CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Polypropylene sources

- Polypropylene homopolymer resin (P700J) was supplied by Thai Polypropylene Co.,Ltd. with reported density of 0.91 g/cm^3 and melt flow rate of 12 g/10min.

3.1.2 Biodegradable additives

- Cassava Starch was purchased from ETC International Trading Co.,Ltd.
- Bleached cotton fabric for preparation of microcrystalline cellulose (MCC) was supplied by Assistant Professor Usa Sangwatanaroj, Ph.D.

3.1.3 Chemical reagents

- 36% hydrochloric acid and 5% ammonium hydroxide analytical grade used for MCC preparation were purchased from Merck, USA. They were used as received.
- Dichloromethane analytical grade for solvation of pyrolysis liquid products was purchased from Merck, USA and used without further purified.

3.1.4 Carrier gas used in pyrolysis study

- High purity nitrogen gas was purchased from Thai Industrial Gas Co.,Ltd. (TIG).

3.1.5 Gas sampling bags

- 300 ml dual-valve gas sampling bags for gaseous products collection were purchased from Cole-Parmer, USA.

3.1.6 Standard gas for GC calibrations

- Agilent Technologies Standard refinery gas (Part number: 5080-8755) with approximate concentrations in %v/v: 15% hydrogen, 5% propane, 1%propylene, 10% iso-butane, 2% iso-pentane, 1% n-pentane, 15% nitrogen, 5% methane, 5% n-butane, 10% 1-butene, 5% trans-2-butene, 5% cis-2-butene, 5% carbon dioxide, 5% carbon monoxide, 1% ethylene, and 10% ethane; was purchased from Petro-Instruments Co.,Ltd., Thailand

3.2 instruments and apparatus

3.2.1 Biodegradable additive characterization

The surface morphology of starch and MCC was evaluated by scanning electron microscopy (SEM). The samples were coated with gold by a sputtering coater model Balzers SCD040. Images were obtained on Scanning Electron Microscope model JSM-5800LV manufactured by Japan Electron Optical Laboratory.

Elemental compositions of starch and MCC were characterized using an elemental analysis technique. Figure 3.1 shows an FISONS elemental analyzer model NA-2000 used in this research.

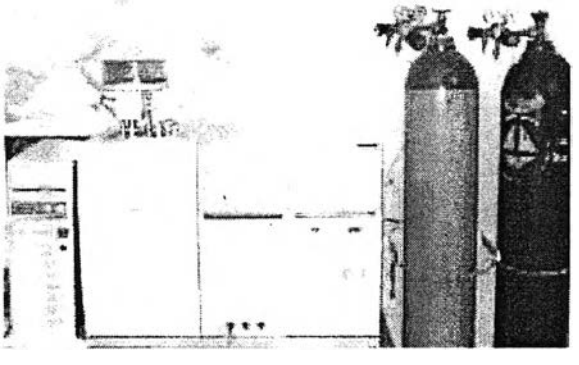

Figure 3.1. FISONS Elemental analyzer

3.2.2 Biodegradable composites processing

PP/biodegradable additive composites were processed through a THERMOPRISM co-rotating twin screw extruder, as shown in Figure 3.2.

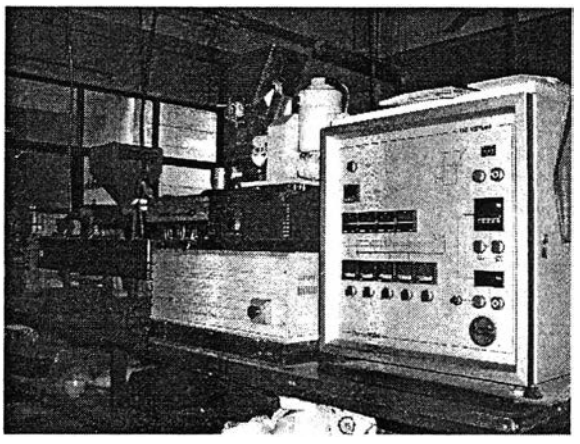

Figure 3.2. THERMOPRISM Twin Screw Extruder

3.2.3 Pyrolysis experiments

The pyrolysis experiments were carried out in a thermogravimetric analyzer (TGA). Figure 3.3 displays the METTLER TOLEDO TGA model TGA/SDTA 851^e with STARe software version 8.1 for data evaluation used in this research.

