

Chapter 3

Materials and Experimental Methods

3.1 Raw Materials

Filler used in this study was calcium carbonate powder which was obtained from Lime Quality Co., Ltd. Blow moulding grade high density polyethylene from Bangkok Polyethylene Co., Ltd. was employed as a matrix. The size of calcium carbonate particles were characterized using Melvern Mastersizer S and the particle morphology was examined using scanning electron microscope (JEOL JSM 5410). The specifications of the materials (supplied by the manufacturers) are shown in table 3.1.

Table 3.1 Characteristics of the materials used in this experiment.

<u>Matrix</u> : High Density Polyethylene (Thai Zex-7000F)		<u>Filler</u> : Calcium Carbonate (Omega)	
Density (kg m ⁻³)	0.956	Density (kg m ⁻³)	2.70
Melt flow index (g/10 min)	0.04	Particle shape	roughly spherical
Melting temperature (°C)	130	Particle size (µm)	5.57

3.2 Sample Preparation

3.2.1 Extrusion Procedure

Calcium carbonate was dried in the oven at 110 °C for 1 hour. Then it was premixed with polyethylene pellets by manual shaking in the bag and subsequently fed into the hopper of the co-rotating twin screw extruder (Betol). Composites with 0.00, 0.10, 0.20, 0.30 and 0.40 filler volume fraction were produced. The composite was extruded from the extruder via a three hole die into a water bath at room temperature. The water bath reduced the temperature of extrudate rapidly in order to prevent the oxidation and degradation of the polymer matrix. Extrudated wires were dried as they went through compressed air jets and then pelletised using the Betol pelletiser. Typical barrel was shown in figure 3.1 and the conditions of temperature profiles were shown in table 3.2.



Figure 3.1 Typical barrel of a co-rotating twin screw extruder.

Table 3.2 Conditions of co-rotating twin screw extruder.

Screw diameter (mm)	40
Die diameter (mm)	12
Standard L/D ratio	21:1
Barrel module length	4D
Screw speed (rpm)	2.7
Motor drive (kN)	40
Barrel temperature profile (feed→die) (°C)	270-270-275-285-285-290
Extrudate cooled in water bath at room temperature.	

The composite pellets were then cooled with liquid nitrogen in a flask before being fed into the centrifugal mill (Retsch) which was periodically cooled with liquid nitrogen to produce a powder. The mesh size of the screen in the mill was 0.5 millimeters, as shown in figure 3.2.



Figure 3.2 Centrifugal mill.

3.2.2 Compression Moulding

Sheets of composite were prepared by compression moulding at 220 °C under a pressure of 1500 psi for 5 minutes. The sheets with the dimension of

160×160×4 mm³ were produced. These plagues were cut into strips and then machined in the form of bars and dumbbells. The compression moulding machine was shown in figure 3.3.

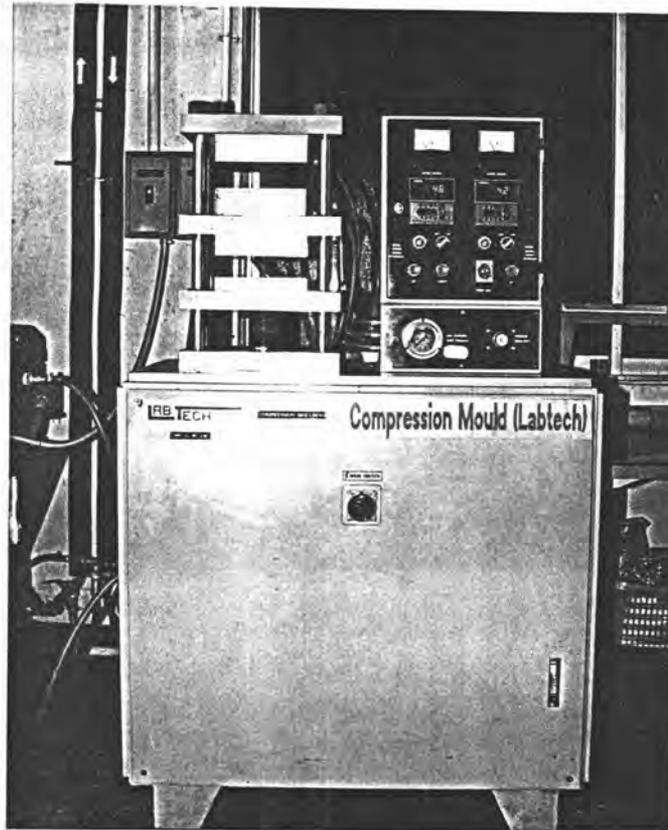


Figure 3.3 Compression moulding machine.

