CHAPTER III

MATERIAL AND METHODOLOGY

Materials

Polypropylene

Polypropylene used in this work is isotactic polypropylene (iPP) under the trade name of Mophen HP400H from Basell Polyolefins in an extrusion grade polypropylene homopolymer. The melt flow index and density are 2 dg/min (230 °C/2.16 kg) and 0.9 g/cm^3, respectively.

Chemicals

Chemicals used and suppliers are listed in Table 1.

Table 1 Chemicals and suppliers

Chemicals	Suppliers
1. Sorbitol $\geq$ 99% $C_6H_{14}O_6$ MW=182.17 g/mol	Aldrich
2. 2-Chlorobenzaldehyde 99% C_7H_5OCl MW=140.57 g/mol	Aldrich
3. Dodecane ($C_{12}H_{26}$): bp 216.2 °C	Aldrich
4. Tetradecane ($C_{14}H_{30}$) : bp 253.0 °C	Aldrich
5. 3-Chlorobenzaldehyde 97% C_7H_5OCl MW=140.57 g/mol	AcrŌs Organics
6. 4-Chlorobenzaldehyde 98.5% C_7H_5OCl MW=140.57 g/mol	AcrŌs Organics
7. 4-Bromobenzaldehyde 98.5% C_7H_5OBr MW=185.02 g/mol	AcrŌs Organics
8. Cyclohexane (C_6H_{12}): AR grade bp 80.2-81.2 °C	Carlo Erba

Table 1 (Cont.)

Chemicals	Suppliers
9. Methanol (CH_3OH): AR grade bp 64.5 °C	Carlo Erba
10. Triethylamine ($C_6H_{15}N$): bp 88.7 °C	Carlo Erba
11. 85% Orthophosphoric acid (H_3PO_4): AR grade	Carlo Erba
12. 99% Potassium permanganate ($KMnO_4$)	Carlo Erba
13. Xylene (C_8H_{10}): AR grade bp 138.5 °C	RCI Labscan
14. Hexane (C_6H_{14}): AR grade bp 69 °C	RCI Labscan
15. 70% Methanesulfonic acid (CH_4O_3S): bp 167 °C	Merck
16. Dimethyl sulfoxide (C_2H_6SO): AR grade bp 189 °C	Fisher Scientific
17. 98% Sulphuric acid (H_2SO_4): AR grade	J. T. Baker
18. 30% Hydrogen peroxide (H_2O_2): AR grade	POCH SA
19. SEBS, Kraton® FG 1901X	Shell Chemical
20. Distilled water	-

Instruments

Instruments, manufacturers and models for this study are listed in Table 2.

Table 2 Instruments, manufacturers and models

Instruments	Manufacturers	Model
1. Melting point apparatus	SANYO	GALLENKAMP
2. Fourier Transform Infrared Spectrometer (FT-IR)	Perkin-Elmer	Spectrum GX
3. Nuclear Magnetic Resonance spectrometer (NMR)	Bruker	400 MHz Advance system
4. Differential Scanning Calorimeter (DSC)	Mettler Toledo	DSC1
5. Heating Block	In house apparatus	PA 4002
6. Scanning Electron Microscope (SEM)	Leo	1455VP
7. Transmission Electron Microscope (TEM)	Phillips	Tecnai12
8. Two-roll mill	Pirom-olarn	110-1E:MGLRM-110-3E
9. Mini-extruder equipped with fiber drawing units	Randcastle	RCP-0625
10. Microtome	SPENCER	820
11. Tensile machine	Testing machine	WDW-5E

Synthesis of sorbitol derivatives

The sorbitol derivatives were prepared by reacting 2 moles of aromatic aldehyde derivative (such as chloro and bromo-benzaldehyde) with 1 mole of D-sorbitol in cyclohexane. An acid catalyst at an elevated temperature was added into the reaction mixture to perform dehydrocondensation at above elevated temperature. For chloro derivatives, different substitutions which are *ortho*, *meta* and *para* were synthesized. The chemical reaction for sorbitol derivatives synthesis was shown in Figure 19. For example 1,3:2,4-di-*p*-chlorobenzylidene sorbitol (*p*-Cl-DBS) was prepared by mixing D-sorbitol (0.1 mol) and 4-chlorobenzaldehyde (0.2 mol). The solution was placed into a round bottom flask equipped with Dean-Stark trap and condenser as seen in Figure 20. Water (6.3 mL) was added into the flask, followed by methanesulfonic acid (1 mL), cyclohexane (200 mL) and dimethylsulfoxide (6 mL). The mixtures were heated until boil with constant stirring. During reflux, white precipitate of the product occurred. The mixture of cyclohexane and water was condensed and separated in the Dean-Stark arrangement. Once no further water was condensed into Dean-Stark trap, the reaction was terminated. The solution was neutralized with triethylamine (6 mL) and then white precipitate was filtered and washed with distilled water until the solution become neutral.

