CHAPTER III
EXPERIMENTAL

3.1 Materials

The materials used in this work are as follows:

1. High Density Polyethylene (HDPE)

High density polyethylene of blow molding grade (Marlex HHM 5502) was kindly supplied by Rianthai Interplas Co., Ltd. Some physical properties are shown in Table 3.1.

Table 3.1 Physical properties of HDPE.

Property	Test method	Unit	Value
Density	D 1505	g/cm^3	0.955
Melt index	D 1238	g/10 min	0.35
Tensile strength at yield, 50.8 mm/min	D 638	MPa	28
Elongation at break at 50.8 mm/min	D 638	%	>600
Shore hardness D	D 2240	-	67
Flexural modulus	D 790	MPa	1380
ESCR, F50	D 1693	Hours	45

2. Ethylene Gas

National Petrochemical Public Company Ltd. (NPC) supplied polymerization grade ethylene gas, used as monomer.

3. Milled Glass Fiber

The milled fiber was purchased from Owen-Corning Co., Ltd. The product description is called 731EC 1/32"; an example of milled glass fibers is shown in Figure 3.1. In addition, a summary of the product data is given in Table 3.2.

Figure 3.1 Example of milled glass fiber.

Table 3.2 Summary of milled glass fiber product data.

Sizing Type	Average filament diameter (μm)	Nominal bulk density (g/cm^3)	Appearance
Cationic	15.8	0.65	Powdery

The characteristics of the glass fiber are relatively free-flowing with a high bulk density. It can be used in formulations which require very uniform dispersions and short fiber lengths.

4. Sodium Dodecyl Sulfate (SDS)

Sodium dodecyl sulfate (purity 99%+) served as a surfactant to form the surfactant template or bilayer for polymerization. It was purchased from Sigma Chemical Co. The material is a white powder, completely soluble in water. A solution of SDS in distilled water was used for all experiments.

5. Initiator

Sodium persulfate (purity 99%+) acted as a water-soluble initiator. It was purchased from BDH Laboratory Suppliers.

6. Solvent

Dimethylformamide (AR-grade) was purchased from J.T. Baker Company Limited. It was used for extracting sizing agent from as-received glass fiber using the soxhlet extraction method.

3.2 Instrumentation

1. The Bench Top Parr Reactor

Polymerization reactions were carried out in a 600 ml Parr reactor (Parr Instrument Company), equipped with a pitch-blade turbine impeller with a speed controller, external heating jacket, thermowell, and pressure transducer (Figure 3.2). The impeller speed, outer jacket temperature, and internal reactor temperature as well as pressure are digitally displayed on the front panel.

Figure 3.2 Bench-top Parr reactor.

2. Brabender Plasti-Corder

Each type of glass fiber was mixed with HDPE in a Brabender Plasti-Corder, PL-2100, torque rheometer with a set of removable roller rotors and measuring mixer W50 having a volumetric capacity of 55 cm^3 in heat and shear stability mode.

3. Instron Universal Testing Machine

Tensile and flexural tests of the glass fiber reinforced HDPE composite samples were carried out on an Instron Universal Testing Machine model 4206.

4. Zwick Pendulum Impact Tester

Impact tests of HDPE/glass fiber composite samples were performed on a Zwick Pendulum Impact Tester model 5113.

5. Scanning Electron Microscopy (SEM)

Scanning electron micrographs were taken to identify the morphology of all glass fiber samples. Samples were characterized using a JEOL JSM 5000 scanning electron microscope at a magnification of 5000X.

