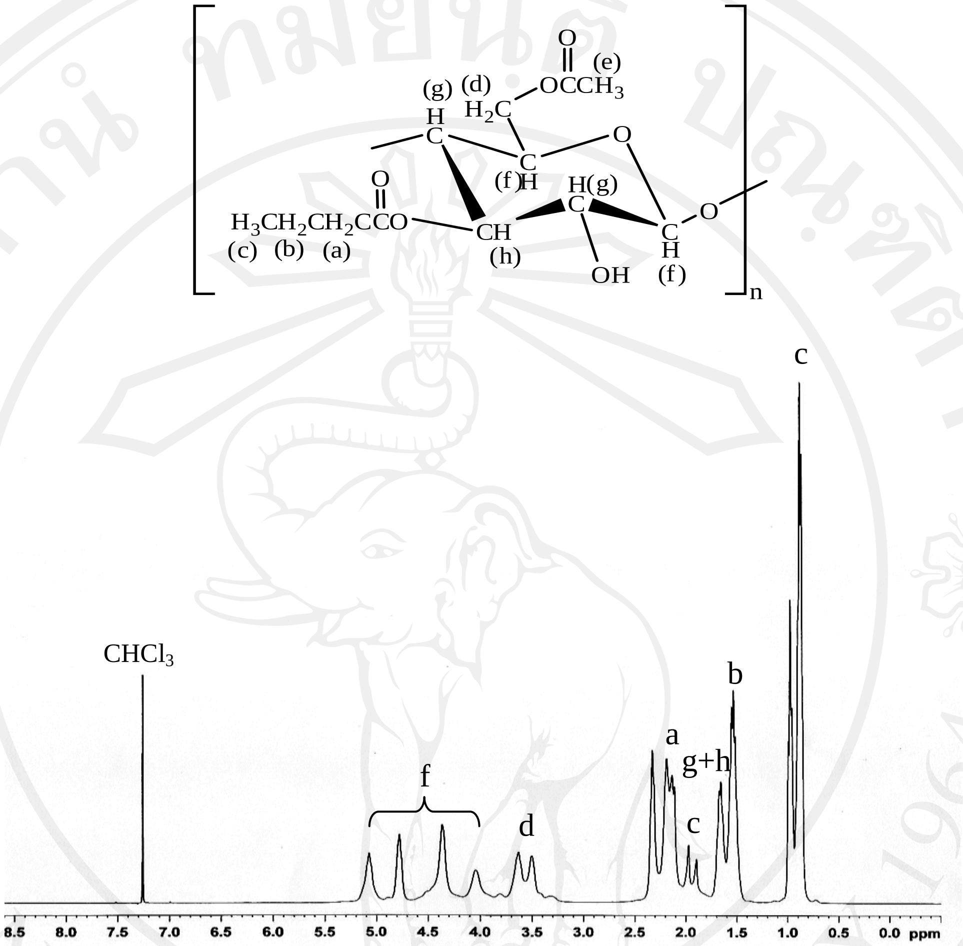
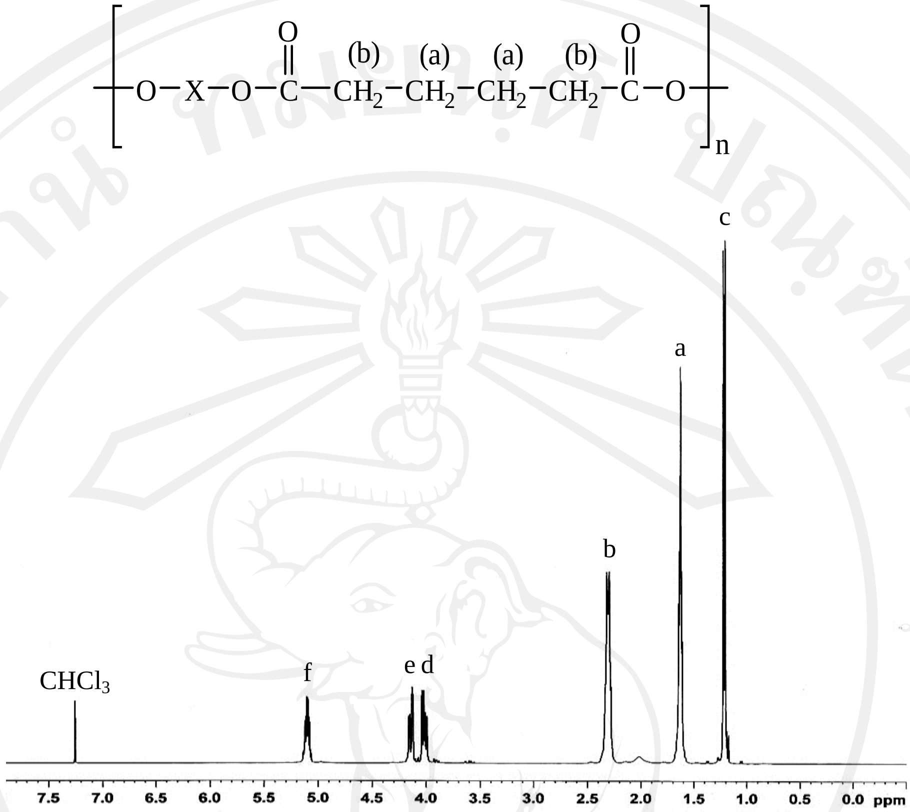


Figure 2.2 400 MHz ^{1}H -NMR spectrum of CAB commercial in $CDCl_3$ as solvent at 21 ºC.

