



Chapter 3

Experiment

Experimental Discription

The experiment was concerned with the application of two different HAPs that MP had lower thermal expansion coefficient than TP after sintering and the TP material showed superior mechanical strength to the MP material (Kochawattana,1993). An appropriate combination of both must be therefore used in search of a good material for either a body or a coating.

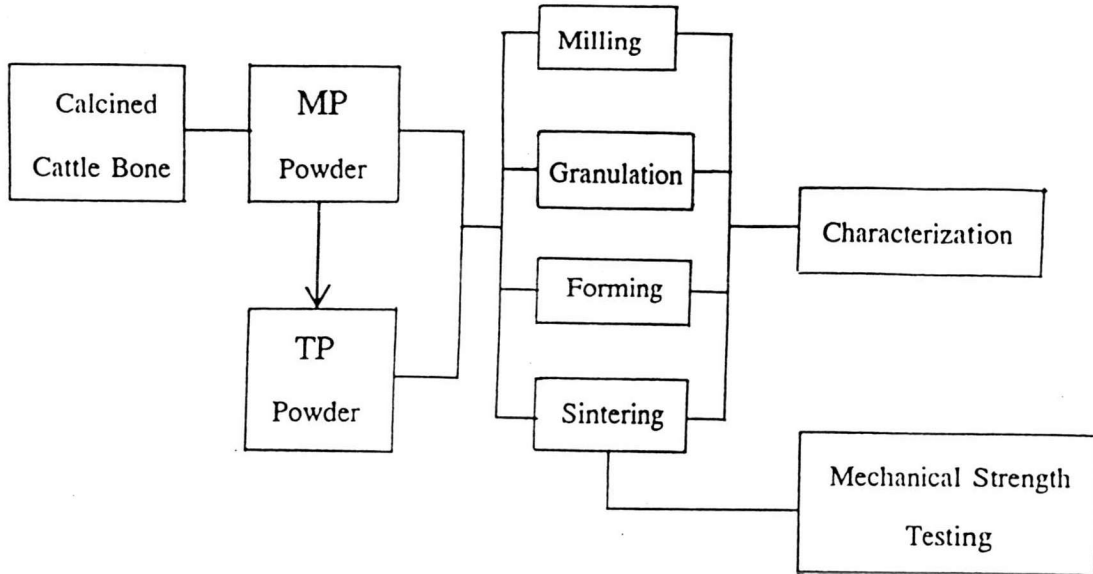
The experimental procedure consists of three sections as follows:

1. HAP preperation and process.
2. HAP mixtures preperation and process.
3. Strengthening of HAP by coating

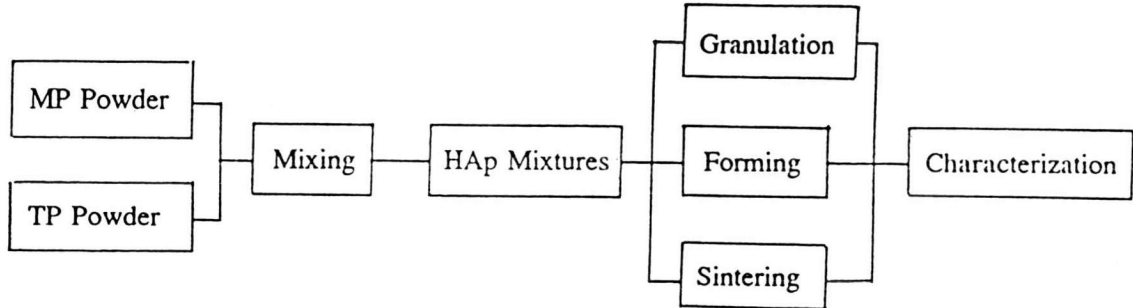
Each section was described stepwise in the following flow chart in

Fig.3.1.