6. Wabash Compression Molder

Test specimens of glass fiber/HDPE composites, 3 mm in thickness, were prepared by compression molding in a 50 ton capacity Wabash V50H compression molder.
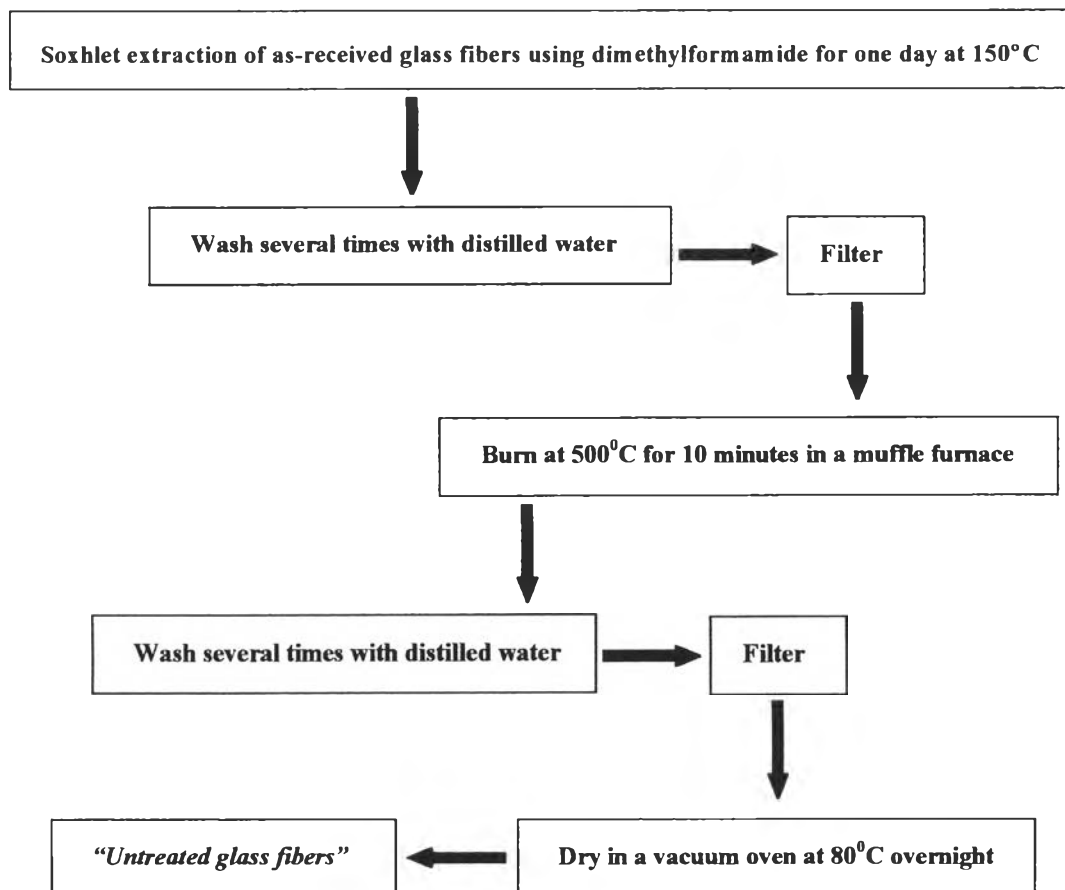
3.3 Methodology

3.3.1 Fiber Preparation

In this experiment, three types of glass fibers were used:

1. As-received glass fiber—used directly without any further surface treatment.

2. Untreated glass fiber—the as-received glass fiber after removal of sizing agent by soxhlet extraction followed by heating the fibers to 500°C for 10 minutes.

3. Admicellar-treated glass fiber—surface modified glass fiber (after removal of the original sizing) via admicellar polymerization.

A schematic of the preparation of untreated glass fibers is shown in Figure 3.3.

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┌─────────────────────────────────────────────────────────────────────┐
│ Soxhlet extraction of as-received glass fibers using                  │
│ dimethylformamide for one day at 150°C                                │
└─────────────────────────────────────────────────────────────────────┘
                              │
                              ▼
┌────────────────────────────────────┐        ┌──────────┐
│ Wash several times with distilled   │  ───▶  │  Filter  │
│ water                               │        │          │
└────────────────────────────────────┘        └──────────┘
                                                     │
                                                     ▼
                    ┌────────────────────────────────────────────┐
                    │ Burn at 500°C for 10 minutes in a muffle    │
                    │ furnace                                      │
                    └────────────────────────────────────────────┘
                                     │
                                     ▼
┌────────────────────────────────────┐        ┌──────────┐
│ Wash several times with distilled   │  ───▶  │  Filter  │
│ water                               │        │          │
└────────────────────────────────────┘        └──────────┘
                                                     │
                                                     ▼
┌────────────────────────────┐        ┌────────────────────────────────────┐
│   "Untreated glass fibers"  │  ◀───  │ Dry in a vacuum oven at 80°C        │
│                            │        │ overnight                           │
└────────────────────────────┘        └────────────────────────────────────┘
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Figure 3.3 Schematic of the preparation of untreated glass fibers.