3.3 Dispersion of Filler

The optimal properties of composite cannot be achieved without a satisfactory dispersion of filler in the matrix. The characterization of filler dispersion was carried out by immersing a composite bar in liquid nitrogen and then breaking it immediately in air. The surface of fractured bar was then coated with gold and examined using a scanning electron microscope (JEOL JSM 5410).

3.4 Density Measurement

The density of composites was determined using Archimedean principle in which a solid immersed in a liquid is exposed to the force of buoyancy. The value of this force is the same as that of the weight of the liquid displaced by the volume of the solid. Hydrostatic balance, figure 3.4, was used to weigh a solid in air and in water. The density of the specimens was calculated from the following equation:

$$\text{Density} = \left(\frac{W_1}{W_1 - W_2} \right) \rho_0 \quad (3.1)$$

where:

W_1 = weight of a specimen in air

W_2 = weight of a specimen in water

ρ_0 = density of water at experimental temperature

3.4.1 Measuring Procedure

1. Determining the weight of a sample in air.

-Tare the balance.

-Place the sample on the upper pan on the frame and weigh.

-Record the weight as W_1 .

2. Determining the weight of a sample in water.

-Tare the balance.

-Place the sample in the sample holder.

-Record the weight as W_2 .

3. Calculating the density.

-Read off the temperature of the liquid.

-Using the table as shown in table 3.3, find the density ρ_0 which corresponds to the temperature measured for the water.

-Calculate the density by eq. 3.1

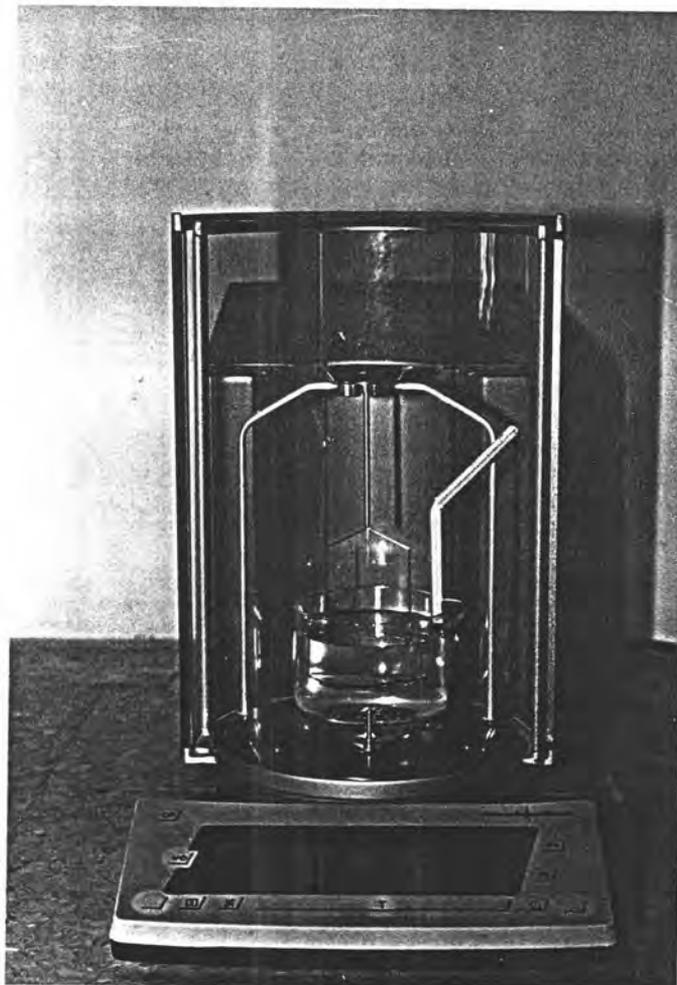


Figure 3.4 Density determination kit.