HAp Preperation and Process



HAp Mixtures Preperation and Process



Strengthening of HAp by Coating

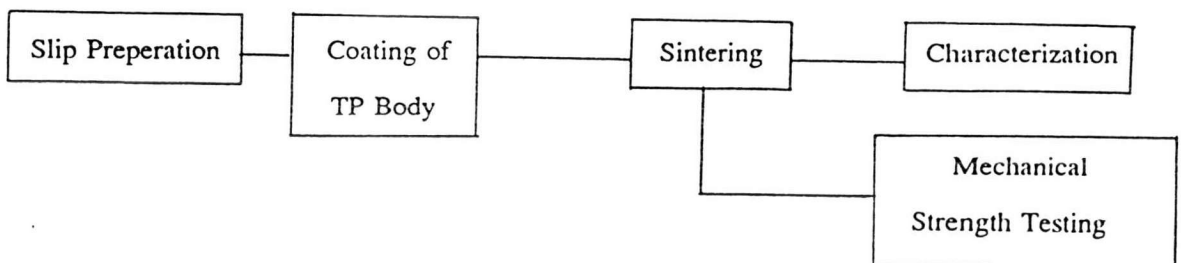


Figure 3.1 Flow chart of experimental procedure.



Experimental Procedure

3.1 Hydroxyapatite Preparation and Process

3.1.1 Hydroxyapatite prepared from cattle bone ash (MP)

MP was prepared as described in the method of Lorpayoon (1986). A central part of cattle leg bone was selected (as shown in Fig. 3.2) and boiled in water for at least one day to eliminate fat. The defatted bone was then calcined in an electric furnace at 700°C for 3 h in order to remove all organic matters. Afterwards, the white calcined bone was ground in a porcelain mortar to yield the desired MP powder.

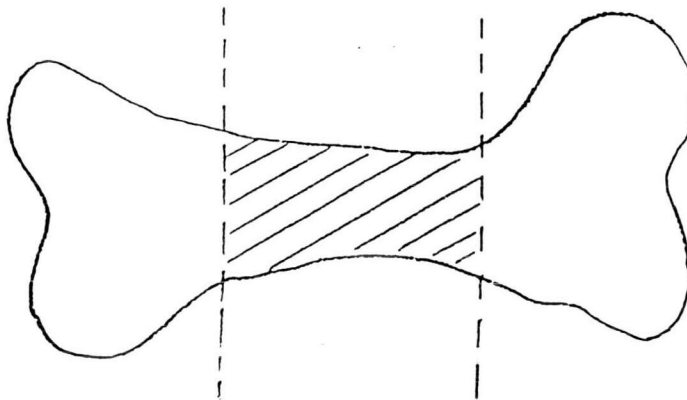


Figure 3.2 Selected part of cattle leg bone.

3.1.2 Chemically treated hydroxyapatite (TP) from MP powder

TP was prepared as described in the method of Lorprayoon (1989). To the MP powder (prepared in 3.1.1) an aqueous solution of calcium nitrate⁺ (10% w/v) was added. The mixture was then dissolved in 1 M nitric acid[#] solution at pH 1. The solution was basified to pH 10.5 with concentrated ammonium hydroxide^{*} solution (35%) resulting in a white precipitate and was gently boiled for 15 min. The precipitate was collected by filtration using a filter paper no. 40 and then washed with several portions of hot distilled water until neutral. The filter cake was dried in an oven and then calcined in an electric furnace at 550°C for 2 h. The product was ground in a porcelain mortar to yield the desired TP powder.

3.1.3 Attrition milling of MP and TP powders

The powder was added in attrition mill using ZrO₂ balls and distilled water as medium (powder:water= 1:1 by weight) and then a solution of dispex (0.1% by weight) as a dispersing agent and a solution of polyvinylalcohol (1.6% by weight) as a binder were added respectively. Afterwards, the mixture was milled for 30 min at a speed of 600 rpm to obtain the desired powder. The MP and TP powders were characterized prior to use.