3.3.2 Admicellar Polymerization of Polyethylene onto Glass Fiber

The following reaction mixtures were prepared:

(i) 0.5857 g $Na_2S_2O_8$ + 0.7094 g SDS (initiator to surfactant ratio = 1:1)

(ii) 0.1714 g $Na_2S_2O_8$ + 0.7094 g SDS (initiator to surfactant ratio = 2:1)

(iii) 1.7571 g $Na_2S_2O_8$ + 0.7094 g SDS (initiator to surfactant ratio = 3:1)

Untreated glass fiber (25 g) was added to 300 ml of each of the above solution mixtures. The mixture was adjusted to pH 4 using 0.1 M HCl, then poured into a Parr reactor which was then closed and sealed. After purging the reactor with nitrogen gas, ethylene gas was introduced into the reactor and the pressure adjusted to 150 psi. For the adsolubilization process, the mixture was stirred at 20 rpm for 24 hours at 25°C. If a pressure drop was observed, the reactor was then repressurized with ethylene gas to keep the pressure at 150 psi before proceeding to the admicellar polymerization step. To start the polymerization reaction, the temperature of the mixture was raised to 70°C and the stirrer speed changed to 60 rpm for a further 24 hours to ensure complete polymerization. The decrease in pressure versus time was recorded at one hour intervals to follow the ethylene consumption during the reaction. When equilibrium was established, i.e. the pressure remained constant, the reactor was cooled down to room temperature. The supernatant liquid was carefully decanted from the reactor and the fibers washed several times with distilled water to remove traces of surfactant and initiator. Lastly, the fibers were dried in a vacuum oven at 80°C overnight.

3.3.3 Surface Morphology of Glass Fibers

Surface morphology of the different kinds of glass fiber samples was characterized using a scanning electron microscope (SEM). Samples were mounted on stubs on the sputtering device and sputter coated with gold for 4 minutes. The surfaces of the coated samples were observed by SEM at an accelerating voltage of 15 kV and magnification X5000.

3.3.4 Gravimetric Analysis (Percentage Weight Loss)

This characterization method is based on the difference in weight of the surface-modified glass fibers before and after burning in a furnace at 500°C for 15 minutes to remove the PE-coated film from the glass fiber surface. The percentage of coating is equal to the percent weight loss which was determined using equation 3.1.

$$\% \text{ Wt. loss} = \frac{\text{Wt. of glass fiber before burning - Wt. of glass fiber after burning}}{\text{Wt. of glass fiber after burning}} \times 100 \qquad (3.1)$$

3.3.5 Polymer Composite Preparation

The mixing of HDPE with the three types of glass fiber, i.e., as-received glass fiber, untreated glass fiber, and admicellar-treated glass fiber, was carried out using a Brabender Plasti-Corder, PL 2100. A rotor speed of 50 rpm and mixing chamber temperature of 150°C was used. The batch composition blends were calculated using equations 3.2 and 3.3.

$$D_{Total} = \frac{M_{Total}}{V_{Total}} \qquad (3.2)$$

where:

D_{Total} = density of the mixed blend

M_{Total} = mass of the mixed blend

$V_{Total} = \{(M_1/D_1) + (M_2/D_2) + (M_3/D_3) +...\}$.

And

$$\text{Batch size (g)} = V_c \times F \times D_{Total} \qquad (3.3)$$

where:

V_c = volume of chamber

F = fill factor of blending system (0.8)

D_{Total} = density of blend.

Table 3.3 Batch composition of each component for glass fiber reinforced HDPE composites.

Glass fiber content (%)	HDPE (g)	Glass fiber (g)
20	40.3	10.1

Sheets of composites, 3 mm thick, were prepared by compression molding at 180°C in a Wabash V 50H compression press. The molding cycle was (a) preheat for 5 minutes (b) compress under a force of 10 tons for a further 3 minutes, and (c) cool under load using cold water and air, until the mold reached 40°C.

3.3.6 Mechanical Properties of HDPE/Glass Fiber Composites

3.3.6.1 Tensile Property Testing

The tensile strength of the glass fiber reinforced HDPE composites were determined using an Instron Universal Testing Machine. Type I dumbbell specimens were cut out using a pnuematic specimen cutter. Tests were carried out according to ASTM D638 using a 100 kN load cell and 50.80 mm/min cross-head speed. Ten specimens were determined for each sample and the results averaged to obtain a mean value.

3.3.6.2 Flexural Property Testing

The flexural strength of the composites were measured using an Instron Universal Testing Machine according to ASTM D 790 in three-point bending method mode. Measurements were carried out using a 5 kN load cell, 11.52 mm/min cross-head speed and a 43.2 mm support span. Eight specimens were tested for each sample and the results averaged to obtain a mean value.

3.3.6.3 Impact Property Testing

Izod impact strength was measured using a Zwick Impact Test instrument with 2.7 joules pendulum according to ASTM D 256 test method. The results were reported by evaluating a mean value from seven specimens.