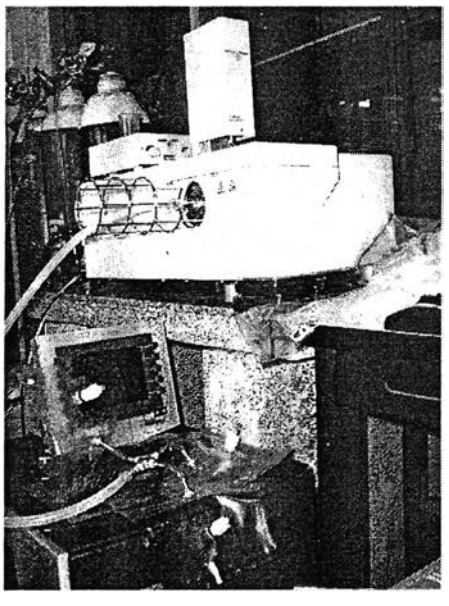

Figure 3.3 METTLER TOLEDO TGA equipped with gas sampling bag.

3.2.4 Pyrolysis products verification

Pyrolysis gas and liquid products were analyzed by gas chromatograph technique in an Agilent Technologies 6890N gas chromatograph equipped with a flame ionization detector (FID), as shown in Figure 3.4. Its capillary column is HP-5 with 0.25 μm thickness coating of 5% phenyl methyl siloxane, 0.32 mm inner diameter and 30 m long.

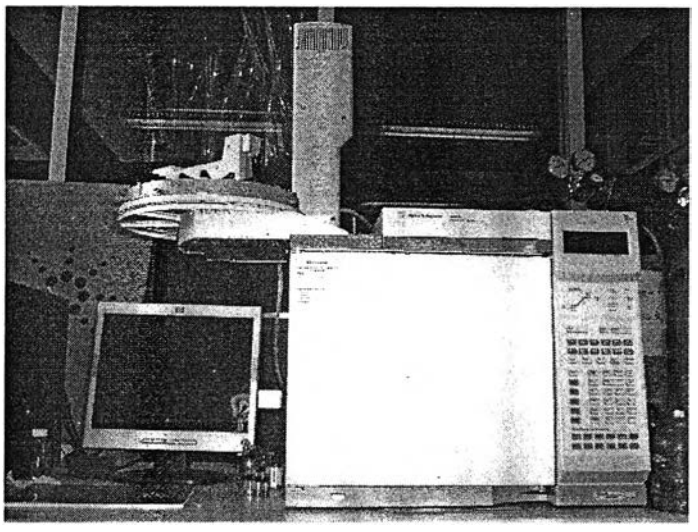

Figure 3.4. Agilent Technologies 6890N gas chromatograph.

In addition, pyrolysis gas and liquid products identification were performed by gas chromatography-mass spectrometry (Varian CP-3800 gas chromatograph coupled to Varian Saturn 2200 mass spectrometer) using a CP-Sil 8 CB low bleed capillary column with 1.0 μm thickness coating of 95% dimethyl polysiloxane, 0.32 mm inner diameter and 30 m long, as shown in Figure 3.5.

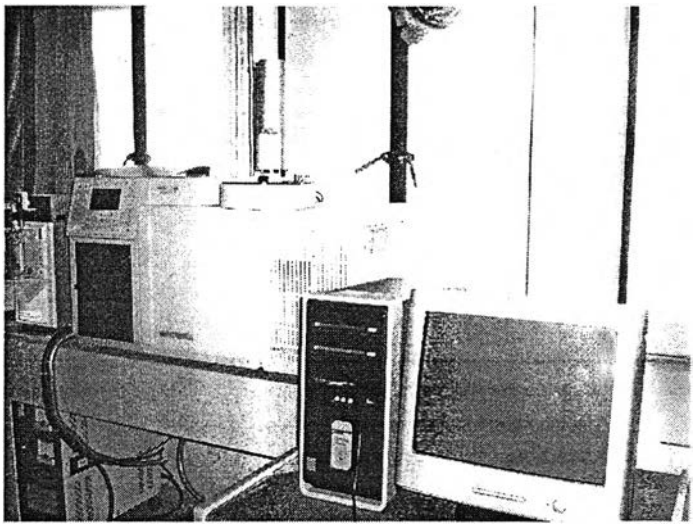

Figure 3.5. Varian CP-3800 gas chromatograph coupled to Varian Saturn 2200 mass spectrometer.