Table 3.3 Density of H₂O at Temperature (in °C).Density of H₂O at Temperature T (in °C)

T/°C	0.0	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
10.	0.99973	0.99972	0.99971	0.99970	0.99969	0.99968	0.99967	0.99966	0.99965	0.99964
11.	0.99963	0.99962	0.99961	0.99960	0.99959	0.99958	0.99957	0.99956	0.99955	0.99954
12.	0.99953	0.99951	0.99950	0.99949	0.99948	0.99947	0.99946	0.99944	0.99943	0.99942
13.	0.99941	0.99939	0.99938	0.99937	0.99935	0.99934	0.99933	0.99931	0.99930	0.99929
14.	0.99927	0.99926	0.99924	0.99923	0.99922	0.99920	0.99919	0.99917	0.99916	0.99914
15.	0.99913	0.99911	0.99910	0.99908	0.99907	0.99905	0.99904	0.99902	0.99900	0.99899
16.	0.99897	0.99896	0.99894	0.99892	0.99891	0.99889	0.99887	0.99885	0.99884	0.99882
17.	0.99880	0.99879	0.99877	0.99875	0.99873	0.99871	0.99870	0.99868	0.99866	0.99864
18.	0.99862	0.99860	0.99859	0.99857	0.99855	0.99853	0.99851	0.99849	0.99847	0.99845
19.	0.99843	0.99841	0.99839	0.99837	0.99835	0.99833	0.99831	0.99829	0.99827	0.99825
20.	0.99823	0.99821	0.99819	0.99817	0.99815	0.99813	0.99811	0.99808	0.99806	0.99804
21.	0.99802	0.99800	0.99798	0.99795	0.99793	0.99791	0.99789	0.99786	0.99784	0.99782
22.	0.99780	0.99777	0.99775	0.99773	0.99771	0.99768	0.99766	0.99764	0.99761	0.99759
23.	0.99756	0.99754	0.99752	0.99749	0.99747	0.99744	0.99742	0.99740	0.99737	0.99735
24.	0.99732	0.99730	0.99727	0.99725	0.99722	0.99720	0.99717	0.99715	0.99712	0.99710
25.	0.99707	0.99704	0.99702	0.99699	0.99697	0.99694	0.99691	0.99689	0.99686	0.99684
26.	0.99681	0.99678	0.99676	0.99673	0.99670	0.99668	0.99665	0.99662	0.99659	0.99657
27.	0.99654	0.99651	0.99648	0.99646	0.99643	0.99640	0.99637	0.99634	0.99632	0.99629
28.	0.99626	0.99623	0.99620	0.99617	0.99614	0.99612	0.99609	0.99606	0.99603	0.99600
29.	0.99597	0.99594	0.99591	0.99588	0.99585	0.99582	0.99579	0.99576	0.99573	0.99570
30.	0.99567	0.99564	0.99561	0.99558	0.99555	0.99552	0.99549	0.99546	0.99543	0.99540

3.5 Mechanical Testing Method

3.5.1 Tensile Testing

One of the most informative mechanical experiments for any materials is the determination of stress-strain curve in tension mode. This is widely used to provide basic design information on the strength of materials and a guide to how a polymer will behave in a finished product. A tensile test involves pulling or stretching a test specimen and measuring the corresponding load applied. Normally, the load and

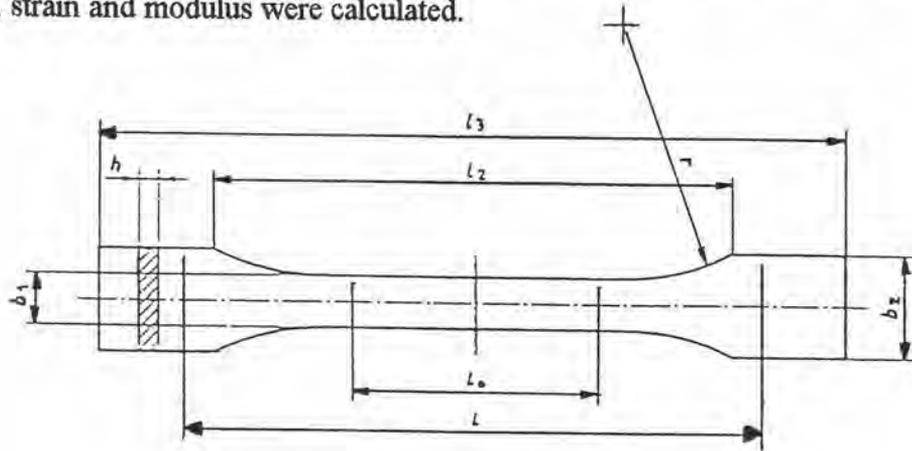
the corresponding extension is plotted out during the test. Metals generally show simple relationships, between stress and strain. So if a graph is plotted of stress versus strain, a straight line is obtained.

