CHAPTER III
EXPERIMENTAL

3.1 Materials and Chemicals

1. Cellulose fibers (CF) were prepared by disintegrating the sulfite pulp pads supplied by Weyerhaeuser in WA USA. The pads were soaked in water overnight and then put into an agitator to make pulps.

2. Cellulose microfibril (CMF) was supplied by Fluka.

3. Four different types of alcohol: 1–Butanol, 1–Decanol, 1–Octadecanol (18OH) and 1–Docosanol, supplied by Sigma Aldrich at ≥99.0% purity, were used as a grafting agent or a hydrophobic modifier.

4. Tolylene 2,4–diisocyanate (TDI) and Epichlorohydrin (EP), supplied by Sigma Aldrich, were used as the coupling agents.

5. o–Xylene with ≥99.0% purity was used as a solvent for TDI coupling agent meanwhile; acetone was used as a solvent for EP coupling agent.

6. Ethanol, 95% purity, and Acetone were used as a washing agent.

7. Sodium hydroxide (NaOH) was used as a catalyst in EP coupling agent reaction.

3.2 Equipment

1. Round–bottom flasks (as a reactor)
2. Egg-shaped magnetic stir bars
3. Silicone oil bath
3. Hot plate and stirrer
4. Condenser
5. Syringes and needles
6. Glass and rubber stoppers
7. Vacuum pump
8. Thermometer
9. Hose clamp

Figure 3.1 shows the experimental set up of the grafting reaction (left; the overall picture and right; the close–up picture).

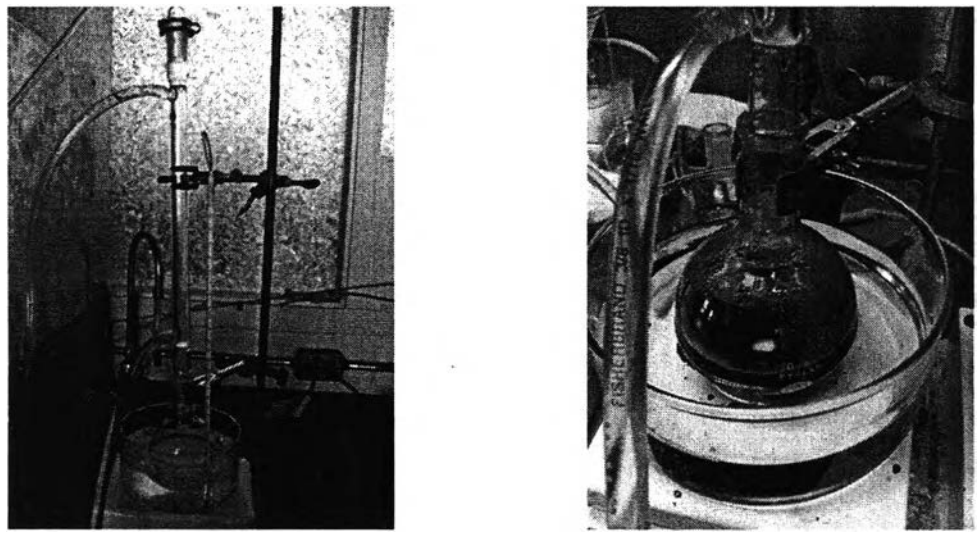

Figure 3.1 Picture of the experimental set up of the grafting reaction.

3.3 Experiment Procedures

The overall picture of the cellulosic materials modification as a reinforce material for biocomposites is shown in Figure 3.2. The modified CF/CMF was blended with polypropylene resin by a plastic extrusion process. The modified–composites will be in a bead formed.

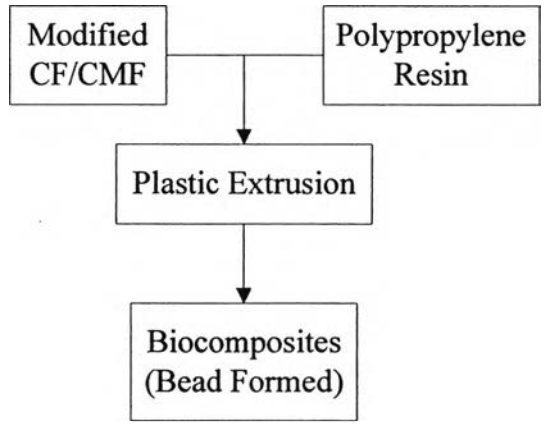

Figure 3.2 The overall route of the modification of cellulosic fibers.