Table 2.5 Interpretation of the ^{1}H -NMR spectra of the Paraplex G40 commercial.

Proton Assignment	Chemical Shift*, δ (ppm)
a	1.63
b	2.30
c	1.21
d	4.00
e	4.12
f	5.10

* given as the peak centre



$$\left[-O-X-O-\overset{O}{\overset{\|}{C}}-\overset{(b)}{CH_2}-\overset{(a)}{CH_2}-\overset{(a)}{CH_2}-\overset{(b)}{CH_2}-\overset{O}{\overset{\|}{C}}-O- \right]_n$$

Figure 2.3 400 MHz ^{1}H -NMR spectrum of Paraplex G40 commercial in $CDCl_3$ as solvent at 21 ºC.

2.2.3 Polymer Molecular Weight Determination

2.2.3.1 Dilute-Solution Viscometry

A secondary method used for the determination of polymer molecular weights is that based on solution viscosity measurements, since the viscosity of a polymer solution is dependent both on solution concentration and on the average molecular weight for the polymer. However, this method is not an absolute method since it requires the prior determination of an empirical relationship that relates the molecular weight to the viscosity of the polymer solution [Rabek, 1980]. Dilute-solution viscosities are usually measured at concentrations of up to 1 g/100 ml of solvent (1 %w/v) at constant temperature (25 ± 0.1 ºC) by determining the *flow-time* of a certain volume of solution through a capillary of fixed length [Rosen, 1975].

Table 2.6 Dilute-solution viscosity data using chloroform as solvent at 25 ± 0.1 ºC for the PBS commercial.

Concentration (g/dl)	Flow-Time* (sec)	η_{rel}	η_{sp}	η_{red} (dl/g)	η_{inh} (dl/g)
solvent	107.3	-	-	-	-
0.200	134.3	1.252	0.252	1.258	1.122
0.400	165.3	1.541	0.541	1.351	1.080
0.600	205.3	1.913	0.913	1.522	1.081
0.800	248.7	2.318	1.318	1.647	1.051
0.100	289.0	2.693	1.693	1.693	0.991

* average of at least 3 reading which agreed to within ± 0.2% of this average value

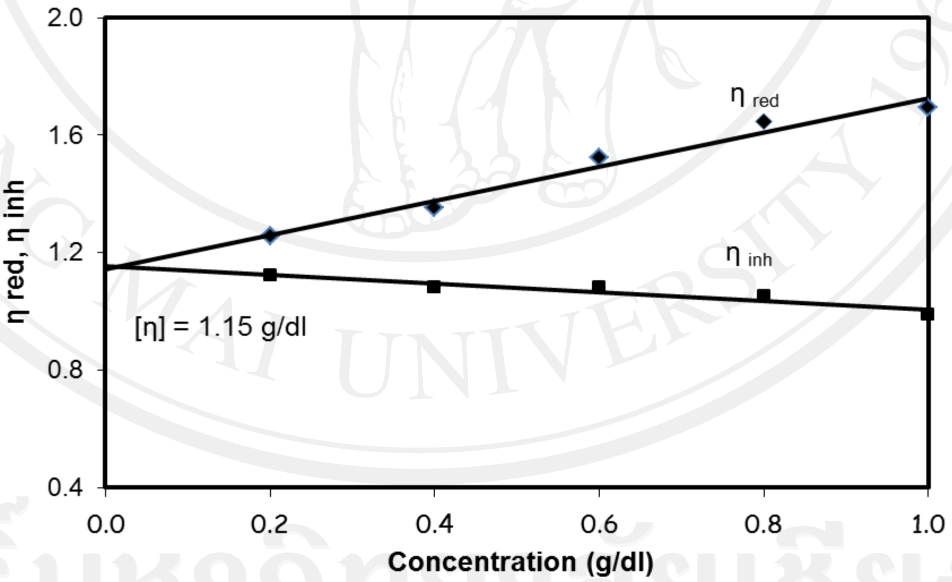


Figure 2.4 Reduced (η_{red}) and inherent (η_{inh}) viscosity-concentration plots for PBS commercial. (♦ η_{red} and ■ η_{inh}) (data from Table 2.6).

Table 2.7 Dilute-solution viscosity data using ethyl acetate as solvent at 25 ± 0.1 ºC for the CAB commercial.

Concentration (g/dl)	Flow-Time* (sec)	η_{rel}	η_{sp}	η_{red} (dl/g)	η_{inh} (dl/g)
solvent	439.4	-	-	-	-
0.213	580.6	1.325	0.325	1.525	1.321
0.410	750.2	1.714	0.714	1.743	1.316
0.602	955.7	2.185	1.185	1.970	1.299
0.800	1218.2	2.786	1.786	2.232	1.281

[*] average of at least 3 reading which agreed to within ± 0.2% of this average value

when this value of [η] is substituted into the Mark-Houwink-Sakurada Equation for CAB in acetone as solvent at 25 ± 0.1 ºC [Brandrup *et al.*, 1997] of: $[\eta] = 1.13 \times 10^{-4} \overline{M}_v^{0.83}$ dl/g.