⁺ reagent grade: MERK 2121.0500

[#] MERK 456

^{*} BDH prod 10012

3.1.4 Granulation of MP and TP powders

A powder containing a moisture content of about 10-15% was granulated by using ASTM standard sieves no. 35, 50 and 140 mesh respectively. The formed granules were separated in each sieve as illustrated in Fig. 3.3. The granules of 50 mesh were mixed with those of 140 mesh in the ratio of 9:1 and was then aged for 5 days until the moisture in the granules was maintained an amount of 13-14%. Characteristics of the desired granules were examined before the forming was proceeded.

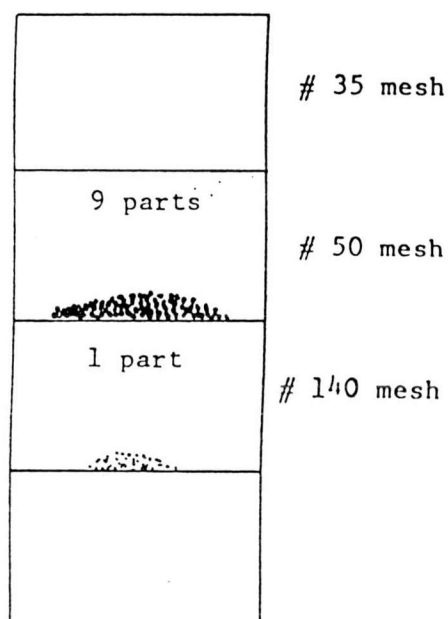


Figure 3.3 Illustration of granule size selection.



Figure 3.4 MP powders.



Figure 3.5 MP granules.

3.1.5 Forming of MP and TP granules

The granules(prepared in 3.1.4) were hydraulically pressed* in a metal mould under a pressure of 1 ton/cm^2 and finally rectangular bar was obtained.

In the process of pressing, the granules (MP 2.2 g or TP 1.8 g) were added in a mould and pressed 80% of desired pressure (1.5 ton). After the spacer of the mould was removed, the pressing of the granules was repeated under a desired pressure (1.9 ton) and then the resulting bar was removed from the mould and dried at 110°C for 24 h. The desired compact bar with a dimension of $4.5 \times 4.5 \times 44.2 \text{ mm}^3$ was obtained after each edge was removed by abrasion with sand paper no. 1000 (as shown in Fig. 3.8).

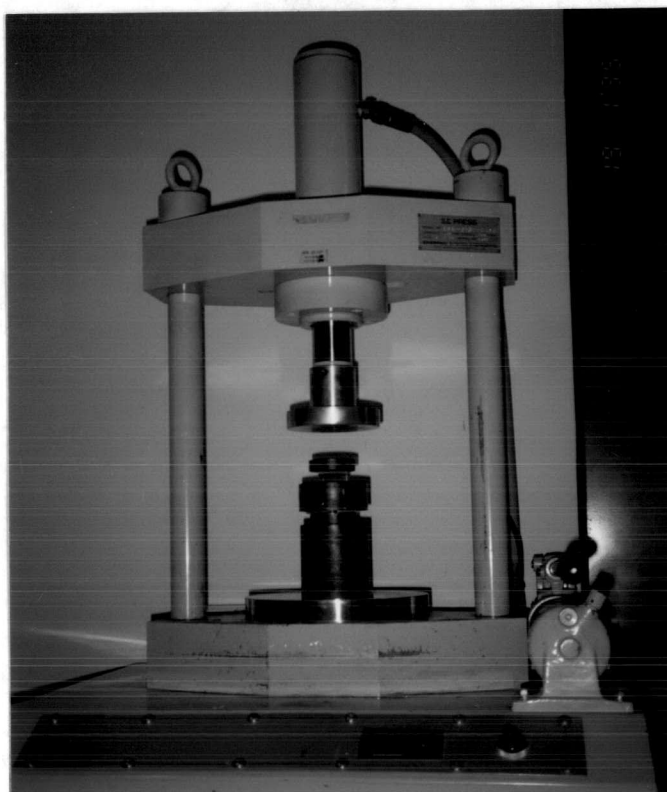


Figure 3.6 Hydraulic pressing machine.

