CHAPTER III

Preparation and Properties of Calciumhydroxyapatite reinforced Dental Composites

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ABSTRACT

From the previous work showed that the ratio between base and diluent monomers did not play important role for enhancing the mechanical properties. The amount and type of filler did more influence to mechanical properties of dental composite. Synthetic calciumhydroxyapatite (CHA) is the most attractive filler for dental restorative filling material from the biocompatibility and bioactivity for tooth tissue. CHA was synthesized by wet method and characterization the structure by XRD and SEM. The big crystal CHA of average size 27.62 µm containing some amorphous small or crystals on surface were obtained. Content of CHA were varied from 1-20 %wt in pure UDMA resin. Increasing content of CHA (when filler was the minor phase) showed the prominent improvement in diametral tensile strength (DTS) up to 34 MPa, which was opposite to those of treated silica about 29-30 MPa (when used as major phase of 60 %wt). The high DTS was attributed to big crystal filler and good adhesion which was evident by plastic deformation inside the holes when CHA

particle were resided. Vicker hardness was not significantly improved by filler content. The optimum content of CHA was 15 %wt determined by DTS.

KEYWORDS: **Dental Materials, Composites, Calciumhydroxyapatite**

1.INTRODUCTION

Hydroxyapatite (HAP) or calcium hydroxyapatite (CHA), with the structural formula of $Ca_{10}(PO_4)_6(OH)_2$, is the major constituent of human bone and teeth. Synthetic calcium hydroxyapatite has excellent biocompatibility and bioactivity and is widely used in many biomedical applications such as implants and coating of prostheses [Lim *et al.*, 1999: Ishikawa *et al.*, 2000]. It is the bioceramics with crystal structure similar to natural bone and teeth minerals. Hydroxyapatite, a material having closed chemical structure as human teeth and bone has been studied intensively to use in the body [Ahn *et al.*, 2000; Tanaka *et al.*, 1997]. Lebugle *et al.* (1994) have modified CHA with hydroxyethyl-methacrylate phosphate and dodecanol phosphate by coprecipitation method and achieved improved dispersion of CHA particles in polymers to use as filler cement in dental and medical therapies. A dental resin reinforced with dispersed hydroxyapatite (HAP) crystals seem, in principle, a favorable restorative material for human tooth tissue, as it for bone tissue [*Saito et al.*, 1994]. The use of hydroxyapatite in restorative dentistry offers several promising advantages, including intrinsic radiopaque response, enhance polishability an improved wear performance, since synthetic HAP has hardness similar to that of natural teeth [Arcis *et al.*, 2002]. Finally, this material is less expensive than most of the fillers commonly used (e.g. barium or zinc glass, quartz, zirconia, silica or alumina [William *et al.*, 1992; Gladys *et al.*, 1997]). The main disadvantage of HAP

is its high refractive index when compared to those of light-activated polymers normally used in dental restoration [Labella *et al.*, 1994]. The aesthetic appearance of HAP reinforced composite was considered worse than that observed for conventional composites filled with quartz or glass powder [Arcis *et al.*, 2002].

This study tries to examine the optimum composition of CHA for optimum strength in order to use as second filler in hybrid composite which contains silanized silica and delaminated silica layered of clay mineral. The dental composite with CHA is expected to provide aesthetic, high mechanical properties and biocompatibility to teeth tissue.

2.MATERIALS AND METHOD

The monomers employed in this work were urethanedimethacrylate (UDMA) were supplied by Esstech (Essington, PA) and were used as received. Camphorquinone and dimethylaminoethyl methacrylate (DMAEMA) were purchased from Fluka Chemical, Switzerland. Calcium hydroxide and orthophosphoric acid were purchased from Carlo Chemical Company and were used as received. The structure of monomer is shown in Figure 1.

(Figure 1)

2.1 Calciumhydroxyapatite synthesis

The method used was following Ishikawa method [Ishikawa *et al.*, 2000]. Specifically, $Ca(OH)_2$ (0.405 mol) was dissolved into 20 dm^3 distilled water free from CO_2 in a seal flask. After the flask was stirred for 24 hours at room temperature, 0.249 mole of H_3PO_4 was added to the $Ca(OH)_2$ solution, and resulting

suspensions were stirred for further 24 hours at room temperature and then aged at 100°C for 48 hours. The CHA particles generated were filtered off, thoroughly washed with distilled water, and finally dried in an air oven at 70 $^{\circ}$C for 16 hours.