3.3.1 Modification of Cellulosic Materials (CF and CMF) via TDI Coupling Agent

3.3.1.1 CMF Grafting with 1–Octadecanol

The following steps are a grafting reaction of cellulose microfibrils (CMF) with 18OH at 120°C reaction temperature and three hours reaction time. The two approaches are, TDI first coupling with 18OH and TDI first coupling with CMF, which is illustrated in Figures 3.3 and 3.4.

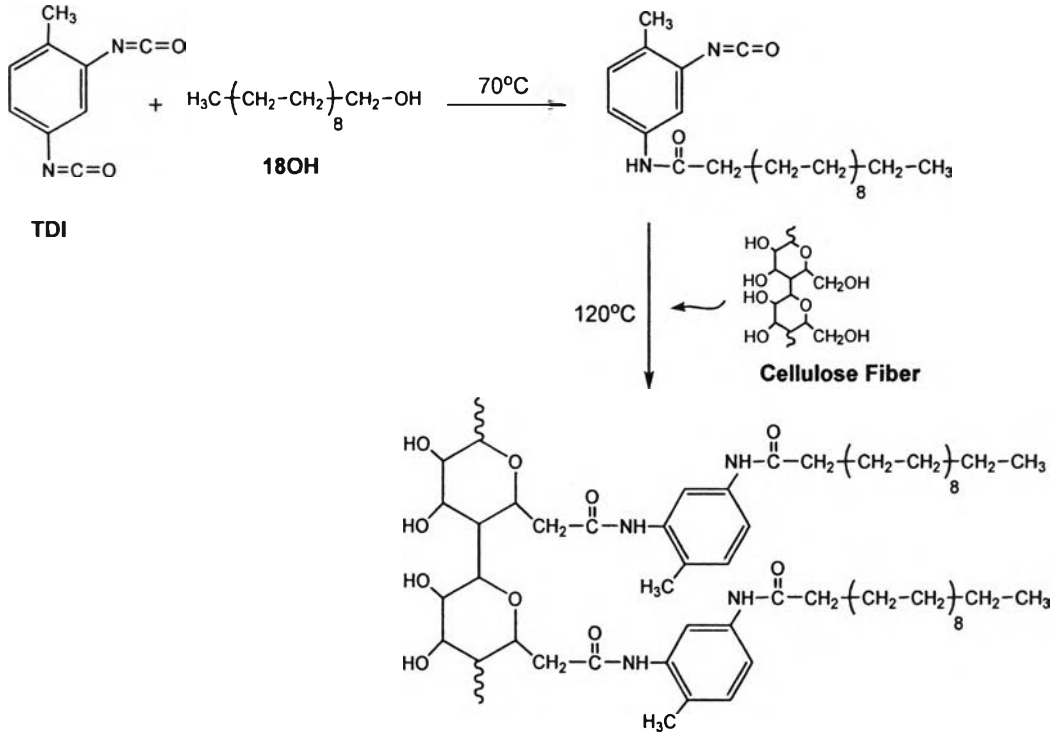

Figure 3.3 Grafting reaction of cellulose fiber with TDI and 1–Octadecanol (first approach).

The first approach, TDI coupling first with 18OH, the solution of 18OH (15.03 g) and o–Xylene (200 ml) was prepared. Then, TDI (7.97 ml) was injected and kept reacting at 70°C (in a constant temperature bath) for three hours. The hydrophobic–grafting of dried CMF (20 g, kept drying in the oven at 110°C overnight to remove water or moisture in CMF) was carried out in a 500 ml a three–necked round bottom flask. The grafting reaction was carried out at 120°C by adding

the prepared solution into a reaction flask and maintaining the reaction temperature at 120°C for another three hours. The grafted–product was filtered, washed with ethanol and dried in the oven at 110°C overnight.