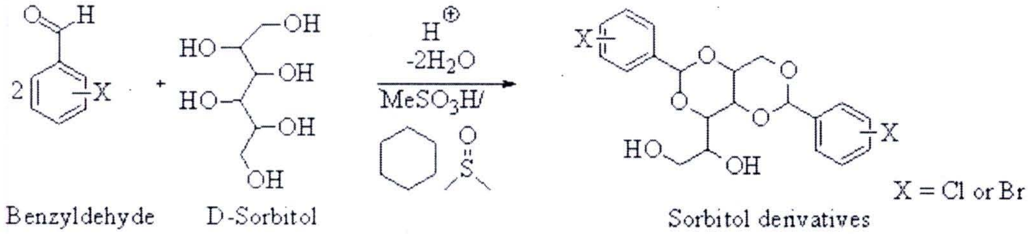

Figure 19 Synthesis of sorbitol derivatives (DBS)

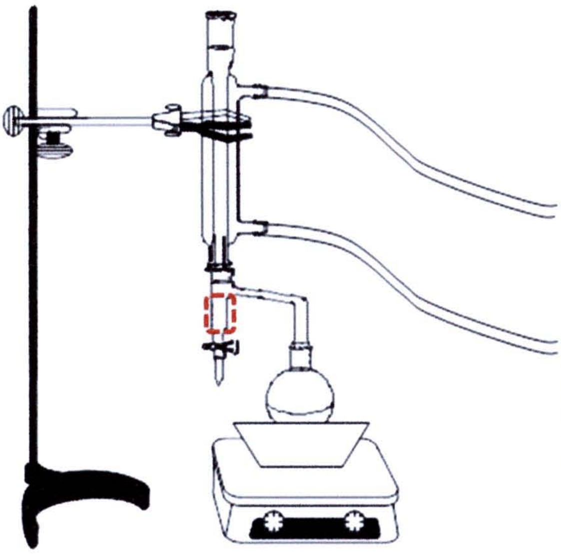

Figure 20 The equipment used in the synthesis

Purification

Sorbitol derivatives were dissolved in methanol (10% w/v) and placed into a round bottom flask. The mixture was heated and stirred at boiling temperature of methanol for about 1 hour. After that, the precipitate was filtered and washed with methanol and then dried in vacuum oven at 60 °C for 2 hours. All derivatives are in a white powder form.

Characterization of sorbitol derivatives

In this study, four types of sorbitol derivatives were used for investigation the effect of sorbitol derivatives on mechanical properties and morphology of iPP fibers. Before all sorbitol derivatives were used, the physical properties of sorbitol derivatives were characterized as following.

Melting point determination

The melting temperature of sorbitol derivatives were investigated by Differential Scanning Calorimeter (DSC, Mettler Toledo DSC1) and melting apparatus. For DSC, about 10 mg to 15 mg of each sample was placed in aluminium pan. The samples were heated from 120 °C to 260 °C with heating rate of 10 °C/min. After that they were cooled down to 120 °C with cooling rate of 5 °C/min and reheated again with heating rate of 10 °C/min. For melting apparatus, about 0.5 mg to 1 mg of each sample was placed into the closed end of the capillary tube. The samples were heated until begin to melt. The temperatures that the materials start to melt were recorded as start temperature. While the temperature that all materials melt were recorded as end temperature. Each sample was repeated 3 times.

Fourier Transform Infrared Spectroscopy (FT-IR)

Sorbitol derivatives were characterized by Fourier Transform Infrared Spectroscopy (FT-IR, PerkinElmer Spectrum GX). About 2 mg of each sample was mixed with KBr (200 mg) and then, pressed the mixture with hydraulic press. The sample was scanned from 400 to 4000 cm^{-1} for 16 times.

Nuclear Magnetic Resonance (NMR)

The chemical structure of each sorbitol derivatives was characterized by Nuclear Magnetic Resonance (NMR, 400 MHz Advance system). About 4 mg of each sample was dissolved in Deuterated-DMSO (1 mL), and then loaded sample directly into NMR tubes.