On the other hand, plastic does not show this simple linear stress-strain relationship, it will produce a curved line. Moreover, polymer's properties are time dependent because of the viscoelastic nature so the shape of the observed curve will also depend on the strain rate and temperature. In order to compare the result of each sample, testing should be done at the same condition. The generalized stress-strain curve for plastic serves to define many useful quantities, including modulus or stiffness (the slope of the curve), yield stress, strength and elongation at break.

The tensile specimens were machined from compression-moulded sheets, in accordance with ISO 527 as shown in figure 3.5. The machined surface was smoothed using a fine abrasive paper.

Tensile test was performed on an Universal Testing Machine (Instron, model 5583), using 5 kN load cell, at a crosshead speed of $5.0 \text{ mm}\cdot\text{min}^{-1}$ (figure 3.6). In order to determine Young's modulus of test specimen, an extensometer ($l_0=25 \text{ mm}$) was used. On the other hand, in the case of strength at break measurement, an Instron extensometer was removed. Testing was performed at room temperature. The system used was controlled via a computerized control console which incorporated a series IX automated materials testing system. The specimens were mounted between the face of grips, they were held firmly to

minimized slippage without crushing the ends. During this test, the test specimen is extended along its major longitudinal axis at constant speed until the specimen fractures. The mean value of five measurements was taken. Finally, the values of stress, strain and modulus were calculated.



Symbol	Description	Dimensions in millimetres
l_3	Overall length	75
r	Radius	60
l_2	Distance between broad parallel-sided portions	57
b_2	Width of ends	10
b_1	Width of narrow portion	5 ± 0.5
h	Thickness	4
L_0	Gauge length	25
L	Initial distance between grips	60

Figure 3.5 Dimensions of tensile test specimen.

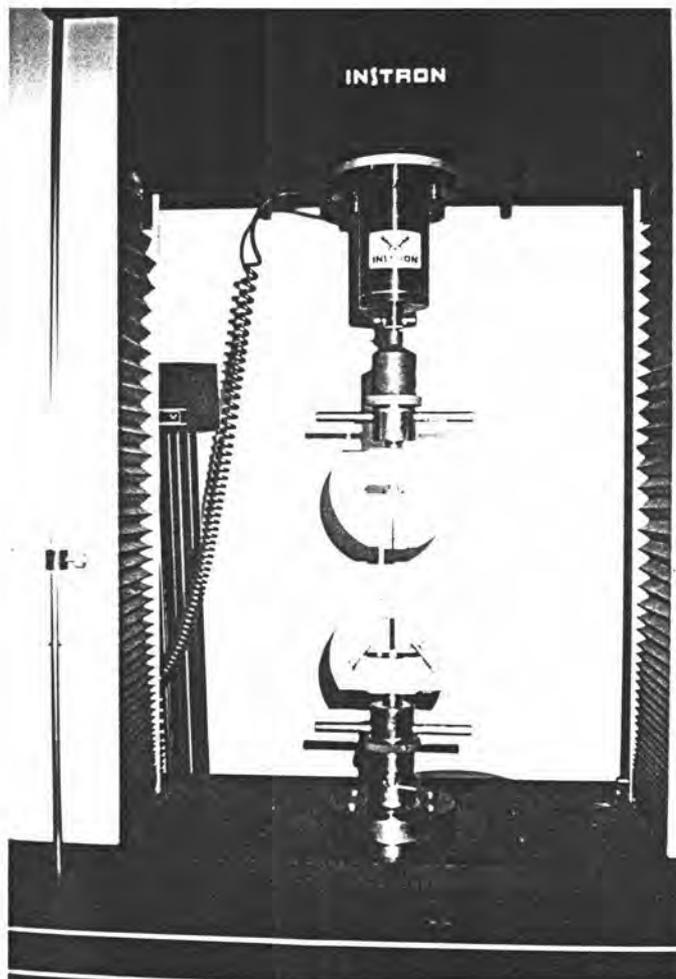


Figure 3.6 Experimental arrangement for tensile test.