The second approach, TDI coupling first with CMF, the solution of CMF (20 g, dreid in the oven at 110°C overnight to remove water or moisture in CMF) and o–Xylene (200 ml) was prepared. Then, TDI (7.97 ml) was injected and kept reacting at 70°C (in a constant temperature bath) for three hours. Then 18OH (15.03 g) was added and the grafting reaction was carried out at 120°C for another three hours. The grafted–product was filtered, washed with ethanol and dried in the oven at 110°C overnight.

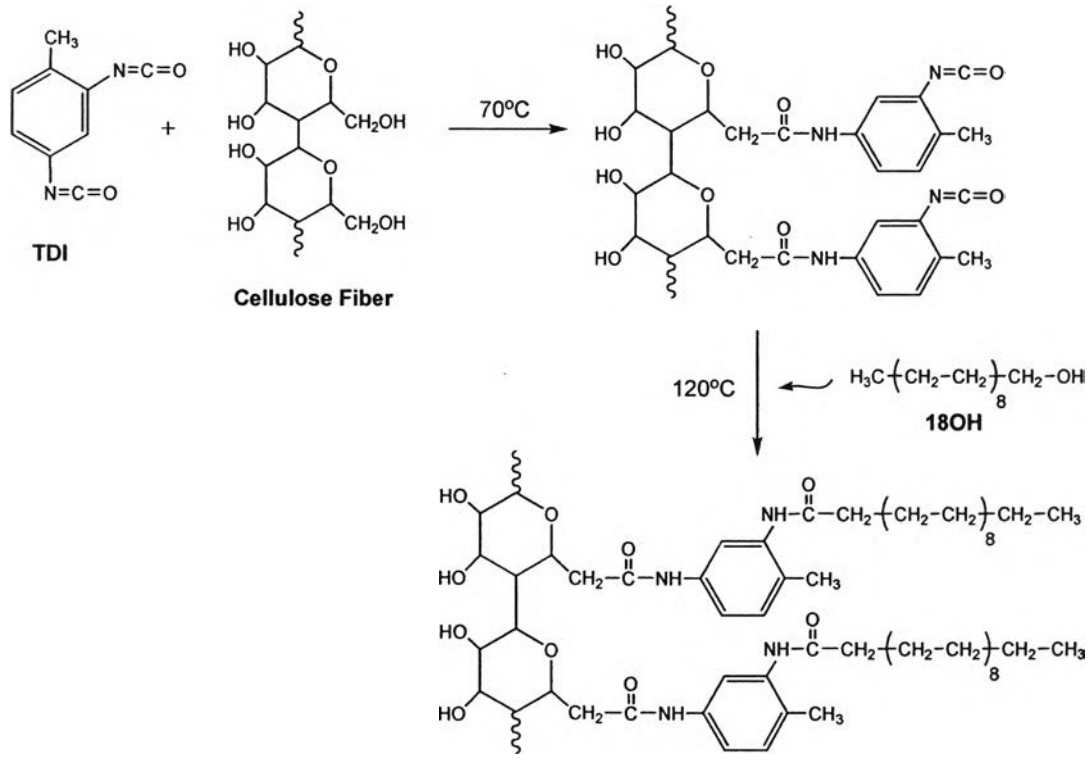

Figure 3.4 Grafting reaction of cellulose fiber with TDI and 1–Octadecanol (second approach).

3.3.1.2 CF Grafting with 1–Octadecanol

The grafting procedures of CF grafted 18OH are similarly with CMF grafted 1–Octadecanol as shown in 3.3.1.1. The different steps are the water removal and the preparation, as shown in Figure 3.5, because CF is a pulp like fiber which contained significant amounts of water. The moisture content in CF was also determined, 9.02%. The specific amount of wet pulp was weighted (221.73 g) and washed three times by 400 ml of acetone. The remaining acetone was distilled out with 500 ml of xylene at 120°C for an hour.