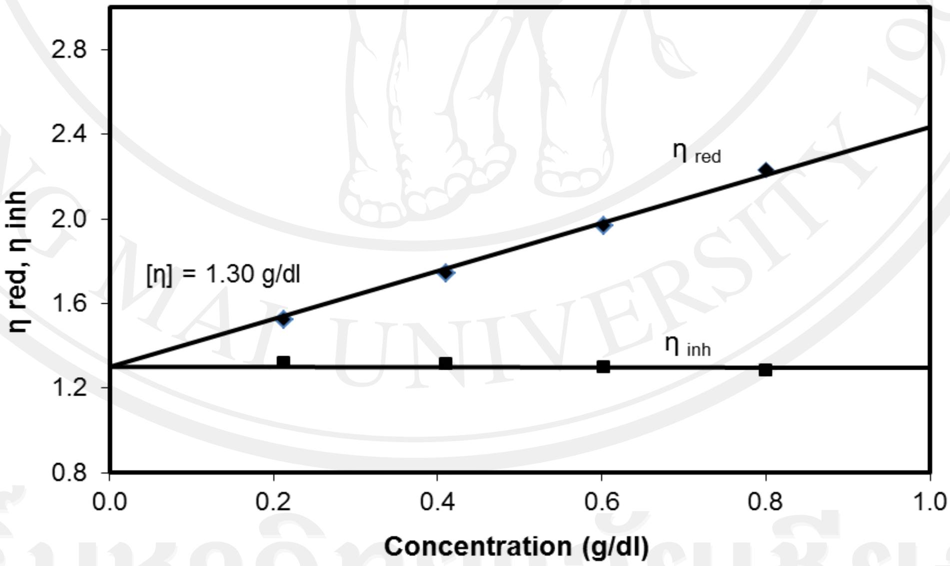


Figure 2.5 Reduced (η_{red}) and inherent (η_{inh}) viscosity-concentration plots for CAB commercial. (♦ η_{red} and ● η_{inh}) (data from Table 2.7)

The viscosity-average molecular weights ($\overline{M}_v$) of PBS and CAB commercial were determined from flow time measurements in a dilution series of solutions (0.2-1.0

%w/v) in solvent using Schott-Gerate AVS300 Automatic Viscosity Measuring System. The results obtained are shown in the following Tables 2.6-2.7 and Figures 2.4-2.5. An example of CAB of flow-time data obtained, derived viscosity parameters, and reduced/inherent viscosity-concentration graphs are shown in Table 2.7 and Figure 2.5. The double extrapolation of the 2 graphs in Figure 2.5 to their common intercept at zero concentration (c = 0) gives the value of the intrinsic viscosity, [η], from which the value of $\overline{M}_v$ is calculated as follows:

Sample calculation of $\overline{M}_v$ **:**

From Figure 2.4 on the following page

$$[\eta] \quad = \quad (\eta_{red})_{c = o} \quad = \quad (\eta_{inh})_{c = o} \quad = \quad 1.30 \quad \mathrm{dl/g}$$

When this value of [η] is substituted into the Mark-Houwink-Sakurada Equation for CAB in acetone as solvent at 25 °C (±0.1 °C) of:

$$[\eta] \quad = \quad 1.13 \times 10^{-4}\ \overline{M}_v^{\,0.83} \quad \mathrm{dl/g}$$

it yields

$$1.30 \quad = \quad 1.13 \times 10^{-4}\ \overline{M}_v^{\,0.83}$$

from which

$$\overline{M}_v \quad = \quad 7.80 \times 10^{4}$$

Table 2.8 Molecular weight and intrinsic viscosity data of the starting material.

Polymer	Viscosity-Average Molecular Weight ($\overline{M}_v$)^a	($\overline{M}_n$)^b (g mol^{-1}) from References
Poly(butylene succinate)	none	3.00 x 10^4
Cellulose acetate butyrate	7.80 x 10^4	6.50×10^4

^{a} data from experimental, ^{b} data from References

2.3 Film Production by Solution Blending

2.3.1 Preparation of Polymer Blend Films

The polymer blend films of uniform thickness are easily prepared by solution-casting techniques. The solvent-casting process consists of preparing a homogeneous polymer solution in a volatile solvent, preparing a thin, uniform layer of this solution on a suitable substrate, and evaporating the solvent while maintaining a well-defined tension profile [Neblette, 1962].