Gel formation and fibril morphology

Physical gel of sorbitol derivatives were prepared by dissolving at a specific concentration (expressed in mass percent) in dodecane and tetradecane at elevated temperature and cooled down to room temperature. Scanning electron microscopy (SEM, Leo1455VP) and transmission electron microscopy (TEM, Philllips Tecnai12) were used to investigate the fibril network of sorbitol derivatives. For SEM technique, a drop of sorbitol derivatives solution was placed on nylon membrane filters 0.2 μm (ϕ = 25 mm) and dried at ambience temperature for one week. Samples for TEM analysis were prepared by drop-casting the samples onto a carbon coated copper grid and examined under instrument operating at an accelerating voltage of 80 kV.

Preparation of polypropylene blend with sorbitol derivatives

In this study, iPP/sorbitol derivatives blend were prepared by two methods.

Solution blending

Isotactic polypropylene (iPP) was blended with sorbitol derivatives at different concentration in xylene. The materials were heated until reach the boiling point of xylene. After 1 hour, the homogeneous solution was precipitated in cold hexane. The sample was filtered out and then dried in vacuum oven for 30 min. The compounds were compressed with hot press molding into film thicknesses 2 mm. In this study, molding temperature was set at 175 °C for 5 min. The compounds were cut into small pieces, and then investigated the effect of sorbitol derivatives on crystallization and melting temperature of iPP by DSC technique.

Melt blending

Due to solution blending technique gave a small amount of sample, it is not enough for the next process. So, in this study the blend samples were prepared by two-roll mill technique.

Isotactic polypropylene (iPP) and sorbitol derivatives were melt-blended using two-roll mill (Pirom-olarn, 110-1E) at 140 °C for 5 min. The compounds were then compressed with hot press mold into film thickness 2 mm using mold temperature at 175 °C for 5 min. The compounds were cut into small pieces, and then investigated the effect of sorbitol derivatives on crystallization and melting temperature of iPP by DSC technique.

Investigation the effect of sorbitol derivatives on crystallization and melting temperature of iPP by DSC technique

The effect of sorbitol derivatives on crystallization and melting temperature of iPP were investigated in term of amount (0.1 to 1 wt% of *p*-Cl-DBS) and type (Cl and Br). The samples were placed in aluminium pan about 10 to 15 mg of each sample. The samples were heated from 25 °C to 180 °C with heating rate of 10 °C/min, and then cooled down from 180 °C to 25 °C with cooling rate 5 °C/min, and reheated again with heating rate of 10 °C/min.

Fiber preparation

The process used a mini-extruder (Randcastle RCP-0625) equipped with a fiber line having a single hole spinneret (Figure 21). An aluminium tube was connected with the die to retain a temperature inside during the process. The temperature profiles were fixed at 123, 180, 190, and 225 °C for feed zone, compression zone, metering zone, and die, respectively. The processing condition for fiber forming was shown in Table 3.

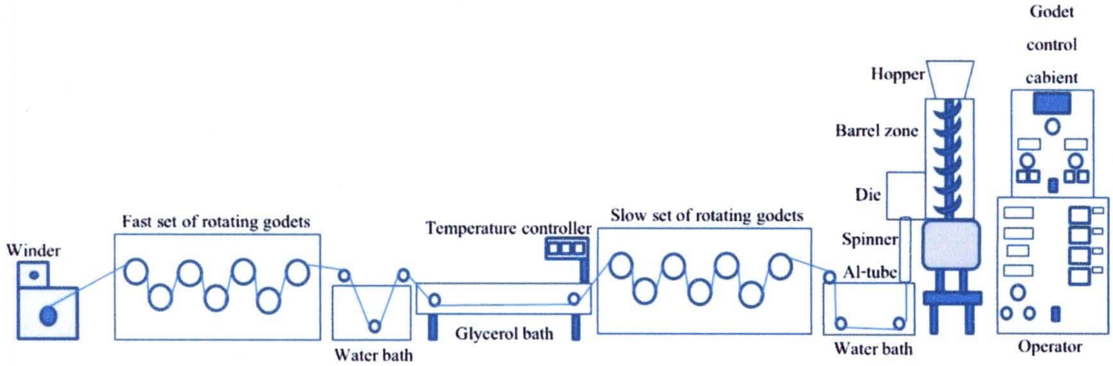

Figure 21 Schematic of mini-extruder and fiber line diagram

Table 3 Extrusion condition for sample preparation of neat iPP fiber and iPP/sorbitol derivatives fiber