* ENERPAX model no. ESE-373-00 SEFS 20.

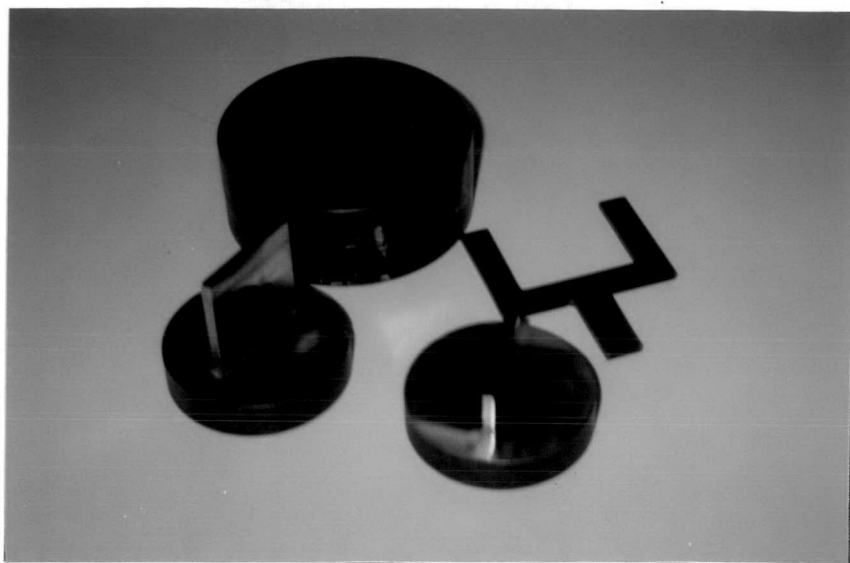


Figure 3.7 Metal mould.

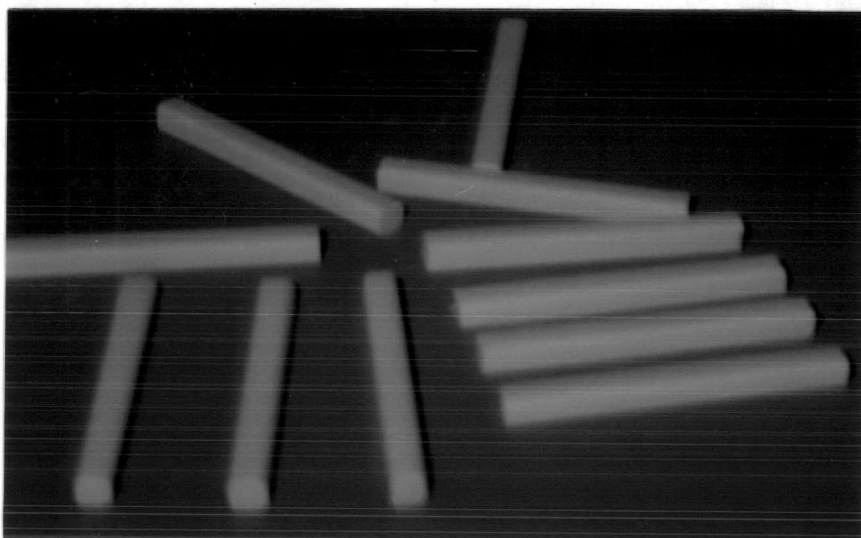


Figure 3.8 Compact bars (MP).

3.1.6 Sintering of MP and TP compact bars

The above specimens (MP and TP) prepared in 3.1.5 were sintered in an electric furnace* (as shown in Fig.3.9) which was heated up to 1150° , 1200° and 1250° C with a rate of 6° C per min and soaked at the maximum temperature for 2 h. The specimens were allowed to cool to room temperature in the furnace.