Having established the most suitable blending solvent as being chloroform, 0.5 g combined weight of PBS/CAB were dissolved in 10 mL of solvent. The solution was continuously stirred with a magnetic bar for at least 4 hours at room temperature to ensure complete dissolution. Polymer ratios were calculated to give blend compositions to obtain blend solutions with varying PBS/CAB mass ratio of 100/0, 70/30, 50/50, 30/70, 60/40, 50/50, 40/60, 30/70, 20/80, 10/90, and 0/100. Each solution of PBS/CAB was poured into clean, dry, 100×20 mm Petri dish. Care was taken to avoid air bubbles in the solution. The Petri dish was taken left for the chloroform solvents evaporate off slowly to form solid films at room temperature for 3 to 4 days. After each film was formed, it was dried in a vacuum oven at 30 °C to constant weight to remove the last traces of solvent and moisture. The same procedure was used for blends containing 10, 20, and 30% by weight of plasticizers (Paraplex G40).

2.3.2 Property Testing of Polymer Blend Films

2.3.2.1 Mechanical Properties

According to American Standard for testing materials (ASTM) the data for tensile properties may be acquired in the form of load-time profile a typical load displacement or stress-strain profile. Tensile strength is defined as the maximum load that a material can withstand without fracture when being stretched, divided by the original cross-sectional area of the material. Tensile strength has the dimensions of force per unit area expressed in units of pound per square inch (psi). When stress less than the tensile strength are removed, a material reaches either completely or partially to its original shape and size. As the stress reaches the values of the tensile strength, however, a material, if ductile, that has already begun to flow plastically rapidly forms a constricted region called a neck, where it then fractures. Young’s modulus is measure of the ability of a material to withstand changes in length when under lengthwise tension or compression. Sometime referred to as the modulus of elasticity, Young’s modulus is equal to the longitudinal stress divided by the strain. Materials are described as soft, hard, tough, weak, brittle or strong upon the characteristic of stress-strain curve [Vaithiyalingam, 2001].

Polymers can show various mechanical properties largely dependent upon their molecular structures and relative arrangements. A particular polymer can also show all the features of properties such as glassy, brittle, weak or rubbery depending on the conditions of testing, *e.g.* the rate of application of load, temperature, and time scale of measurement. It is therefore difficult to classify polymers as particular types of materials. However, it is helpful to specify their properties at a particular condition at testing from their stress-strain diagrams as described below [Channuan, 2006]. Figure 2.6 illustrates typical stress-strain curves obtained from polymers processing different properties such as softness, brittleness, hardness and toughness. The area under the stress-strain curve is measure of toughness of the polymeric material [Seymour, & Carraher, 1984; Chanda, & Roy, 1993]. Definitions of all other terms are as followed.

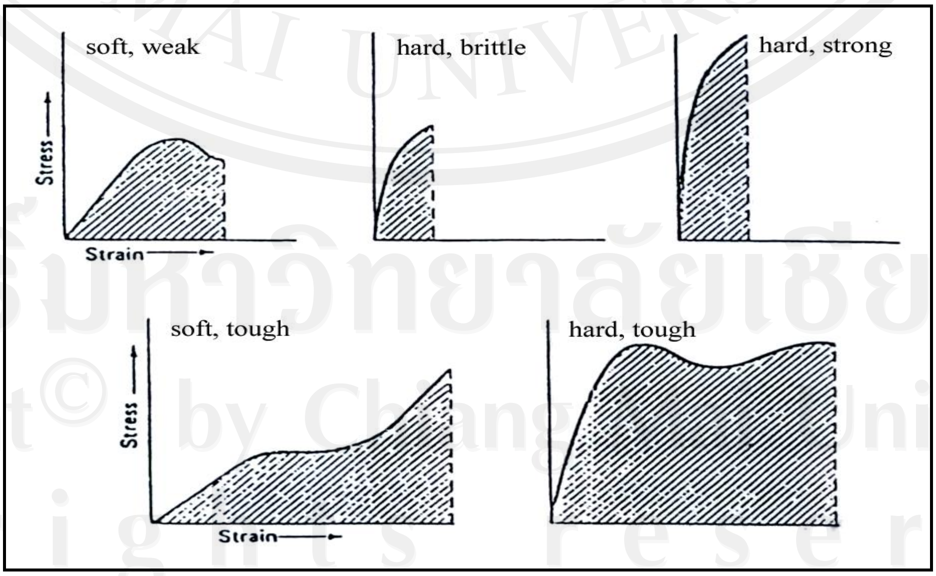


Figure 2.6 Typical stress-strain curves [Brown, 1988].

A soft and weak material is characterized by low modulus, low (or no) yield point and moderate elongation at break.

A hard and brittle material is characterized by high modulus, high yield stress, high ultimate strength and relatively low elongation at break.

A hard and strong material has high modulus, high yield stress, high ultimate strength and relatively low elongation at break.

A soft but tough material shows low modulus, low yield point but very high elongation and high stress at break.

A hard and tough material is characterized by high modulus, high yield stress relatively high elongation at break and high ultimate strength

Tensile properties of thin plastic sheeting, primary film test method: ASTM D882; additional test methods: ASTM D638; D1708, and ISO 527. The primary test method, ASTM D882, is used for the determination of tensile properties of plastics in the form of thin sheeting (less than 1.0 mm in thickness). This includes film which has been arbitrarily defined as sheeting having nominal thickness not greater than 0.25 mm [Massey, 2004].

Figure 2.7 Lloyd Instruments LRX universal mechanical testing machine used for tensile testing according to the ASTM D882-91.

