Chapter 3

Materials and Methods

Materials

A range of particulate composites were prepared by mixing blow molding grade high density polyethylene powders from BP Chemical Ltd. with calcium hydroxyapatite from calcined bone ash from Podmore and Sons Ltd. In addition some fillers consisted of synthetic hydroxyapatite from British Charcoal and Macdonalds Ltd. for assessment in comparison. The details of the materials are shown in Table 3.1.1 and Table 3.1.2 shows the various types of materials tested.

Table 3.1.1 Materials used in the experiment.

Matrix Phase : High Density Polyethylene (BP Chemical Ltd. ; Rigidex H060-45P)	
Density (Kg m^{-3}) [a]	945
Melt index (g/10 min) [a,b]	6.0
Molecular weight ($\overline{M_w}$) [c]	412000
Molecular weight distribution($\overline{M_w}/\overline{M_n}$) [c]	13.3

Particulate Filler : Calcined Bone Ash (Podmore and Sons Ltd. ; P3305)	
Density (Kg m^{-3}) [d]	3160
Atomic calcium : phosphorus ratio [e]	1.67
Particle shape [f]	Approximately spherical
Particle size [g]	95 % less than 30 μ m
: Synthetic Hydroxyapatite (British Charcoal and Macdonalds Ltd.)	
Theoretical density(Kg m^{-3})	3156
Median particle size(μm) [h]	2.16-3.07
Surface area(m^2 g^{-1}) [h]	11-18
Particle shape [f]	Approximately spherical

[a] BP Chemicals Ltd. published data. [b] 190 °C, 21.6 kg load.

[c] By GPC at RAPRA, Polymer Supply and Characterization center.

[d] True powder density determined using a helium displacement pycnometer by Coulter Electronics Ltd.

[e] By X-ray spectrometry at British Ceramic Research Association.

[f] By scanning electron microscopy.

[g] By sedigraph particle size analyzer at British Ceramic Research Association.

[h] British Charcoal and Macdonalds published data.

Table 3.1.2 Types of composite materials tested

Type of filler	Method	Volume fraction of filler
Calcined Bone Ash	Injection moulded	0.10,0.20,0.25,0.30,0.35, 0.40,0.45,0.50
Synthetic Hydroxyapatite	Injection moulded	0.10,0.20,0.35,0.40,0.50

Processing Methods

The two components were compounded with Betol co-rotating twin screw extruder model BTS40 to make a series of composites with various volume fraction. The typical barrel was shown in Fig.3.2.1 and also the conditions of temperature profiles were shown in Table 3.2.1.

The composite was extruded through an 3 mm round die and quickly cooled in water bath and then cut into pellets about 5 mm lengths. Then, the pellets were frozen in liquid nitrogen before being fed into the grinding mill to produce a powder.

Table 3.2.1 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
Feed rate (kg/hr)	2.7
Screw speed (rpm)	40
Motor drive (kW)	7.8
Barrel temperature profile (feed→die)(°C)	270-270-275-285-285-285-290
Extrudate cooled in water bath at room temperature.	
Material residence time on barrel (min.)	≈ 2