3.5.2 Flexural Testing

Flexural testing is performed on an Universal Testing Machine, the same type of machine as used for tensile testing. The test consists of bending a relatively long and flat specimen of rectangular cross-section. The results from the test can give a good indication of rigidity or stiffness of the material, technically known as

the material's flexural modulus. The flexural strength and flexural strain at yield can be also reported.

Flexural tests can be performed using 3-point bending or 4-point bending modes as shown in figure 3.7. With 3-point bending, the maximum stress occur in the specimen where the centre support is. In a 4-point bending test the stress is spread over the region between the two centre supports (load span). Nevertheless, 3-point bending tests are the most common type of flexural tests performed. Considering the stresses present in a test specimen during a 3-point flexural test, there will be a tensile stress on the outer surface and a compressive stress on the inner surface.

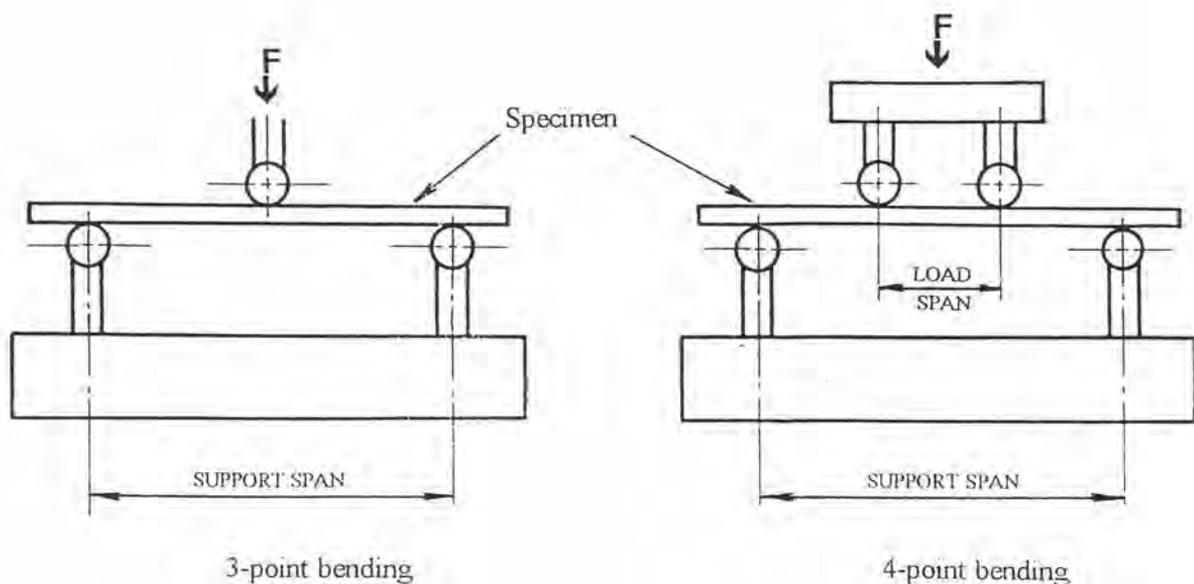
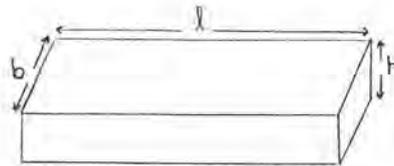


Figure 3.7 The 3-point and 4-point fixture configuration.

The test specimens were cut from compression-moulded sheets into strips with the dimensions in accordance with ISO 178 as shown in figure 3.8. The cross-section was rectangular, with no rounded, and the machined surface was smoothed by using a fine abrasive paper.



length : $l = 80 \text{ mm}$

width : $b = 10.0 \text{ mm}$

thickness : $h = 4.0 \text{ mm}$

Figure 3.8 Dimensions of flexural test specimen.

Flexural test was carried out at room temperature using Universal Testing Machine (Instron , model 5583), according to ISO 178, using 150 kN load cell and a crosshead speed of $5.0 \text{ mm} \cdot \text{min}^{-1}$ (figure 3.9). In the test, the specimen was symmetrically placed on two supports and the force was applied at midspan. The span for a 3-point flexural test was 64 millimeters. The test specimen is deflected at constant rate at the midspan until the specimen fractures or until the deformation reaches predetermined values. The force applied to the specimen and the corresponding deflection of the specimen were recorded. The mean value of five

measurements was taken. The modulus, strength, and strain at yield point or end of test were calculated.