Char residues were analyzed by elemental analysis and their morphology was observed using SEM (JSM-5800LV, Japan Electron Optical Laboratory), as presented in Figure 3.6

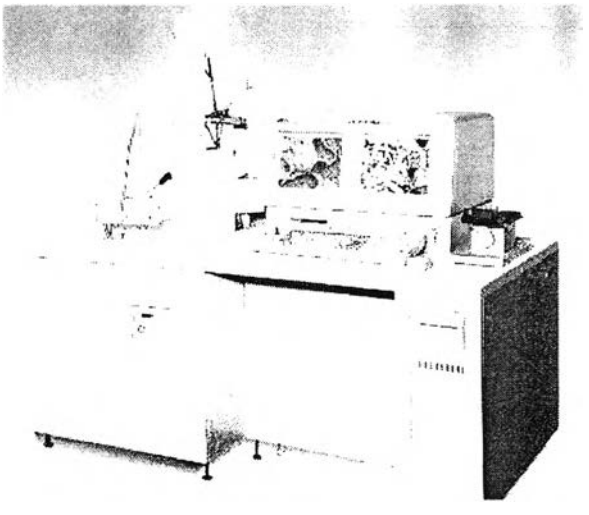

Figure 3.6. JSM-5800LV scanning electron microscope.

3.3 Methodology

The flow chart of the entire experimental procedure is shown below in Figure 3.7.

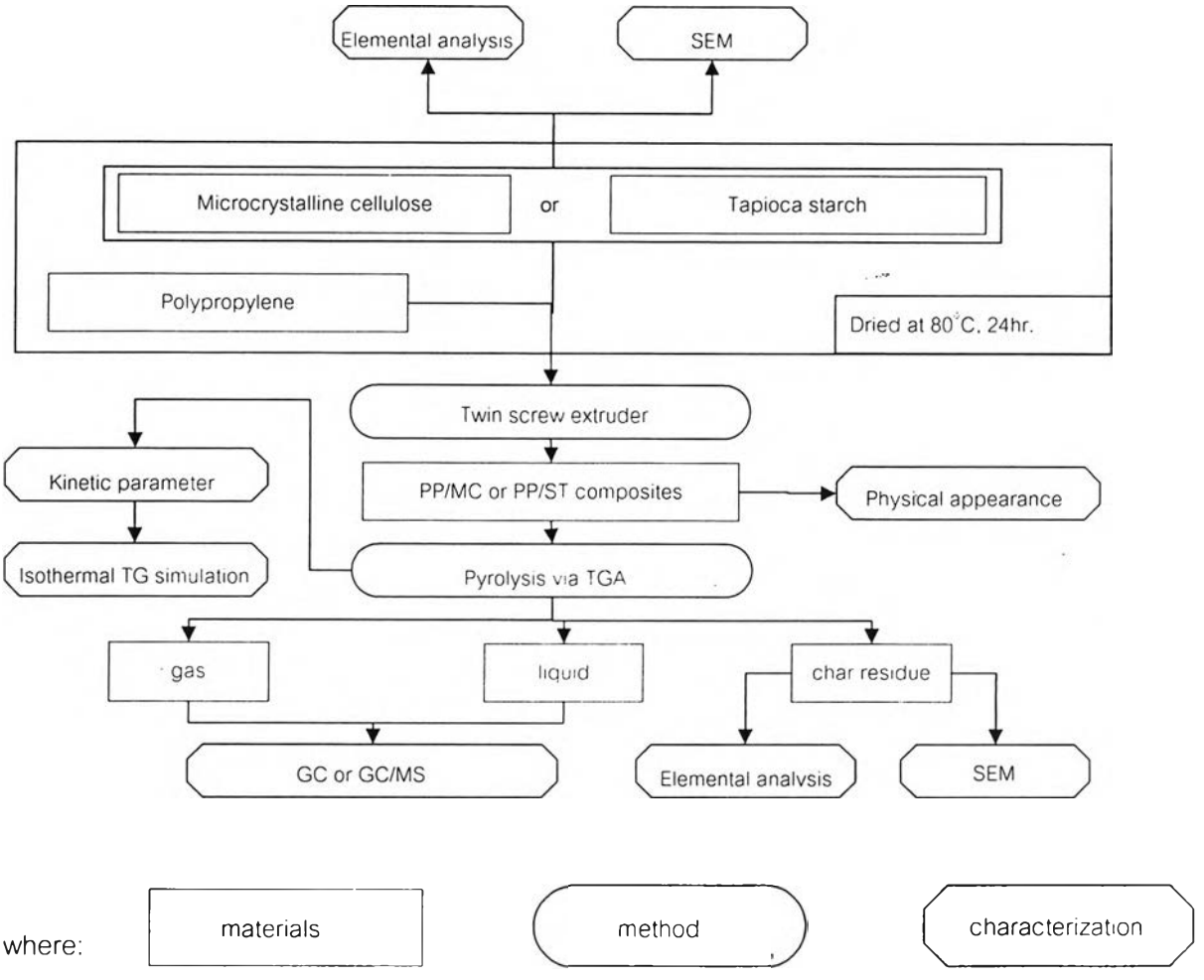

Figure 3.7. Flow chart of experiment procedure.