Mechanical properties of polymer thin films with size of 50 mm x 10 mm x 40-60 µm were evaluated on a universal mechanical testing machine (LRX, Lloyd Instruments, and see in Figure 2.7) according to the ASTM D882-91 [ASTM D882-91], with a crosshead speed of 50 mm/min. The gauge length was 50 mm, and each sample's width and thickness were measured before testing. The experiments were used to determine the tensile strength and %elongation at break (%EB). At least five specimens were conducted for each sample, and the results were reported as average values.

2.3.2.2 Thermal Properties

The thermal properties of polymer thin films were characterized by a differential scanning calorimetry (DSC 822^e, Mettle Toledo) shown in Figure 2.8. The samples were sealed in aluminum pan (3-5 mg) and scans were carried out from -60 to 200 °C at heating rated of 10 °C/min. The first and second scans were recorded in all cases and were heated and cooled under nitrogen atmosphere. The glass transition temperature (T_g), crystallinity temperature (T_c), melting temperature (T_m) and degree of initial crystallinity were determined from the second heating scans. The T_m and T_c were taken at the peak value of the respective endotherms and exotherms, and the T_g at the mid-point of heat capacity changes.

Figure 2.8 The Mettle Toledo DSC 822^e differential scanning calorimeter used for thermal transition.

2.3.2.3 Morphology

Scanning electron microscopy (SEM) is another popular technique for assessing the morphology in a polymer blend. This method focuses an electron beam into a surface, and the emission of electrons from the specimen is defected and amplified to obtain an image. The according voltage is typically in the range of 1-40 kV. The resultant image is often viewed on a video monitor. The resolution achievable ranges down to 2 nm. SEM exhibits a relatively large depth of field, thus can show topological features better than other microscopy methods (except perhaps atomic force microscopy). Sample require surface conductivity, thus a thin layer (~10 nm) of a conductive metal (gold or platinum) is sputtered onto the surface. Staining and etching processes can be employed to provide improved contrast. SEM is particularly useful for observation of fracture surfaces. In order to accentuate the surface feature chemical (solvent or acid exposure) or plasma etching is often employed. Cryogenic fracture is also employed to provide surfaces with better defined topological features than possible with higher temperature fracture. Particles, such as impact modifiers, will often be exposed and deboned during cryogenic fracture providing the desired contrast [Da Silva, & Bretas, 2003; Robeson, 2007].

Figure 2.9 The Jeol JSM 5910-LV scanning electron microscope used for morphology.

The morphologies of selected polymer thin films (PBS, CAB and their blends) was investigated using JSM5910-LV (Figure 2.9) with accelerated voltage of 15 kV at magnification of 2000 times.

2.3.2.4 Optical Properties

The measurement of the transparency of the polymer thin films, a light transmittance test was Lambda 25 UV-Vis spectrometer (Perkin-Elmer, and see in Figure 2.10) using wavelength of 500 nm by transmission mode which compared to air as a standard.

Figure 2.10 The Perkin-Elmer Lambda25 UV-Visible spectrometer used for transparency measurements.

2.4 Sheet Formation Preparation by Melt-Mixing

2.4.1 Preparation of Polymer Blend Sheets

The polymers (PBS and CAB) were initially dried in an oven at 60 °C for at least 24 hr to eliminate moisture content and stored in a desiccator prior to compounding. Drying is necessary to minimize the hydrolytic degradation of the polymers during melt processing. Melt-blends with composition PBS/CAB 100/0, 70/30, 50/50, 30/70 0/100 % by weight with 10% Paraplex G40 as plasticizer were prepared by a 310 cc internal batch mixer (Rheomex 252p, HAAKE Polylab Internal Mixer, and see in Figure. 2.11). Dried polymers of PBS, CAB and plasticizer were mixed in a container before blending in internal batch mixer. A mixing temperature 175 °C, a mixing time of 20 minutes, and a rotor speed of 20 rpm were employed to compound the sample. These conditions were chosen as approximately optimal on the basis of several pre-trials. The obtained compound was again dried at 60 °C in oven for at least 24 hour before compression. The compound was composed into flat sheet with 0.5-1.0 mm thickness by a compression-molding machine (LP-S-20, LabTech Engineering, and see in Figure 2.12). The molding temperatures for PBS/CAB and PBS/CAB/Paraplex G40 compound were 145 °C and 125 °C, respectively for 5 minutes under constant pressure 16-20 MPa. Molded specimens were then cooled to room temperature for 5 minutes before removal from the mold.

Figure 2.11 The HAAKE Polylab internal mixer used in melt-mixing method.

Figure 2.12 The compression molding LabTech Engineering used for preparation flat sheet polymer.

2.4.2 Property Testing of Polymer Blend

2.4.2.1 Melt-Flow Index

Melt flow index (MFI) is a measure of the ease of flow of the melt of a thermoplastic polymer. It is defined as the mass of polymer, in grams, flowing in ten minutes through a capillary of a specific diameter and length by a pressure applied via prescribed alternative gravimetric weights for alternative prescribed temperatures. Melt flow rate is an indirect measure of molecular weight, with high melt flow rate corresponding to low molecular weight. At the same time, melt flow rate is measure of ability of the material's melt to flow under pressure. Melt flow rate is inversely proportional to viscosity of the melt at the conditions of the test; through it should be borne in mind that the viscosity for any such material depends on the applied force [Encyclopedia, 2011].