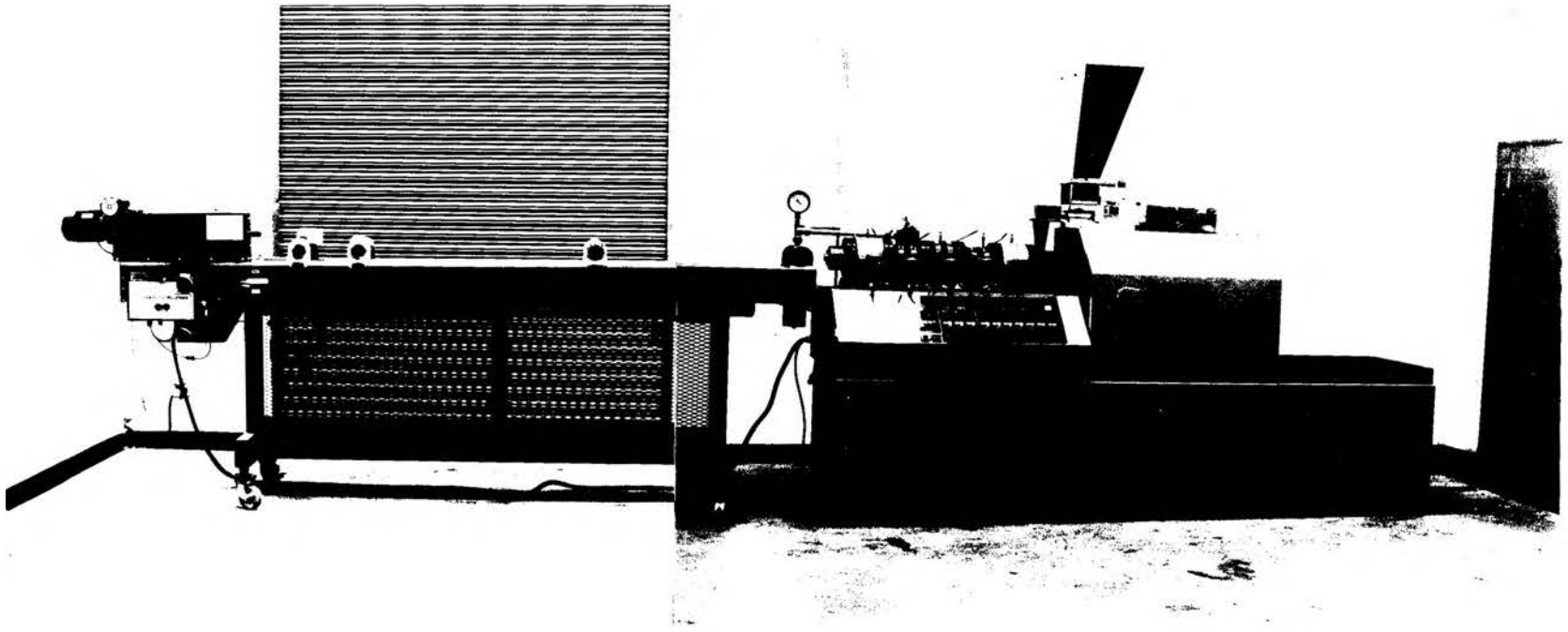
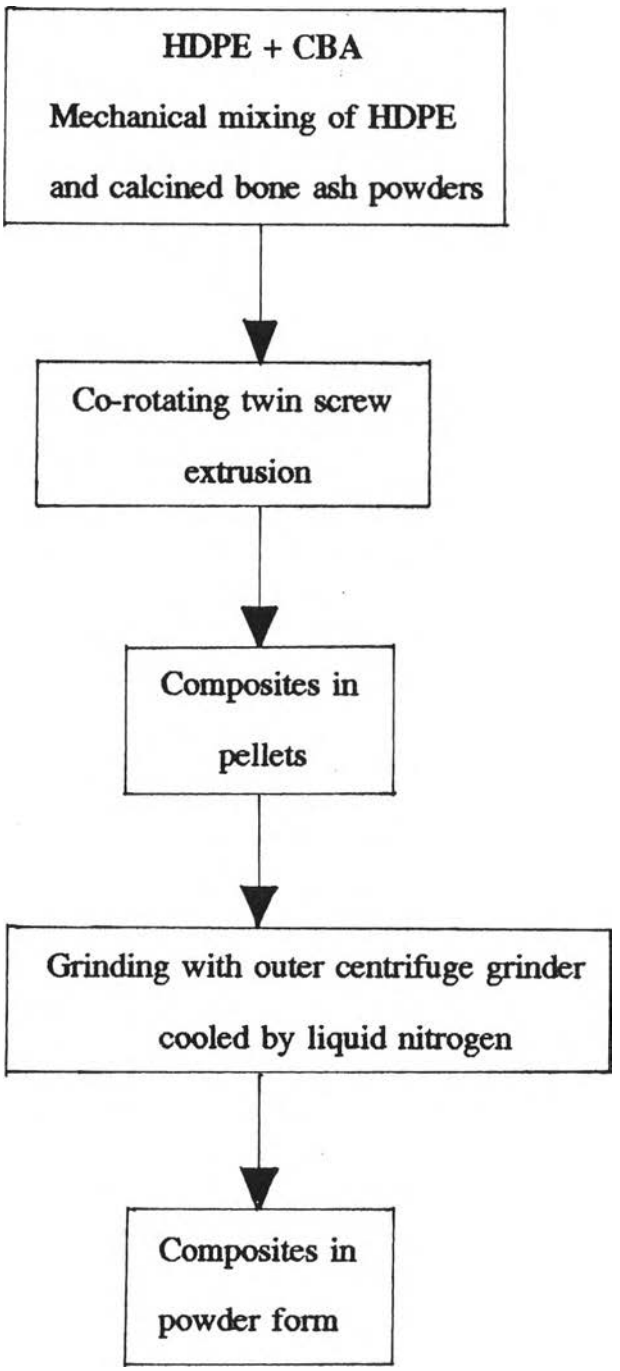


Figure 3.2.1 Typical barrel configuration of Betol co-rotating twin screw extruder model BTS40.