2.2 Dental resin Preparation

Dental resins were prepared by mixing UDMA monomer with 0.2 %wt camphorquinone and 0.8 %wt dimethylaminoethyl methacrylate. Prepolymerized dental resin was blended with CHA by mixer ALC-sL with four twisted-blade turbine at 500 rpm for 20 minutes.

2.3 Microstructural studies

Filler particles were studied by Cu K-α X-ray diffractometer Rigaku D/MAX-2000 series at 40 kV/30 mA. The standard sample holders were applied to powder samples. The experiment was operated in the 2θ range of 5-70 degrees at the scan speed 5 degrees/min with 0.02 degrees 2θ-stepwise increment. The microstructural analyses were performed by using a JEOL 520 scanning electron microscope (SEM) at a voltage of 10 kV and 500x magnifications. Particle size was measured by Masterxizer X vesion 2.15, Malvern with range lens 45 mm.

2.4 Diametral tensile strength

The specimens were prepared by pouring the unpolymerized dental resin into a stainless steel mold. Resin disk (3 mm thick by 6 mm diameter) were photopolymerized between glass slide and translucent polycarbonate strip in a dental curing unit (3M Curing Light XL3000) with a light intensity of approximately 300

mW/cm^2 measured by a radiometer for 40 seconds on each side. They were subjected to test in a Universal Testing Machine following the procedure in American Dental Association-Specification No. 27 for Direct Filling Resins. Five specimens for each sample type were tested and their mean values were determined.

The diametral tensile strength (DTS) test was therefore utilized by placing a sample disk vertically between flat grips. Compressive load was applied to failure with a crosshead speed of 10 mm/min, using 25 kN load cell. DTS were determined by the following standard formula (1)

$$DTS = 2f/(\pi dl) \qquad \dots\dots\dots\dots\dots(1)$$

Where f = load at failure; d = specimen diameter; l = specimen thickness

2.5 Microhardness test

The microhardness of the samples was measured using FM-700e Digital Microhardness tester (Future-tech corp. Japan) with 500-gram load, dwell time 15 seconds and 136° pyramidal diamond indenter (Vicker Hardness Scale). The specimens were prepared in the same way as the DTS specimen followed by polishing the surface with 0.3 μm slurry alpha alumina (Imptech, South Africa). The pyramidal shaped indenter was applied on the surface of specimens within dwell time then the force was removed. For the Vickers method, the indentation length of vertical and horizontal axes is measured and averaged. The experiment was repeated five times for each sample set of parameters. The impression length was measured microscopically and the test load was used to calculate a hardness value automatically by the instrument calculation programme.

3.RESULT AND DISCUSSION

Structure of Synthesized CHA

According to Ishikawa's method, this CHA posses high surface energy due to OH^{-1} and PO_4^{3-} groups on its crystal surface. This provides good adhesion between CHA and acrylate resin. The XRD pattern of synthesized calcium hydroxyapatite in Figure 2 shows sharp complex diffraction peaks particularly appearing below $2\theta = 40°$ and which is matched with the crystal structure of nanostructure processing by high temperature sintering of hydroxyapatite-base bioceramics as reported by Ahn *et al.* 2001.

(Figure 2)

It is surprising that our preparation can provide excellent composition homogeneity and phase purity (low amorphous part) without high temperature sintering at 1000 – 1300 °C.

The morphology observed by SEM is shown in Figure 3ab

(Figure 3ab)

The particles are rather square in shape, having a characteristic lateral size of 10-50 microns long and somewhat less in thickness. The crystal shows stacked like shape that should be ordered stacking of hydroxyapatite layer [Vallet-Regi and Ramila (2000) and Yamashita *et al.*, 1996]. However, the mean particle size was 26.70 $\pm$ 3.492 μm measured by Martersizer X. The superior densed packed crystal structure associated with large particle size can bring about improved mechanical properties without sacrificing biocompatibility so it is applicable for dental restorative filling material. Ahn *et al.* (2001) reported that the nanostructure CHA possesses excellent

strength beyond conventional CHA e.g. compressive strength of 879 MPa, bending strength of 193 MPa and fracture toughness of 1.3 MPa.m $^{1/2}$. The big densed crystal CHA prepared in this work is quite astonishing since most works have not achieved to obtain big size but rather nano or micro size with pores.