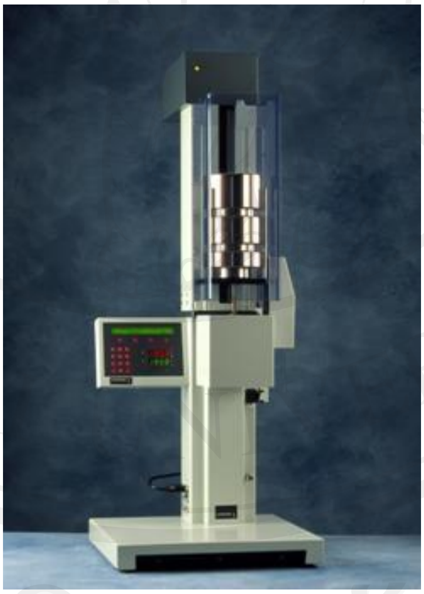


Figure 2.13 The Lloyd Instruments MFI-10 melt flow indexer used for melt flow measurement.

MFI measurements of polymer blends were obtained using a model MFI-10 davenport (Lloyd Instruments). The test was carried out according to ASTM D1238 [ASTM D1238 and see in Figure 2.13. A small amount of the polymer sample (around 4 to 6 grams) is taken in the specially designed MFI apparatus which is nothing but a miniature extruder. The apparatus consists of a small die inserted into the extruder, with diameter of the die generally being around 2 mm. The material is packed properly inside the extruder barrel to avoid formation of air pockets. A piston is introduced which acts as the medium that causes extrusion of the molten polymer. The sample is preheated for a specified amount of time: 3 min at 175 °C for polymer sample. After the preheating a 2.16 kg weight is introduced onto the piston. The weight exerts a force on the molten polymer and it immediately starts flowing through the die. A sample of the melt is taken after desired period of time and is weighed accurately. MFI is expressed as grams of polymer/10 minutes of flow time [Encyclopedia, 2011].

2.4.2.2 Mechanical Properties

The mechanical properties were evaluated by universal tensile testing machine (Instron 55R4502, see in Figure 2.14) equipped with a 1kN cell, according to ASTM D638 Type V. A crosshead speed of 50 mm/min was used. The specimens were prepared and cutting with a dumbbell-shaped cutter. The gauge length was 63 mm, and the thickness and width of the specimens were 0.5-1.0 mm and 62±1 mm, respectively. At least five specimens were used for each blend condition.

Figure 2.14 The Instron 55R4502 universal tensile testing machine used for tensile testing according to the ASTM D638 Type V.

2.4.2.3 Thermal Properties

2.4.2.3.1 Differential Scanning Calorimetry

Procedure detail in 2.3.2.2

2.4.2.3.2 Dynamic Mechanical Analysis

Polymers are viscoelastic materials, whose mechanical behavior exhibits characteristics of both solids and liquids. Thermal analysts are frequently called on to measure the mechanical properties of polymer for a number of purposes. Of the different methods for viscoelastic property characterization, dynamic mechanical techniques are the most popular, since they are readily adapted for studies of both polymeric solids and liquids. They are often referred to collectively as dynamic mechanical analysis (DMA). Thermal analysts often refer to the DMA measurements on liquids as rheology measurement.

Dynamic mechanical analysis involves imposing a small cyclic strain on a sample and measuring the resulting stress response, or equivalently, imposing a cyclic stress on a sample and measuring the resultant strain response. In most commercial DMA instruments strain is the controlled input, while the resulting stress is measured. DMA is used both to study molecular relaxation processes in polymers and to determine inherent mechanical or flow properties as function of time and temperature.

Figure 2.15 The Metler-Toledu SDTA861^{e} dynamic mechanical analyzer used for dynamic mechanical properties.

Dynamic mechanical properties were determined as a function of temperature using a DMA testing machine (SDTA861^{e}, Metler-Toledu) as shown in Figure 2.19. The relaxation spectrum was scanned from -60 to 120 °C with a frequency of 1 Hz and a heating rate of 4 °C/min. Storage modulus (E'), loss modulus (E'') and tan d were recorded as a function of temperature. The glass transition temperature, T_g was evaluated from the peak position of the tan d versus temperature curve. Applications for which DMA is used are listed in Table 2.9.