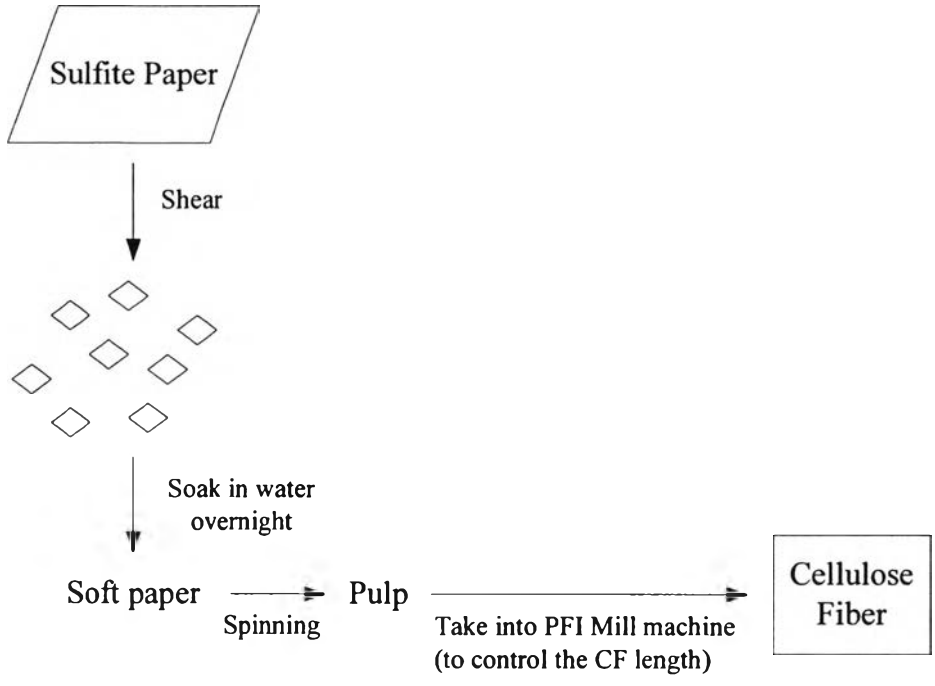

Figure 3.5 The preparation of CF pulp from sulfite paper.

3.3.2 Modify Cellulose Microfibril (CMF) via EP Coupling Agent

The grafting reaction was performed by an EP coupling agent in order to compare the grafting efficiency with the previous coupling agent, TDI. The schematic is shown in Figure 3.6.

A mixture of EP (0.29 ml of EP with 20 ml of acetone) and 15% NaOH solution (0.051 g of NaOH and 10 ml of water) which gave a pH of 11 was added in to a reaction flask at room temperature. The reaction was carried out at 55°C while add-

ing dried CMF (1 g) at intervals. The pH was increased during the reaction. The reaction was maintained for four hours under stirring. After reaction, the CMF–grafted–EP was washed with acetone in order to remove HCl produced and dried at 80°C overnight. Then, CMF–grafted–EP was immersed in a mixture of acetone (20 ml), a desired amount of NaOH solution acting as a catalyst (0.01 g/ 10 ml) and 18OH (0.07 g) was added under continuous stirring. The reaction was carried out at 55°C for another four hours. After reaction, the product was washed with acetone and dried at 80°C overnight, respectively.