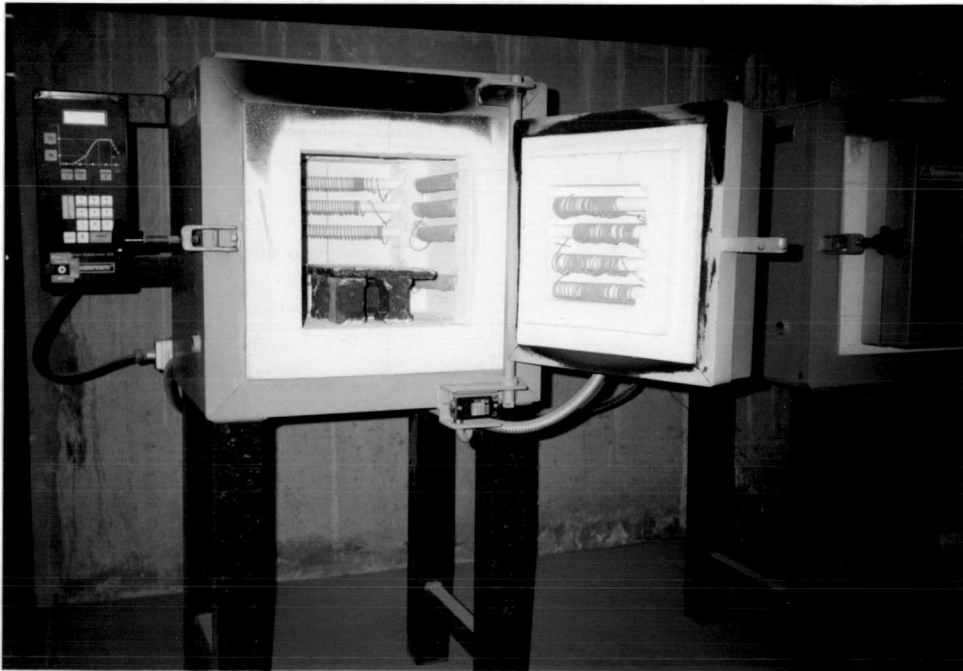


Figure 3.9 Electric furnace (Nabertherm model 20N/H).

* Nabertherm model 20N/H.

3.2 Characterization of Hydroxyapatite

3.2.1 Chemical composition and impurities.

The analyses of calcium and phosphorus of milled MP and TP powders were carried out by wet chemical method and the impurities including trace metals were determined by atomic absorption spectroscopy using a Varian spectrAA 300 atomic absorption spectrometer. All of the analyses were performed by Department of Science Service.

3.2.2 Phase identification

The crystalline phase of HAp was identified by X-ray diffraction method using a Philips PW 1710 X-ray diffractometer (as shown in Fig. 3.10) with cobalt K_{α} radiation and iron filter at 35 kV and 25mA and 2θ was started from 10° to 60° at a scanning velocity of 0.05° per sec.

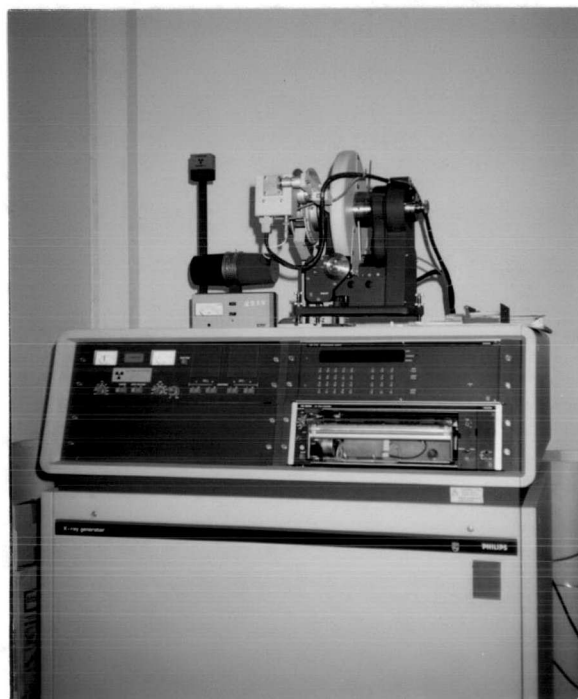


Figure 3.10 X-ray diffractometer (Philips PW 1710).