Table 2.9 Applications of DMA and Structure-Property Characterization

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Dynamic Mechanical analysis

1. Detect transitions arising from molecular motions or relaxations
2. Determine mechanical properties, i.e., modulus and damping of viscoelastic Materials over spectrum of time (frequency) and temperature
3. Develop structure-property or morphology relationships

Polymer structure-Property Characterization

1. Glass transition
2. Secondary transition
3. Crystallinity
4. Molecular mass/crosslinking
5. Phase separation (polymer blends, copolymers, polymer alloys)
6. Composite
7. Aging (physical and chemical)
8. Curing of networks
9. Orientation
10. Effect of additives (plasticizer, moisture)

2.4.2.3.3 Thermogravimetric Analyzer

Thermogravimetry analysis (TGA) or thermogravimetry (TG) is a technique where the mass of a polymer is measured as a function of temperature or time while the sample is subjected to a controlled temperature program in a controlled atmosphere (Earnest 1988). Temperature ranges for commercial TGAs are typically ambient to 1000 °C or more, a sufficient upper limit for polymer applications. A purge gas flowing through the balance creates an atmosphere that can be inert, such as nitrogen, argon, or helium; oxidizing, such as air or oxygen; or reducing, such as forming gas (8-10%hydrogen in nitrogen). With polymers, a reducing atmosphere is rarely needed. The moisture content of the purge gas can vary from dry to saturated.

Figure 2.16 The Perkin-Elmer (TGA7) thermogravimetric analyzer used for thermal degradation.

Polymers generally exhibit mass loss, although mass gain may be observed prior to degradation at slow heating rates in an oxidizing atmosphere. Mass loss may be categorized as volatile components such as absorbed moisture, residual solvents, or low-molecular-mass additives or oligomers that generally evaporate between ambient and 300 °C; reaction products, such as water and formaldehyde from the cure of phenolic and amino resins, which generally from between 100 °C and 250 °C; and generation of volatile degradation products resulting from chain scission that generally require temperatures above 200 °C but not more than 800 °C. All of these mass loss processes may be characterized by TGA to yield information such as composition, extent of cure, and thermal stability. The kinetics of these processes may also be determined to model and predict cure, thermal stability, and aging due to thermal and thermooxidative processes. This the project was used to determine if there was any water in the samples. The Perkin-Elmer (TGA7) using temperature 50 to 600 °C and a scan rate of 50 °C/min.

2.4.2.4 Morphology

Procedure detail in 2.3.2.3

2.4.2.5 Optical Properties

Procedure detail in 2.3.2.4

2.4.2.6 Biodegradation under Laboratory-Scale Composting Conditions

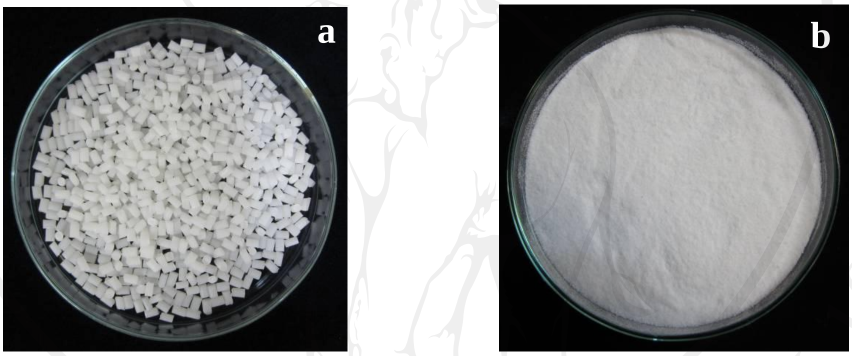
ASTM D5338 is method used to assess biodegradability of biodegradable plastics under simulated or controlled composting conditions which correlates biodegradability to the total mineralization of organic carbon (CO_2 evolved) in the polymer. To meet the ASTM D5338-98 [ASTM D5338-98] standard, 60% of single polymer materials must mineralize in six months, and 90% must do so in blends. Materials should give way to intense microbial activity and be converted from carbon to carbon dioxide, biomass and water. Materials also should begin to fragment, at which point disintegrations begins. In this phase, the material must complete physical and visually disintegrate. Ninety percent of the disintegrated material must not adversely affect the quality of the compost. Finally, even after land application, remaining materials should be safely converted into CO_2 by microorganisms. The resultant compost should not be toxic and should not deter plant growth, ecotoxicity tests are carried out in accordance with ASTM D6400 to certify that it is compostable. ISO 14855-1 [ISO 14855-1] gives similar guidelines to that of ASTM D5338 except that the mineralization of an unknown biodegradable material should be 90% of the value obtained for a reference material to prove its biodegradability. In both methods, the amount of CO_2 evolved due to biodegradation can be measured using acid-base titration, or by using a direct measurement such as infrared or gas chromatography [Kale *et al.*, 2007; Nolan-ITU, 2002].