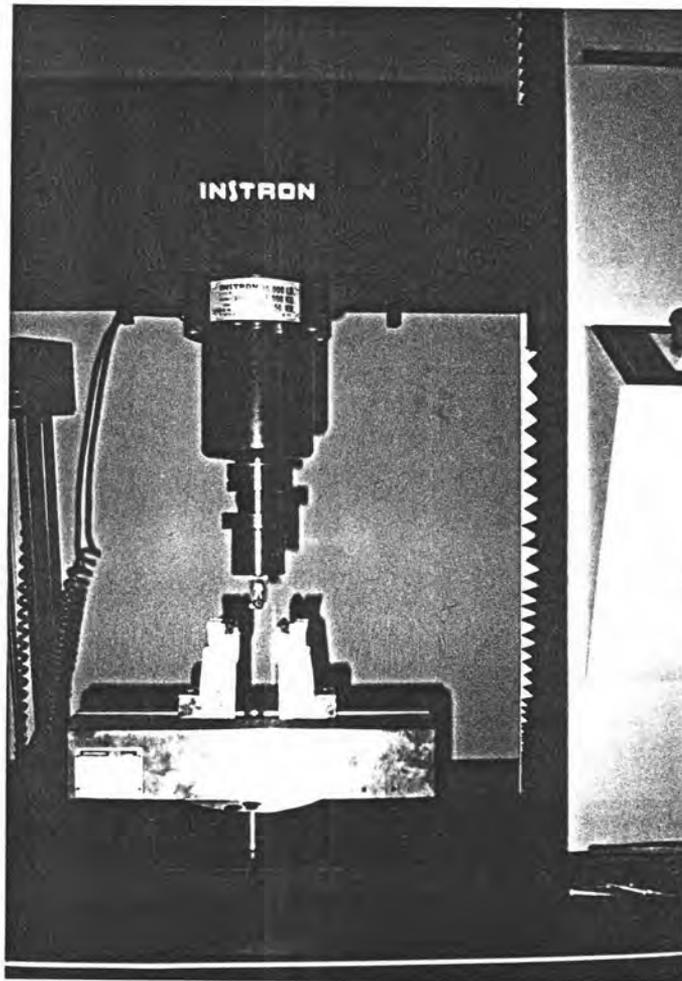
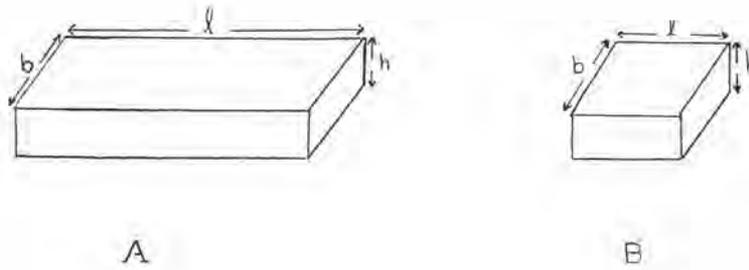


Figure 3.9 Experimental arrangement for a flexural test.

3.5.3 Compressive Testing

Although the compression test ranks low on the list of routine acceptance tests for engineering materials, it can be used to obtain data on the deformation of materials not readily yielded by tensile tests. It can be employed for studying of the stress-strain behavior of materials which, under tension, behave in a brittle manner because of the rapid crack growth may exhibit appreciable ductility in compression. In contrast to tensile mode, the cross-sectional area is increased with increasing strain. The negative sign of stress and strain in the test, however, is generally omitted.

The test specimens were cut from compression-moulded sheets in accordance with the requirements of the ISO 604 as shown in figure 3.10. All surfaces of the test specimens were free from visible flaws, scratches and other imperfections that are likely to influence the results.



Dimensions in millimetres

Type	Measurement	Length , l	Width , b	Thickness , h
A	Modulus	50	10	4
B	Strength	10	10	4

Figure 3.10 Dimensions of compressive specimen.

The compressive test was performed at room temperature using an Universal Testing Machine (Instron , model 5583) which consisted of hardened steel compression anvils, for applying the deformation to the test specimen (figure 3.11), 150 kN load cell was used and a crosshead speed is $5.0 \text{ mm}\cdot\text{min}^{-1}$ for both modulus measurement and strength measurement. In the test, the specimen was placed between the surfaces of the compression plates and align the centreline of the compression plate surfaces. The end surfaces of the specimen are parallel to the surfaces of the compression plates and adjust the machine so that the surfaces of the ends of the test specimen and compression plate are just touching. The mean

value of five measurements was taken. At the end of test, the values of stress, strain and modulus at yield point were determined.