Figure 3.2.2 Processing of calcined bone ash reinforced high density polyethylene composites



Finally, the pulverized composite powders were injection molded with a one gate mold as shown in Fig.3.2.3 and the dimensions of plaques were 120x50x3 mm^3. These plaques were cut into three strips and machined on a template replication machine to the international standard ISO/DIS 6239/1 for tensile tests.

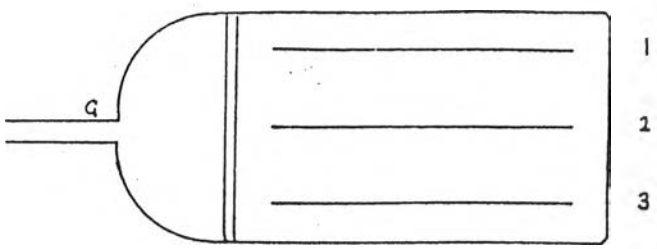


Figure 3.2.3 A diagram to show injection moulded plaques. G indicates the positions of the gates. The numbers represent the positions of the specimens.

Mechanical Testing Methods

1. Tensile testing

The engineering tension test is widely used to provide basic design information on the strength of materials and as an acceptance test for the specification of materials. Obtaining the information required is by means of a tensile test and the tensile stress-strain relationship.

Studies of a materials behaviour made by Robert Hooke in 1678 showed that the relationship between force and distance is linear. When the load is removed, the interatomic forces take the atoms back to their original

equilibrium positions. This behaviour is known as Hooke's law. In other words extension and force are directly and simply proportional to each other.

Metals generally obey a linear load deformation law up to their elastic limit. However, non-metallic materials, such as plastics and rubber, exhibit a non linear load deformation relationship, showing an interdependence of stress and strain with time. The phenomenon of cold drawing can occur in some thermoplastic materials. These drawn materials are much stronger than the original undrawn plastic material due to the alignment of polymer molecules which occurs during drawing.

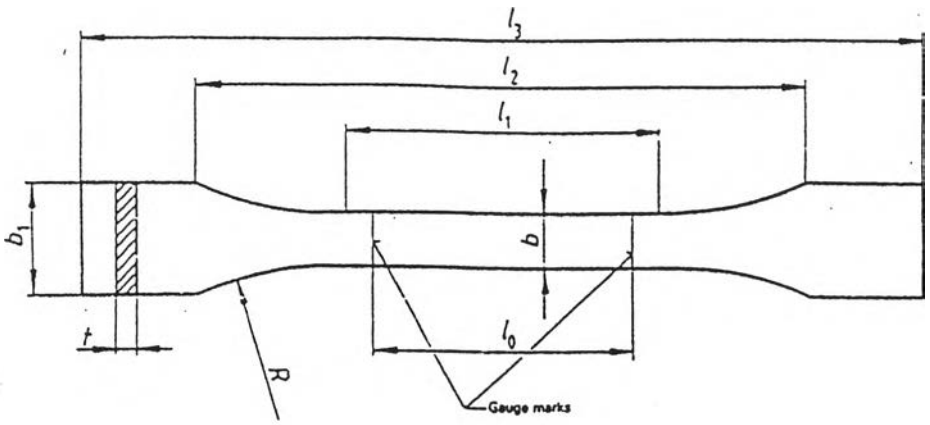
In this section the Young's modulus, tensile strength, strain to failure, energy to failure and toughness is considered.

1.1 Preparation of specimen

The composite materials were cut into strips and machined on a template replication machine to ISO/DIS 6239/1 for tensile tests as shown in Fig.3.3.1.