3.2.3 Microstructure

The microstructures were examined by scanning electron microscopy (SEM) using a JEOL JSM 35 CF scanning electron microscope (as shown in Fig. 3.11) in which the sample was placed on the target stub and sputtered with gold. For the sintered specimen, the sample was previously etched with an aqueous solution of 25% w/v phosphoric acid for 15 sec, rinsed with water and dried before placing on the target stub.

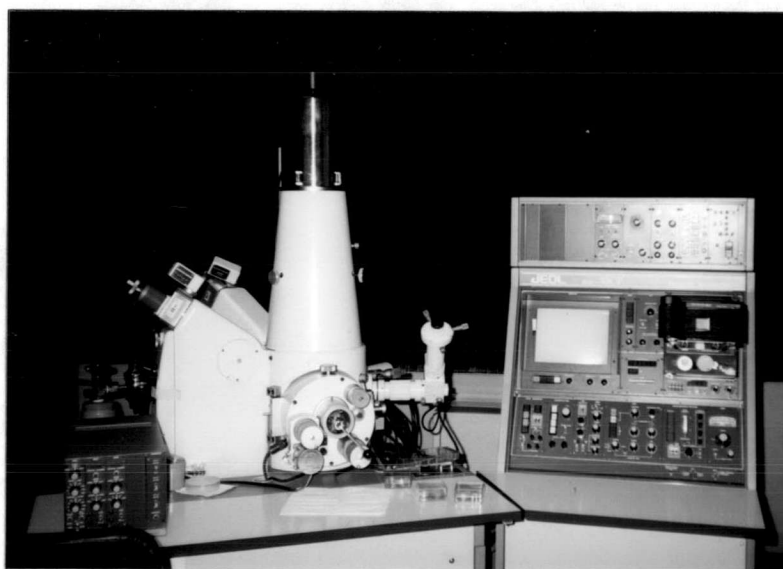


Figure 3.11 Scanning electron microscope (JEOL JSM 35 CF).

3.2.4 Density

The densities of the MP and TP powders were examined by gas pycnometer using a Micromeritics AccuPyc 1330 pycnometer with He gas as medium (as shown in Fig. 3.12).

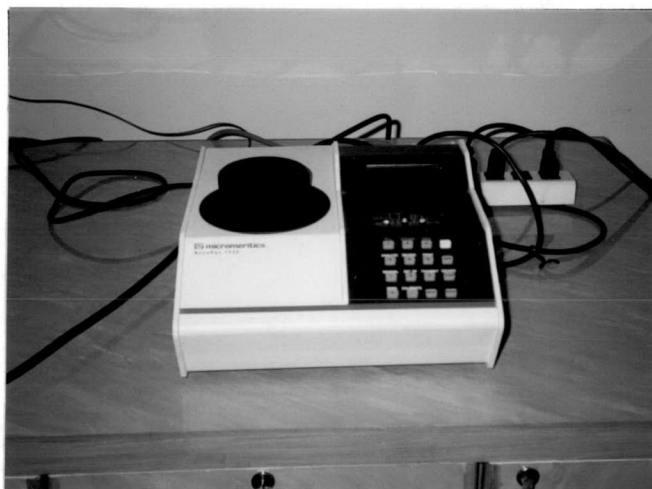


Figure 3.12 Micromeritics pycnometer (AccuPyc 1330).

3.2.5 Surface area analysis

The surface areas of the MP and TP powders were determined by the BET gas adsorption method using a Micromeritics Gemini 2360 surface area analyser.

3.2.6 Particle size distribution

The particle size distributions of the MP and TP powders were examined by sedimentation technique using a Micromeritics sedigraph 5100 particle size analyser (as shown in Fig. 3:13).



Figure 3.13 Sedigraph 5100 particle size analyser.

3.2.7 Flow rate of granules

The flow rates of the MP and TP granules were measured according to the ASTM test method B 213-90 (see Appendix B).