The determination method of the biodegradability as shown in Figure 2.18 is based on ISO 14855-1[ISO 14855-1] and ASTM D5338-93 which are translated by National Metal and Materials Technology Center (MTEC). ISO 14855-1 and ASTM D5338 in respect of: (a) the amount of compost/vermiculite mixture and sample used; (b) the number of blanks; (c) the positive control; (d) the sample bioreactors; and (e) the method of CO_2 measurement. This system was designed to yield percentage of carbon dioxide from organic content of the sample. Three month-old compost was used for biodegradation purpose. The compost was sieved through a 10 mm and inert materials such as glass, stones, and metal were removed. Cellulose power for thin-layer chromatography with a particle size under 20 μm obtained from Merck (Germany) was used as the known reference material (positive control). The organic carbon content of the cellulose was 43.52% determined by elemental analysis. Polymer samples were grinded powder into size particle less than 1000 μm to be used as samples for biodegradability evaluation. The recommend using compost and sample in a ratio of 6:1 and the used quantity is 360 g of compost (dry weight) to 60 g of polymer sample powder (as shown in Table 2.9), and the moisture level was adjusted to about 50±5 % and C/N ratio range between 10 and 40. The current system is comprised of twelve bioreactors; two blanks, two positive control (cellulose), and four samples (PBS and PBS/CAB/Paraplex G40 blend powder; each sample two bioreactors). The compost containing no samples was used as a blank to determine the respiration activity of this compost. The composting vessels are incubated in the dark or in diffuse light for a period of 45 day in an enclosure that is free from vapors toxic to microorganisms. The temperature is maintained at 58±2 °C for 90 days and oxygen (O_2) levels in the composting vessel should be at least 6% at all times. Check CO_2 and O_2 concentrations in the outgoing air at least daily with a minimum time interval of 6 h after the first week for the remainder of the test. Check air flow daily before the composting vessels and at the outlets, ensuring that no leaks are present in the complete system. Adjust air flow to maintain a CO_2 concentration of at least 2% volume over volume to allow accurate determination of CO_2 level in exhaust air. The

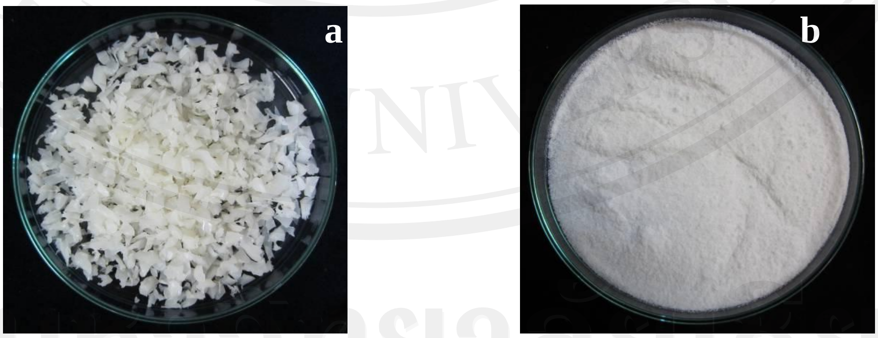
CO_2 produced from the reaction vessels was trapped in alkaline solution bottles. The amounts of trapped CO_2 were determined by titration of acid solution to trap solutions. The percentages of biodegradation were calculated from the produced CO_2 amount which was the called respiration CO_2 amount determined from a blank and theoretically produced CO_2 amount added sample.

Sample : PBS

: PBS/C AB/Paraplex G40 (70/30/10)



PBS



PBS/CAB/ Paraplex G40 (70/30/10)

Figure 2.17 Physical appearance of sample testing: (a) sample obtained and (b) sample for testing (< 1000 μm).

Table 2.10 Mass mixing of compost and sample powder is used testing.

Bioreactor	Compost/Vermiculite		Sample Powder	
	wet weight (gram)	dry weight (gram)	wet weight (gram)	dry weight (gram)
Blank Vessel	757.70	360.13	-	-
Cellulose (Positive control)	757.51	360.07	63.00	60.00
LDPE (Negative control)	772.29	420.05	70.23	70.14
CAB	772.69	420.27	70.02	69.21
PBS	757.39	360.01	61.61	60.00
PBS/CAB/Paraplex G40 (70/30/10)	757.66	360.14	61.00	60.00

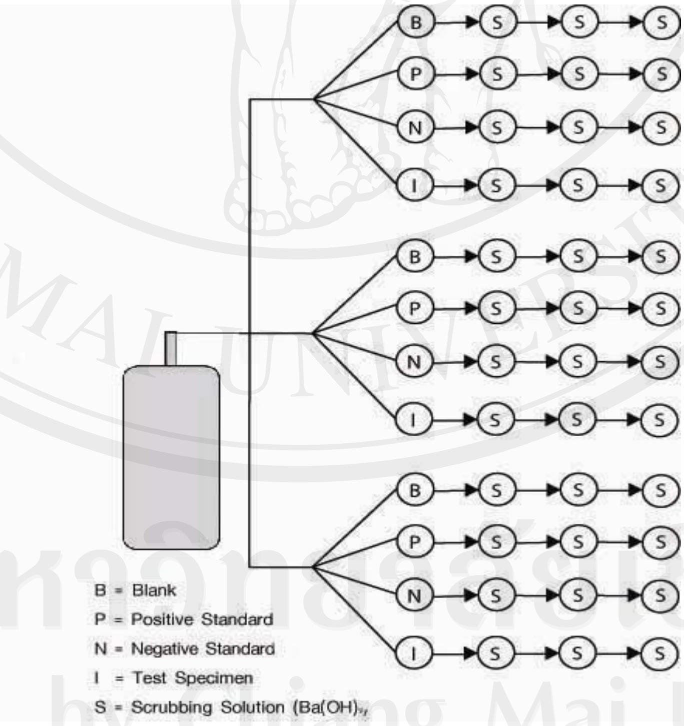


Figure 2.18 Set-up using carbon dioxide-trapping apparatus [ASTM D5338-98].