1.2 Testing procedure

The tensile specimens were tested on an Instron universal testing machine, model 5583, using 5 kN load cell, at crosshead speed of 0.5 and 1.0 mm min^{-1}, to failure (Fig.3.3.2). The system used was controlled via a computerized control console which incorporated a series IX automated materials testing system. Tests were carried out at room temperature (25



Dimensions in millimetres

Symbol	Description	Test specimens	
		B_1 (1 : 2)	B_2 (1 : 5)
l_3	Minimum overall length	75	30
b_1	Width at ends	10 ± 0,5	4 ± 0,2
l_1	Length of narrow parallel portion	30 ± 0,5	12 ± 0,5
b	Width of narrow parallel portion	5 ± 0,2	2 ± 0,2
R	Minimum radius	30	12
l_0	Distance between gauge marks	25 ± 0,5	10 ± 0,2
l_2	Initial distance between grips	58 ± 2	23 ± 2
t	Minimum thickness	2 ± 1	2 ± 1

Figure 3.3.1 A diagram of the ISO/DIS 6239/1 tensile test specimen.

±2°C) and 50% relative humidity. The specimens were mounted between the faces of grips, insuring that they were held firmly to minimize slippage without crushing the ends (Fig.3.3.3). Strain was measured with the use of balanced elastomeric extensometer (Instron Limited Model 2603-070). Tests were stopped at fracture, and values of stress, strain and energy at the yield point and end of test were calculated according to the ASTM D-638 procedure.

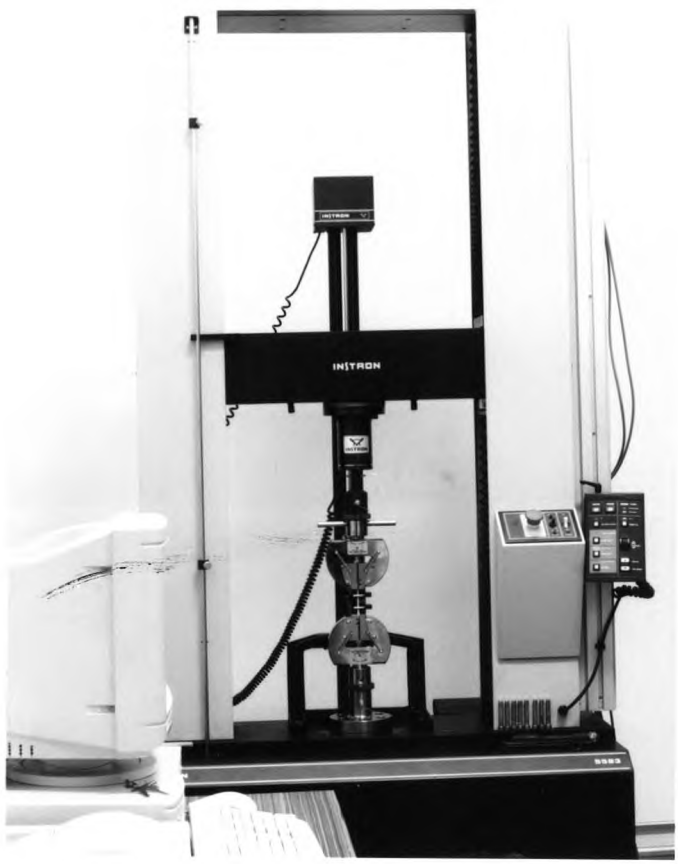


Figure 3.3.2 Instron universal testing machine.

1.3 Effects of strain rate on tensile properties

Viscoelasticity is the term used to describe the behaviour of a material which combines the characteristics of a various liquid and an elastic solid. The model which may represent a Hookean solid is a spring for which stress is linearly related to strain. The rate at which stress is applied to a specimen can have an important influence on the flow stress.