3.2.8 Filled density and Tap density of granules

The filled density and tap density of the MP and TP granules were determined according to the ASTM test method B 527-85 (see Appendix C).

3.2.9 Compact density

The compact densities of the compact MP and TP bars were calculated from the ratio between weight and size of a sample used.

3.2.10 Linear shrinkage

The linear shrinkages of the MP and TP sintered specimens were calculated from the equation below as:

$$\% \text{ Linear shrinkage} = [(L_2 - L_1) / L_1] \times 100$$

where L_1 = Linear of dried specimen before sintering

L_2 = Linear of specimen after sintering

3.2.11 Bulk density, relative density, water absorption and apparent porosity of sintered specimens

All the measurements were carried out according to the ASTM test method C 373-72 (Reapproved 1982) (see Appendix D). The relative density was calculated against the theoretical density of HAp (3.16 g/cm³).

3.2.12 Thermal expansion coefficient

The thermal expansion coefficients of the MP and TP sintered specimens were measured by means of a Adamel Lhomargy DI-24 dilatometer (as shown in Fig. 3.14) in which the heating rate of 10°C per min was used.

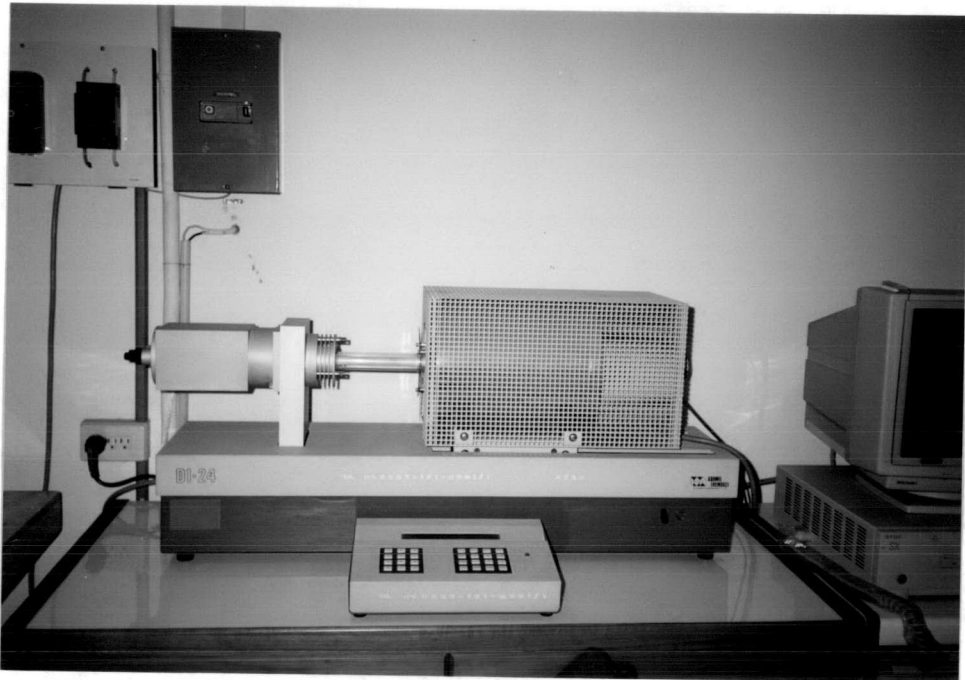


Figure 3.14 Dilatometer (Adamel Lhomargy DI-24).

3.3 Mechanical Strength Testing of Hydroxyapatite

The compressive strength of the MP and TP sintered specimens was determined by using a Shimadzu Autograph AGS-500D universal testing machine (as shown in Fig. 3.15) with the rate of load cell of 0.5 mm/min. Cushion pads were placed on the bottom and top of the specimen.

The specimens were obtained from the cutting of the green compact bar with the ratio of the length to the cross-sectional width of about 2.0 prior to sintering.