Diametral Tensile Strength (DTS)

DTS of CHA macrofilled composite increases obviously with filler content in CHA reinforced dental composite as shown in Figure 4

(Figure 4)

Especially, when 15 %wt CHA was added into dental resin, it gains the highest diametral tensile value which is greater than those of conventional composites, at only half loading. This indicates better compatibility of CHA and the resin. Further increase of filler results in lowering DTS. All diametral tensile strength of CHA reinforcing dental composites are higher than those of conventional dental composites and more closed to those of the commercial ones. Zhang *et al.* (1999) reported that CHA is quite stable on carboxyl substrate but not on NH_2 terminated substrate. For our system using UDMA containing amide group and acrylate group, thus it is expected that CHA and UDMA are compatible. The results are agreed welled with those observed by Arcis *et al.* (2002) that the macrofilled CHA composites gives higher strength than nanofilled CHA composites an unfilled resin, respectively. SEM micrograph in Figure 5 show 20% filled composite morphology. Fillers size is obviously reduced and becomes less than 10 μm.

(Figure 5)

It indicates that the crystal is rather brittle and partially broken during mixing. Plastic deformation is appeared on the crack surface and in the inner surface of holes suggesting toughness matrix associating with good adhesion between filler and matrix.

Microhardness of CHA filled dental composites

Mean and Standard deviation of Vicker hardness for CHA reinforced dental composites are presented in Figure 6

(Figure 6)

The VHN values observed are quite low compared to those (but with higher loading content) reported previously [Arcis *et al.*, 2002]. However, The VHN values for the CHA filled and unfilled resins are not significantly different although CHA bending strength is significantly high as mentioned earlier. CHA tends to induce more hardness to the resin but with the large fluctuation. Considering that the composites contained low filler content and the broken crystal of CHA. This may be the clue of low VHN.

4. CONCLUSION

Calcium hydroxyapatite is utilized as minor phase filler in dental resin composite. The optimum content is 15 %wt smaller amount than those used for the conventional one with higher mechanical properties. Additionally, the high surface energy of densed crystal would offer a good adhesion with the polymer matrix evident by plastic deformation at the interface. Synthetic calcium hydroxyapatite in this work is large densed crystal similar with structure to the nanostructure processing of previous

synthesized hydroxyapatite based bioceramics having chemical homogeneity and microstructure uniformity. However, they are broken down to small size below 10 μm upon mixing causing low VHN values. Hydroxyapatite is successfully prepared with polar surface and by sintering. This micro-macro scale filler provide reinforcement to the resin matrix by well dispersion and good adhesion.