Screw temperature (°C) with screw speed 2 rpm			
Feed zone	Compression zone	Metering zone	Die
123	180	190	225

Neat iPP and iPP/sorbitol derivatives pellets were fed into the hopper of mini-extruder to melt the pellet. The molten polymer was extruded through the spinneret and become an extrudate or as-spun fiber was pulled by slow set of rotating godets, immediately cooled in air and subsequently cooled in water. After the as-spun fiber was passed through water bath, it was continuously fed into a glycerol bath set as 95

°C to draw. The outcoming fiber from the glycerol bath was pulled into the water bath to washout the glycerol by the fast set of rotating godets. Finally, the drawn fibers at minimum to maximum draw ratios were collected by varying the take up velocity. In this work, the draw ratios of all samples were calculated from the ratios of the speeds of fast and slow sets of rotating godets.

Mechanical testing

Mechanical properties were tested by tensile tester (WDW-5E) with full-scale load 100 N and cross head speed 50 mm/min. The specimen gauge length of as-spun and drawn fiber were 20 and 100 mm, respectively. The sand paper No 2000 was used to hold the sample. The average values of mechanical properties of samples were calculated at least eight measurements for each sample. Tensile strength, Modulus and Elongation at break will be reported.

Characterization of as-spun and drawn fibers

Scanning electron microscope (SEM)

In this technique, sample surface is bombarded by electron beam that is generated from cathode-ray tube. The contrastable image was obtained from the scanning of electron beam on the contrastable surface. For polypropylene fiber, all repeating units of molecular chains consist of only carbon and hydrogen atoms. Beside, the densities of crystalline and amorphous orientations are not different. Therefore, the fiber's surface must be etched with permanganic-acid reagent to generate the different heights.

As-spun fiber was sandwiched by two sheets of styrene-(ethylene butylene)-styrene (SEBS) for ease of handing and microtoming (Figure 22). Two sheets of SEBS were fused together by using toluene. The longitudinal surface of fiber was removed with a glass knife on microtome (SPENCER, 820).

For etching, there were two solutions called: solution 1 and solution 2. Solution 1 was a mixture of sulfuric acid (H_2SO_4): orthophosphoric acid (H_3PO_4): water (10:4:1, v/v/v). Solution 2 was mixture of sulfuric acid: water (2:7, v/v). The specimen was placed into 2 mL of 1% (w/v) of potassium permanganate in solution 1 and shaken for 2 hours at room temperature. And then, 2 mL of solution 2 was added into permanganic-acid reagent to decrease the concentration of acid. After that, hydrogen peroxide was dropped into the solution to stop reaction. The solution was changed from dark green to no color. The specimen was washed with distilled water. In this work, the samples were cut into 2 types which are cross section and longitudinal section. After etching the sample was coated with thin layer gold in order to generate conductivity on the measurement surface and observed the morphology with SEM technique.

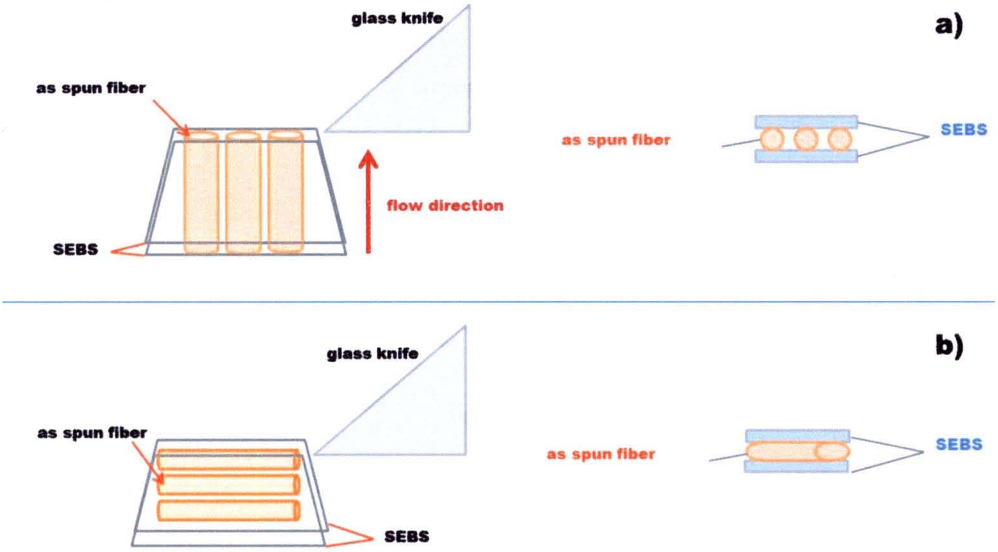

Figure 22 Schematic representation of fiber surface preparation for etching, a) cross section fiber and b) longitudinal section fiber