3.3.1 Microcrystalline cellulose preparation

Microcrystalline cellulose (MCC) was obtained from acid hydrolysis of about 25g bleached cotton fabric using 200ml 2.5N hydrochloric acid at 90°C for 30 min. The product was then neutralized with 5% ammonium hydroxide. MCC was recovered by filtering using no.1 WHATMAN filter paper and dried at 80°C for 24 hr to remove moisture. The obtained MCC was weighed to determine the product yield. The percent yield of MCC was calculated by dividing weight of dried MCC from the hydrolysis

experiment with initial weight of bleached cotton fabric. Figure 3.8 shows the schematic diagram of MCC preparation.

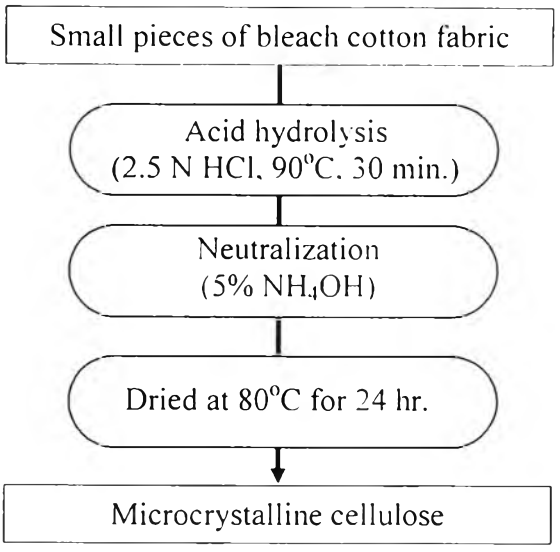

Figure 3.8. Schematic diagram of MCC preparation.

3.3.2 Preparation of biodegradable composites

The samples consisted of PP and biodegradable additives used in the experiments were mixed in different compositions as shown in Table 3.1.

Table 3.1. Biodegradable composites tested in pyrolysis process

Samples	Polypropylene (PP) (%)	Microcrystalline cellulose (MCC) (%)	Starch (STR) (%)
PPURE	100	-	-
P05MC	95	5	-
P10MC	90	10	-
P15MC	85	15	-
P20MC	80	20	-
P05ST	95	-	5
P10ST	90	-	10
P15ST	85	-	15
P20ST	80	-	20

Figure 3.9 presents a schematic preparation of the biodegradable composites. Polypropylene, cassava starch, and microcrystalline cellulose were dried at 80°C for 24 hr, and then mechanically premixed and processed through a co-rotating twin screw extruder with the programmed temperature in feeding, metering, and die sections at 160, 165, and 170°C, respectively. The screw speed was maintained at 25 rpm. The extrudates were cooled in water and cut into pellet with a rotary cutter at the die exit.

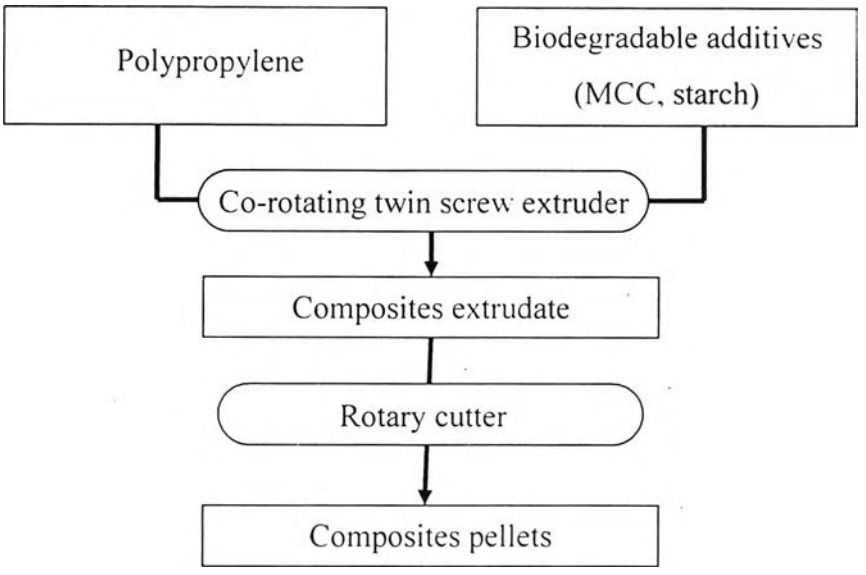

Figure 3.9. Schematic preparation of the biodegradable composites preparation.