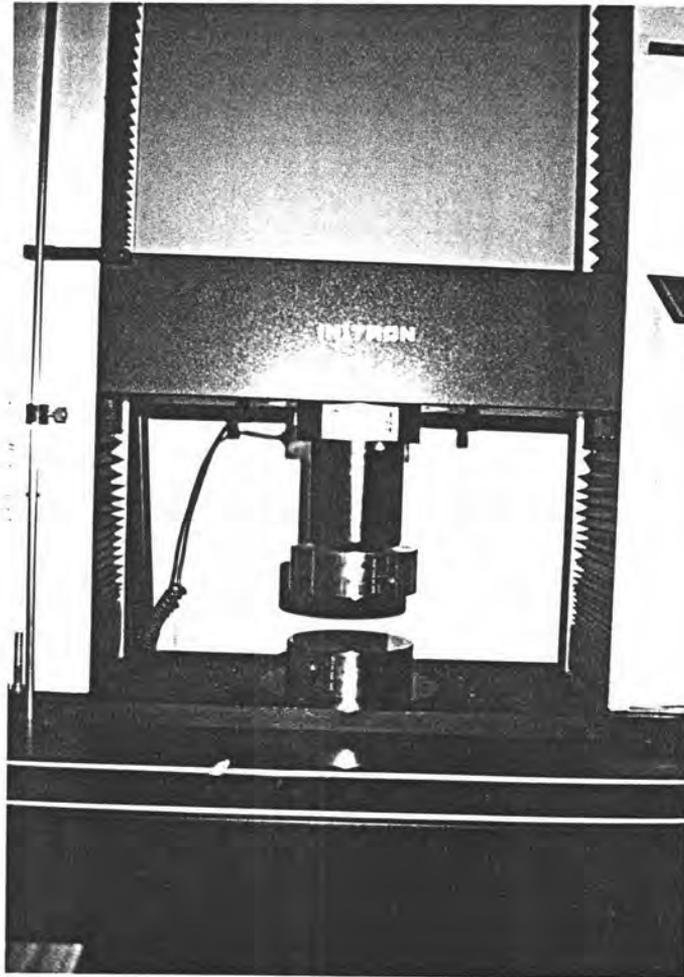


Figure 3.11 Compression testing configuration.

3.6 Annealing Treatment

Annealing implies heating a solid to temperatures approaching its melting point. Annealing of the polymer activates the internal mobility and promotes greater stability by eliminating the stresses and defects in a general movement towards the thermodynamic equilibrium condition. This will influence on the properties of polymer such as mechanical and thermal properties.

Annealing was carried out by placing composite sheets in the window frame sandwiched by two plates. The assembly was then put into the oven at specified annealing temperature for a specified period of time. The assembly was cooled slowly by switching off the oven and leaving it to cool down for 24 hours.

3.7 Differential Scanning Calorimetry (DSC)

Thermal behavior of the specimens was investigated by Differential Scanning Calorimeter (Perkin-Elmer DSC 7). Approximately 9 mg of each sample was put in an aluminium pan and heated from room temperature to 200 °C at the heating rate of 20 °C·min⁻¹. Data were collected continuously and analysed by the DSC analysis programme.

3.8 Thermogravimetric analysis (TGA)

Determination of filler content in composite is necessary to ensure that the composites have a satisfactory ratio. This was achieved by using thermogravimetric analyser (Perkin-Elmer TGA 7). Approximately 2 mg of sample was heated from room temperature, at a heating rate of $20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, up to a temperature of $600\text{ }^{\circ}\text{C}$ in a nitrogen atmosphere. Data were recorded continuously and analysed by TGA analysis programme.

3.9 Raman Spectroscopy

After the extrusion and compression moulding process, the polymer matrix is likely to be oxidized or degraded because of heat. That results in the detrimentally effect on the mechanical properties of the composites. Therefore, the Raman spectroscopic technique used to examine whether oxidation of polymer matrix occurs by determining the carbonyl group. Raman spectra were recorded on a Perkin-Elmer System 2000 from 200 to 3600 cm^{-1} at a resolution of 4 cm^{-1} .