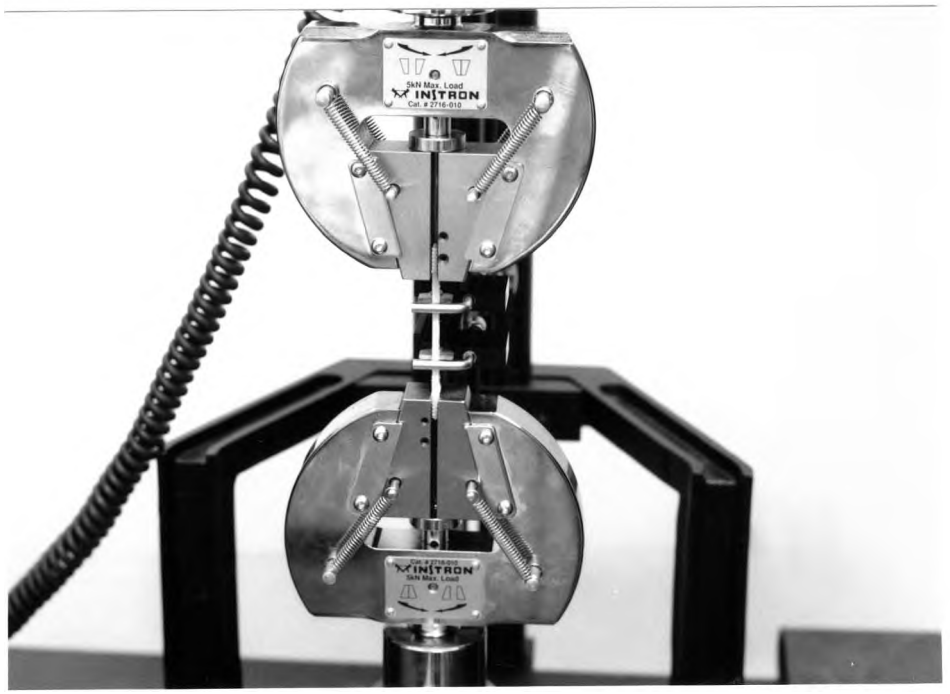


Figure 3.3.3 Test-piece held in the grips.

Strain rate is defined as $\xi = \frac{d\varepsilon}{dt}$ and is conventionally expressed in units of "per second".

Nadai (1950) presented a mathematical analysis of the conditions existing during the extension of a cylindrical specimen with one end fixed and the other attached to a moveable crosshead of a testing machine. The crosshead velocity (V) was expressed as

$$V = \frac{dL}{dt} \qquad (3.3.1)$$

The strain rate was expressed in terms of conventional linear strain is

$$\xi = \frac{d\varepsilon}{dt} = \frac{d(L - L_o)/L_o}{dt} = \frac{1dL}{L_o dt} = \frac{V}{L_o} \qquad (3.3.2)$$

where L is the extended length and L_o is the original length.

Thus, the conventional strain rate is proportional to the crosshead speed. In a modern testing machine in which the crosshead speed can be set accurately and controlled, it is a simple matter to carry out tension tests at constant conventional strain rate. The effect of crosshead speed on tensile properties for calcined bone ash reinforced polyethylene composite were investigated at crosshead speeds of 0.5 and 1.0 mm min^{-1}.

2. Flexural testing

The flexural test is easily performed with a minimum of complex test apparatus, so it is a favorite mechanical test in the development of new materials in the research laboratory. It employs a specimen beam of rectangular cross section resting on two supports near its ends. The load is applied by means of a loading nose midway between the supports (Fig. 3.3.4).

Stresses developed in beams subjected to bending loads are derived from the basic formula :

$$S = Mc/I \qquad (3.3.3)$$

where S is the maximum stress, M is the maximum bending moment, c is the distance from the beam's neutral axis, and I is the moment of inertia of the beam's cross section about its neutral axis.

Stress formulas derived from eq. (3.3.3) will differ according to the nature of the beam's cross section (e.g., rectangular or round) and the manner in which the beam is loaded. Both eq. (3.3.3) and those to be cited subsequently in connection with the flexural testing of plastics are based upon the elastic theory, which, in turn, imposes certain restrictions and assumptions relative to the behaviour of the sample undergoing bending (Loveless, 1966).

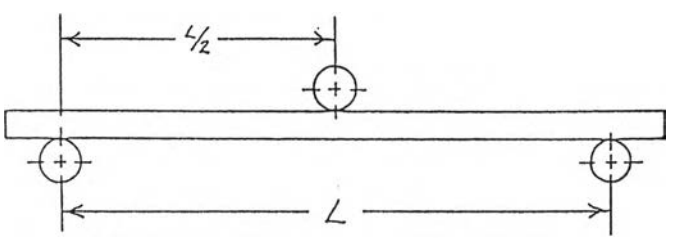


Figure 3.3.4 The three-point fixture configuration.