3.3.3 Pyrolysis studies

The pyrolysis experiments were carried out in a thermogravimetric analysis (TGA) instrument under nitrogen atmosphere at a maintained flow rate of 50 ml/min. The schematic representation of the experiment used is shown in figure 3.10. After the experiment was set up, air remaining in the reactor was purged with nitrogen gas at a flow rate of 50 ml/min for 30 min. Alumina crucible was used as a sample holder and the total mass of sample taken was 25-30 mg for each run of the experiments. Temperature was maintained in dynamic condition between 30 to 600°C at different heating rates of 10, 20 and 30°C/min and held at 600°C for 10 min. The experiments were also carried out in isothermal condition at 490°C for 8 min. Reproducibility of the experiments and the

sensitivity of the results on the sample size were proved by pyrolysis of PP using three different sample sizes (10, 20 and 30 mg) at a heating rate of 20°C.

The pyrolysis products were classified into three groups as gases, condensable liquids, and char residues. The amount of gaseous products was calculated by subtracting the weight of liquid products and char residues from the total weight of sample initially loaded to the TGA.

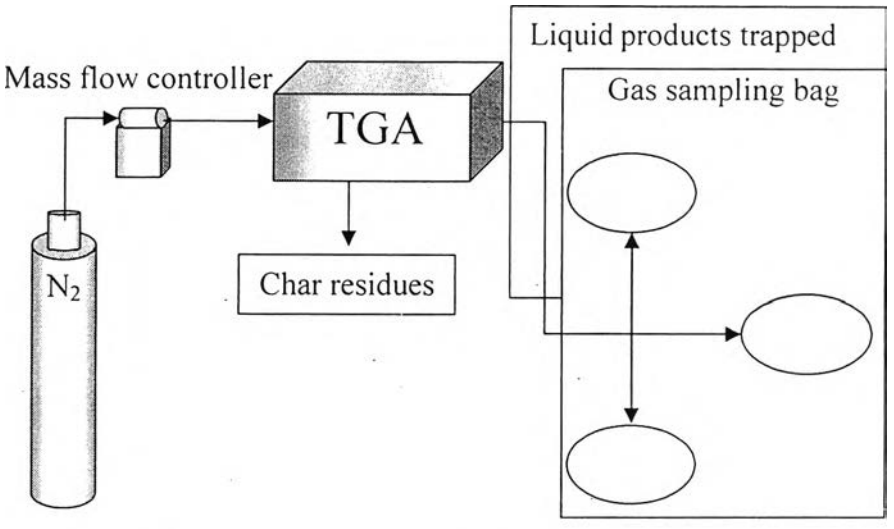

Figure 3.10. Schematic diagram of pyrolysis studies.

3.4 Characterization and testing

Biodegradable additives and their char residues were characterized by elemental analysis to determine the elemental composition.

The morphology of biodegradable additives and char residue were also determined by SEM (JSM-5800LV). The samples were dried at 80°C for 8 hr. before placing on the stub and then sputtering a thin layer of gold onto them to reduce electron charging effects. Sample morphology was obtained in 15 kV mode.

Pyrolysed gas products were kept in gas sampling bag. Condensable liquid products were extracted using dichloromethane as solvent. Both gas and liquid pyrolysis products were analyzed via gas chromatography. Injector temperature was set at 250°C in a splitless mode. The temperature program of the GC column was used from

35°C (held for 5 min) to 280°C at a heating rate of 10°C/min followed by an isothermal stage at 280°C for 15 min under a 1.3 ml/min flow of helium as a carrier gas.

The pyrolysed products were also identified with gas chromatography-mass spectrometry. The temperature program of the GC column was used from 35°C (held for 5 min) to 280°C at a heating rate of 10°C/min followed by an isothermal stage at 280°C for 15 min under a 1.3 ml/min flow of helium as a carrier gas. The mass spectrometer was scanned with the mass range from 10 to 150 m/z.