Small- and Wide-Angle X-ray Scattering (SAXS and WAXS)

Small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) measurements were used to investigate the effect of sorbitol derivatives on the orientation of iPP fiber. Time resolved X-ray scattering measurements were performed on beam-line BL2.2: SAXS at Siam photon laboratory, Synchrotron light research institute (Public organization) (Korat, Thailand), using a beam 0.2 mm in diameter. X-ray scattering data were collected using a CCD (Mar165) X-ray detector and photon energy was operating at 8 keV. The detector was located at a distance from the sample of 250 cm for small-angle X-ray scattering experiments and of 14 cm for wide-angle X-ray scattering experiments. The integration times for most samples were 300 s.

Flow charts of experiment

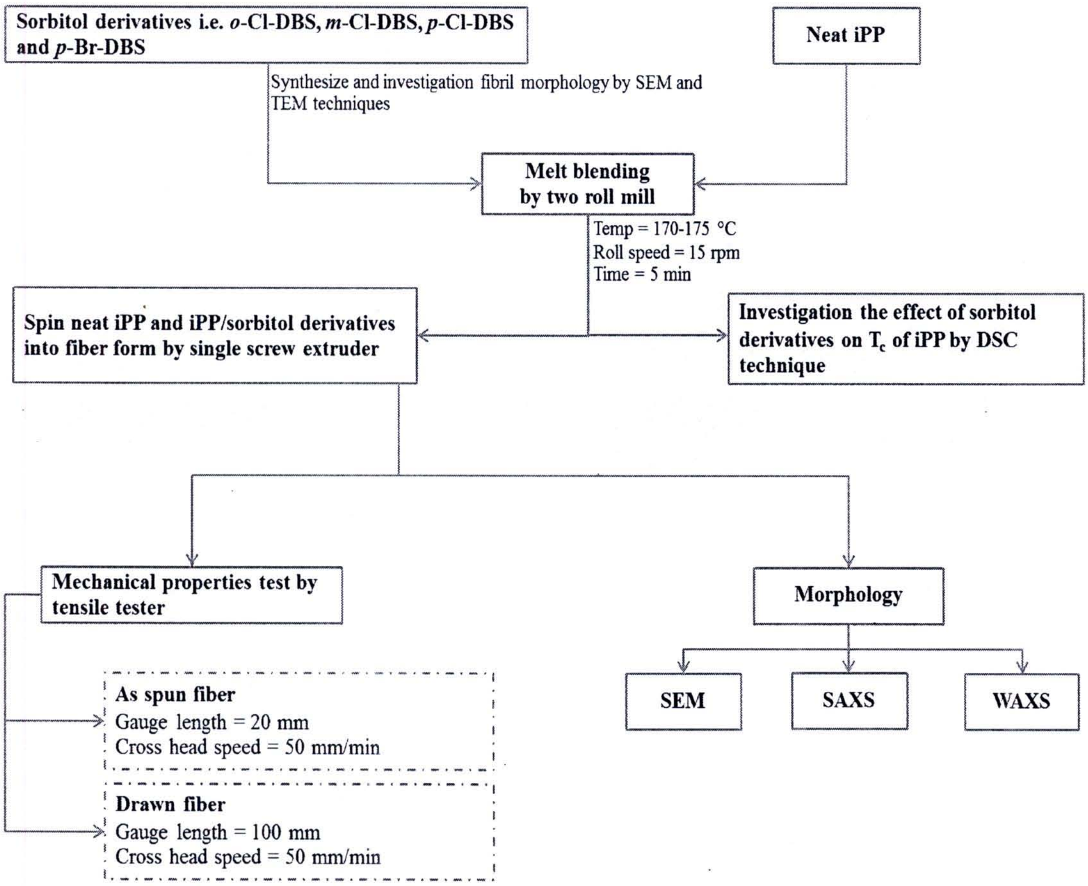

Figure 23 Experiment overview