2.1 Flexural strength

In this case, the maximum bending moment occurs at midspan, and if we denote the load and test span by P and L, respectively, it follows that M will have the value $PL/4$. Assuming the beam to be of rectangular cross section, I then becomes $bd^3/12$, where b and d denote the width and depth of the beam, respectively. Expressed in terms of the beam's thickness, d, $c = d/2$. By direct substitution of these values in eq. (3.3.3), it then follow that:

$$S = 3PL/2bd^2 \qquad (3.3.4)$$

Equation (3.3.4) is normally used to provide an estimate of the maximum stress at midspan when the beam is stressed by some load, *P*. When the beam is loaded to rupture, the maximum stress is based on the breaking load. The stress so calculated is known as the flexural strength, or modulus of rupture, of the material. The flexural test is generally applicable to rigid and semirigid materials.

However, some plastics cannot be broken in flexure, and, hence, do not exhibit the property flexural strength. Such materials may reflect a "yield point" within the imposed 5% strain limitation. In this cases, the flexural yield strength may be calculated in accordance with eq. (3.3.4) by letting *P* equal the load at yield. Beyond 5% strain, this test is not applicable, and some other property such as tensile strength should be used to characterize the material.

2.2 Testing procedure

Standard three-point bending (ASTM D-790) was used in this experiment. The specimens were cut into rectangular bars (3x4x45 mm^3), using a saw-tooth-edge solid carbide circular saw blade. The span used was 40 mm. The loading nose and supports had cylindrical surface having diameter 10 mm as shown in Fig.3.3.5.

Five specimens were prepared at each volume fraction of filler and tested on an Instron universal testing machine, model 5583, at a

crosshead speed of 5 mm min^{-1}. The specimen is deflected until rupture occurs, or until the maximum strain of 5% is reached, whichever occurs first.

Stress-strain curves are used to determine such properties as flexural yield strength, secant or tangent modulus of elasticity, and the total work or energy expanded on the specimen during the test, as measured by the area under the curve. If the specimen does not break within the specified maximum strain, flexural strength cannot be determined by this method.

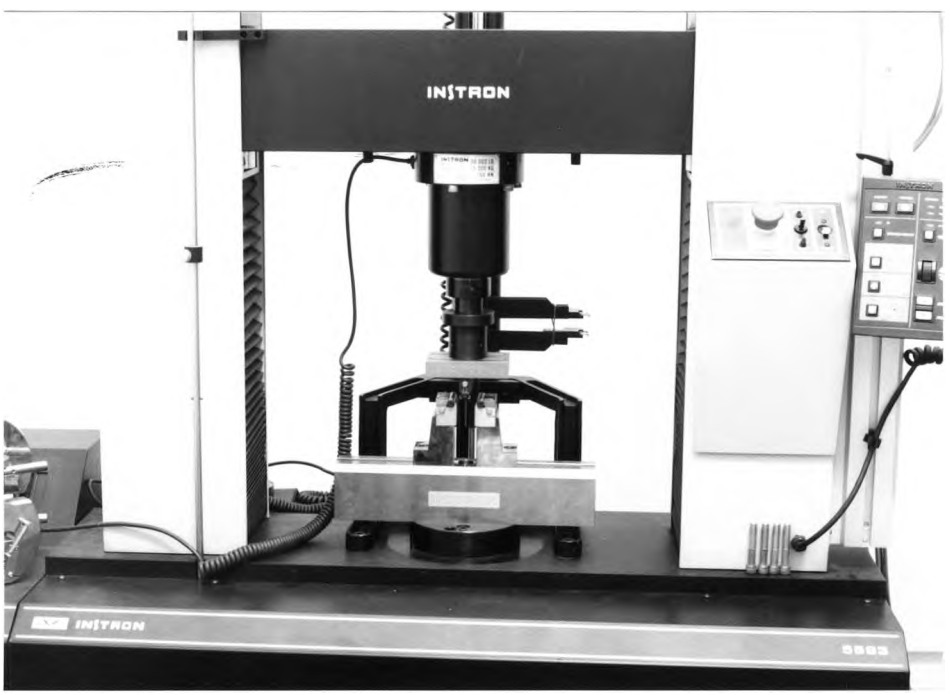


Figure 3.3.5 Experimental arrangement for a flexural test.