The compressive strength was therefore calculated from the equation below as:

$$\text{Compressive strength} \quad = \quad \frac{\text{applied load (kg)}}{\text{cross-sectional area of specimen (mm}^2\text{)}} \\ (\text{kg/mm}^2)$$

The unit kg/mm^2 was multiplied with 9.810001 to convert into a MPa unit.



Figure 3.15 Universal testing machine (Shimadzu Autograph AGS-500D).

3.4 Hydroxyapatite Mixtures Preparation and Process

A mixture of MP and TP powders was prepared in different 6 compositions (as shown in Table 3.1). Each mixture was added in a high speed ball mill using distilled water as medium in the ratio of 1:1 by weight. The powder was mixed for 30 min and dried in an oven. Each of the resulting powders was then granulated, pressed and sintered by the methods similar to the preparation of the MP and TP as described in 3.1.4, 3.1.5 and 3.1.6 respectively. Subsequent characterizations of the MP and TP mixtures were performed in each step.

Table 3.1 Various compositions of MP and TP mixtures.

Mixture	Weight, %	
	MP	TP
MPTP1	90	10
MPTP2	80	20
MPTP3	70	30
MPTP4	50	50
MPTP5	30	70
MPTP6	20	80

3.5 Characterization of Hydroxyapatite Mixtures

3.5.1 Phase identification

The crystalline phases of the MPTP 1-6 sintered specimens were identified by the similar procedure as described in 3.2.2.

3.5.2 Microstructure

The microstructures of the MPTP 1-6 compact and sintered specimens were examined by the similar procedure as described in 3.2.3.

3.5.3 Compact density

The compact densities of the MPTP 1-6 compact bars were measured by the similar method as described in 3.2.9.

3.5.4 Linear shrinkage, bulk density, relative density, water absorption and apparent porosity of sintered specimen

All the measurements were carried out by the same procedure as described in 3.2.10 and 3.2.11.

3.5.5 Thermal expansion coefficient

The thermal expansion coefficients of the MPTP1-6 sintered specimens were measured by the same procedure as described in 3.2.12.

3.6 Strengthening of Hydroxyapatite by Coating

3.6.1 Preparation of a coating slip

An MP slip was prepared by a high speed ball milling for 30 min using distilled water as medium in the ratio of 1:1 by weight. Then the slip was passed through sieve no. 50 mesh to exclude bubbles occurring during the milling. Similarly, mixtures of MP and TP (MPTP 5 and MPTP 6) were prepared as described above.

3.6.2 Preparation of coated TP specimens

TP specimens were obtained from the cutting of a compacted bar with the ratio of the length to cross-sectional width of about 2.0. Each specimen was polished with a fine abrasive paper no. 1000. The whole surface of the specimen was then sprayed with the coating slip prepared in 3.6.1 to obtain an uniform thickness of about 0.2 mm. The coated specimens were dried in an oven for 24 h and finally calcined in an electric furnace at 550°C for 2 h.

3.6.3 Sintering of coated TP specimens

The coated TP specimens were sintered in an electric furnace which was heated up to 1200°C with a rate of 6°C per min and soaked at the final temperature for 2 h. The specimens were allowed to cool to room temperature in the furnace.

3.7 Characterization of Coated Hydroxyapatite

3.7.1 Thickness measurement

The thickness of a coating layer was obtained from the difference between the thickness of the specimen after coating and before coating, measured using a vernier caliper prior to sintering.

3.7.2 Phase identification

The crystalline phases of sintered specimens were identified by the similar procedure as described in 3.2.2.

3.7.3 Bulk density, relative density, water absorption and apparent porosity of sintered specimens

All the measurements were carried out by the same procedure as described in 3.2.11.

3.7.4 Surface condition

The surface conditions of the coated specimens after sintering were observed by scanning electron microscopy using a JEOL JSM 35 CF scanning electron microscope.

3.8 Mechanical Strength Testing of Coated Hydroxyapatite

The compressive strength of the coated TP specimens after sintering was determined by using the same procedure as described in 3.3.