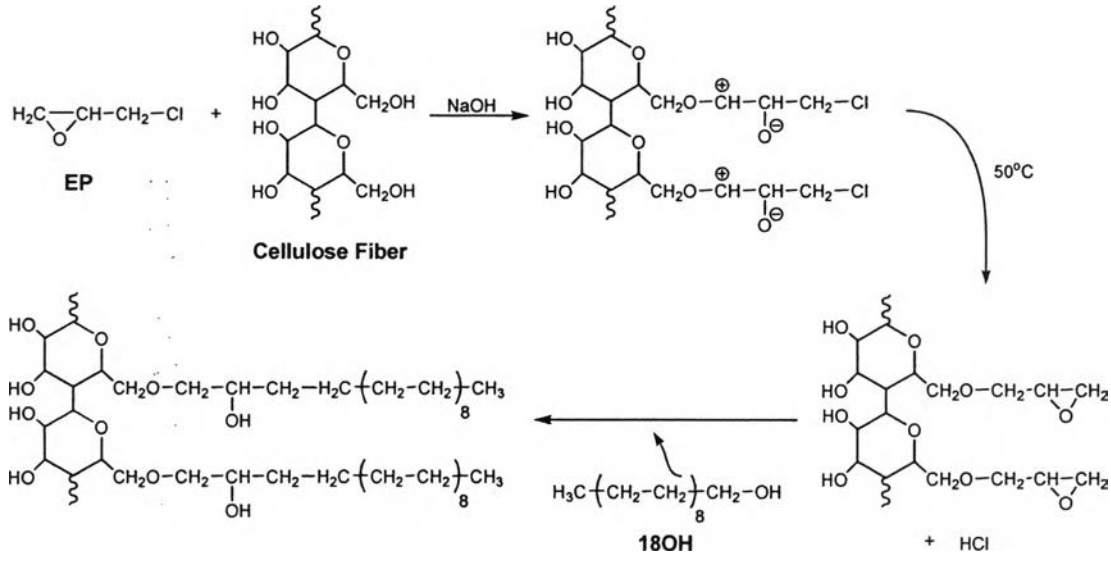

Figure 3.6 Grafting reaction of cellulose fiber with EP and 1–Octadecanol.

3.3.3 Extrusion Process

The preparation of polypropylene–based biocomposites was carried out in a twin–screw extruder (KESUN Co., L/D ratio: 32) at 180°C and 80 rpm. The premix of PP, CMF–18OH and 0.4% antioxidant, Irganox 1010 (Ciba), was addedat a high speed of the mixer, was added to the extruder in order to prepare the biocomposite sample.

The polypropylenes used were Y1600 and EPS30R types at Y1600:CMF–18OH ratio = 49:1 and EPS30R:CF–18OH ratio = 70:30.

3.4 Characterizations

3.4.1 Surface characterizations

The Scanning Electron Microscope (SEM) images were obtained for original and grafted cellulosic materials using a JEOL JSM–6400 scanning electron microscope. The samples were sputter–coated with carbon to avoid specimen charging.

The static contact angle measurements were conducted using a JC200A instrument (PowerEach, China) equipped with a digital photo analyzer. The hydrophobic property of the modified CF and CMF surfaces were qualified.

3.4.2 Qualitative Analysis of the grafting

The FT–IR spectra in the form of KBr pellets of fiber samples were recorded on a Spectrum 100 Perkin Elmer FT–IR spectrophotometer from USA. About 0.01 g of modified fiber was mixed with 0.2 g of dried KBr. and the FT–IR spectra were recorded with 32 scans per sample.

3.4.3 Quantitative Analysis of the grafting

The thermogravimetric analysis (TGA) of the fiber samples was conducted using a TA Instrument SDT Q600 model from USA. About 7 mg of samples, placed in an aluminum pan, were heated from 20 to 600°C at a heating rate of 10 °C/min under a constant flow rate of nitrogen (100 ml/min) and atmosphere conditions. The grafting yield and efficiency of the modified CF and CMF were quantified.

$$\text{Grafting Yield} = \frac{\text{Weight of alcohol grafted}}{\text{Weight of CF or CMF added}} \times 100\%$$

$$\text{Grafting Efficiency} = \frac{\text{Weight of alcohol grafted}}{\text{Weight of alcohol added}} \times 100\%$$

The Element Analysis (EDAX), connected with the scanning electron microscope device, was obtained for ungrafted and grafted cellulosic materials using EDAX Phoenix EDS systems. The samples were prepared similarly with the SEM samples. The alcohols grafted on the cellulosic materials were verified.

3.4.4 Thermal Characterization

The thermal behaviour, Differential Scanning Calorimetry (DSC) measurement, of the polypropylene-modified cellulosic fibers composites was examined with a TA Instrument SDT Q600 model from the USA at a standard heating/cooling rate of 10°C/min, under nitrogen flow.