3. Hardness

Hardness of a material is generally defined as its resistance to penetration by an indenter of which the property is not a fundamental one. The Hardness tests by indentation have the advantage of being simple, cheap, reproducible, and relatively nondestructive (Lysaght and DeBellis, 1969). However, there is a great deal of theoretical and experimental work showing that, if a material is capable of undergoing plastic flow, then hardness is related quite closely to yield stress.

Microhardness is determined by measuring the size of the impression made by a diamond indenter which is pressed into a surface with a small known load. It has been shown previously that microhardness provides a means of quantifying the physical effects of small scale spatial variation in the composition of bone. Thus, this technique is used in the experiment for composite which was similar to bone.

The specimens were polished hand sanded and hand polished using aluminum oxide suspension. All specimens were tested on a Zwick Hardness Tester, model 3212, using a 50 g indenting load for 10 seconds (Fig.3.3.6). Each specimen was indented 10 times, the diagonals of pyramid shaped diamond indenter were measured through optical microscope at 200 x magnification and the Vicker Hardness Number (*VHN*) was calculated using the equation:

$$VHN = \frac{1854.4xP}{d^2} \qquad (3.3.5)$$

where:

P = Indenting load in grams.

d = Mean of the two measured diamonds in microns.

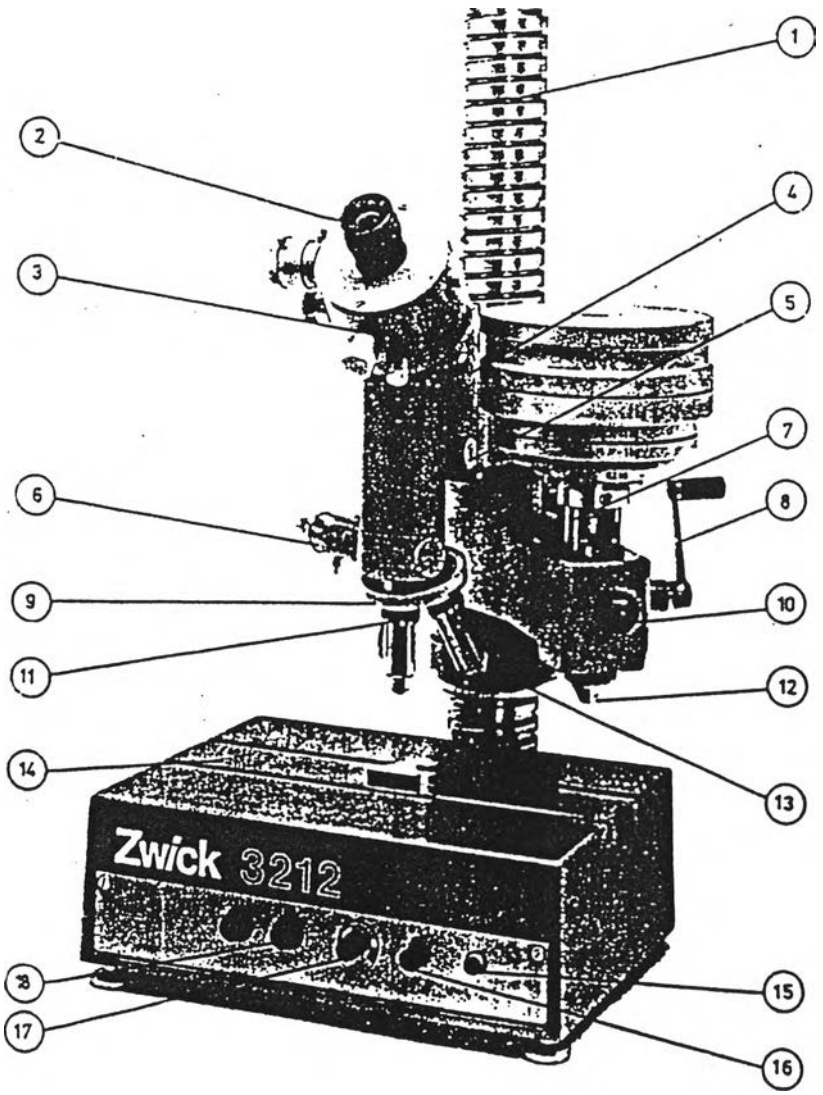


Figure 3.3.6 Zwick hardness tester.

Density Measurements

The density of composite materials was determined using density-gradient technique, showing an equipment in Fig.3.4.1. Suitable pairs of liquids that can be mixed together and filled the gradient tube, starting with the heaviest, by a siphon or pipet. The floats are then carefully dipped in the column until the least dense and most dense floats span the required range of the gradient tube. After 24 hours, the densities of the floats should be plotted graphically against their heights to observe whether or not a continuous and nearly linear curve is obtained. If an irregular curve is obtained, the solution shall be discarded and a new gradient prepared. The specimens are wetted with the less dense liquid and dipped in the liquid column. Allow the tube and specimens to reach equilibrium, which will require to 10 min or more. After equilibrium is attained, read the height of the floats and specimens by using a line through their center of volume. The density of the specimens is calculated from the following equation :

$$\text{density at } x = a + \left[\frac{(x-y)(b-a)}{z-y} \right] \qquad (3.4.1)$$

where :

a and b = densities of the two standard floats,

y and z = distances of the two standard, a and b, respectively, bracketing the unknown measured from an arbitrary level, and

x = distance of unknown above the same arbitrary level.

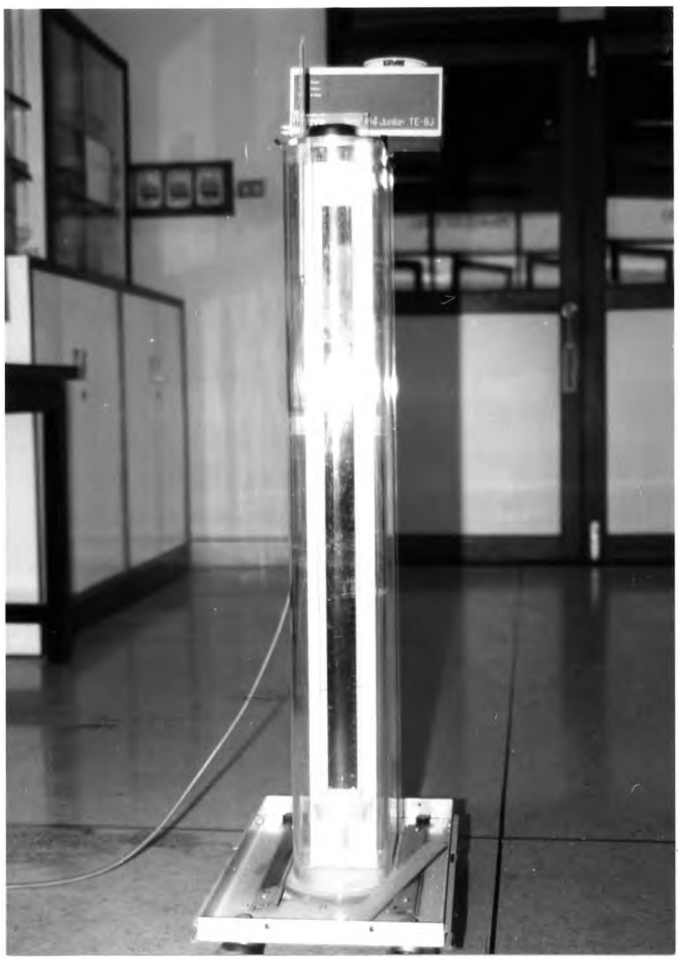


Figure 3.4.1 The density-gradient column used in the experiment.

Dispersion of Filler

The optimal useful properties of composite cannot be achieved without a satisfactory dispersion of the filler in the matrix. First, the specimens were examined at low magnification in order to determine the presence of large scale defects, ensuring that samples for further microscopic evaluation were representative of the bulk material.

Finally, a JEOL JSM-T220A scanning electron microscope (SEM) at Scientific and Technological Research Equipment Centre, Chulalongkorn University (STREC) may be applied to examine the surface of specimens after etching in xylene at 85°C for 15 min (Švehlová, 1986). It gave enhanced contrast between the matrix and the filler.

Fractography

Fractography is the study of fracture surfaces, being a subdivision of failure analysis. The purpose of fractography is to reveal the mode of failure, and when this information is combined with other data, it can identifies the cause of failure. It relies upon visual interpretation of a fracture surface, with examinations beginning at the macroscopic level and proceeding to the microscopic level. The SEM was used for analyzing the fracture surface obtained from the tensile and the flexural tests. Specimens were coated with gold under vacuum to make the surface conductive.