5. ACKNOWLEDGEMENTS

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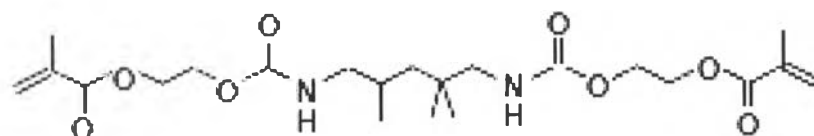
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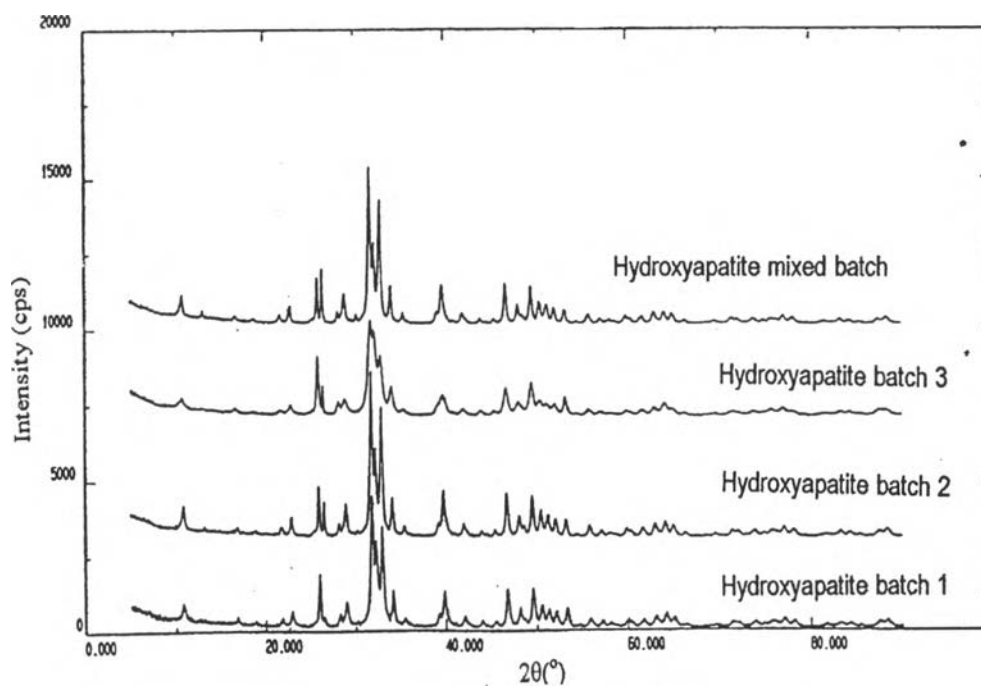
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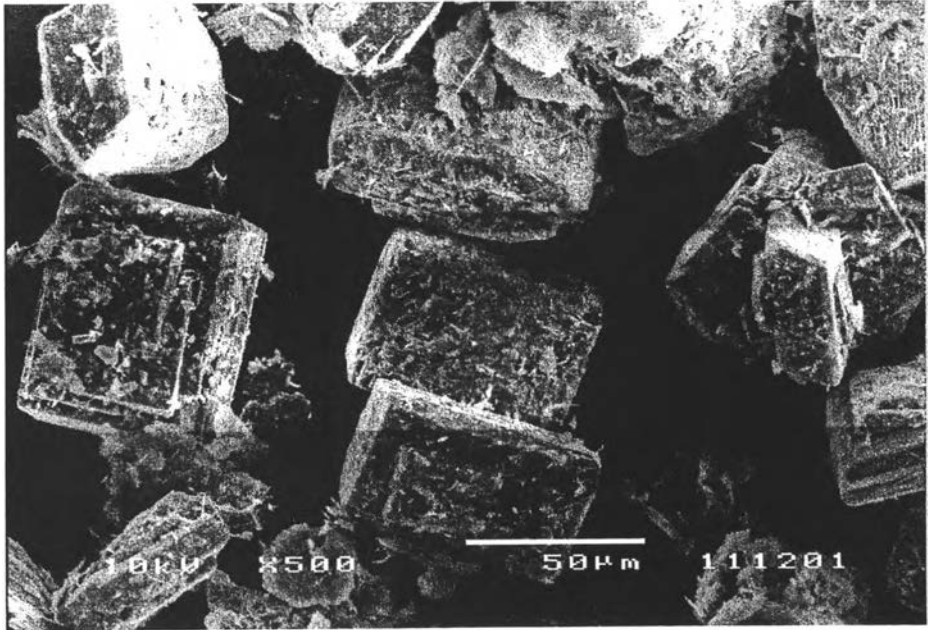
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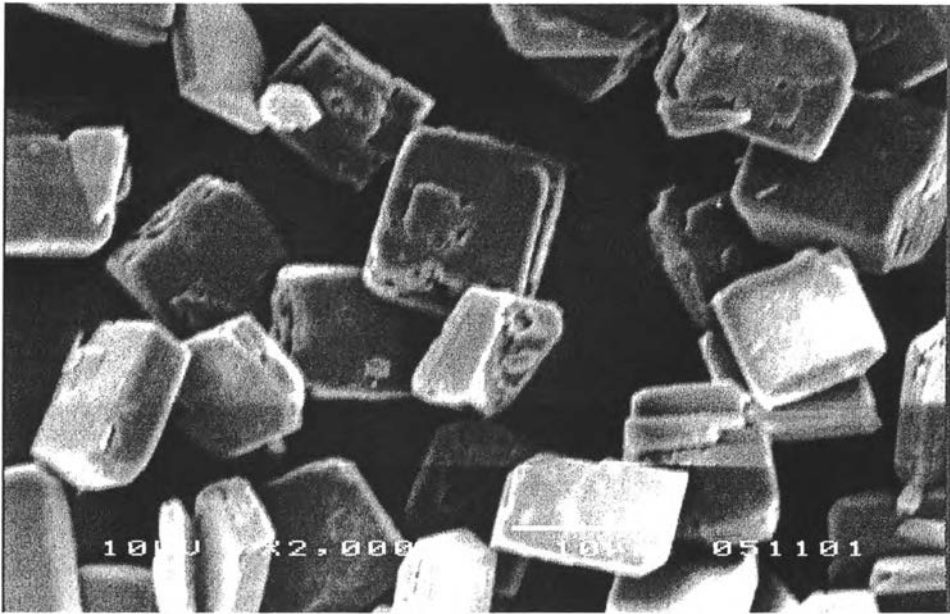
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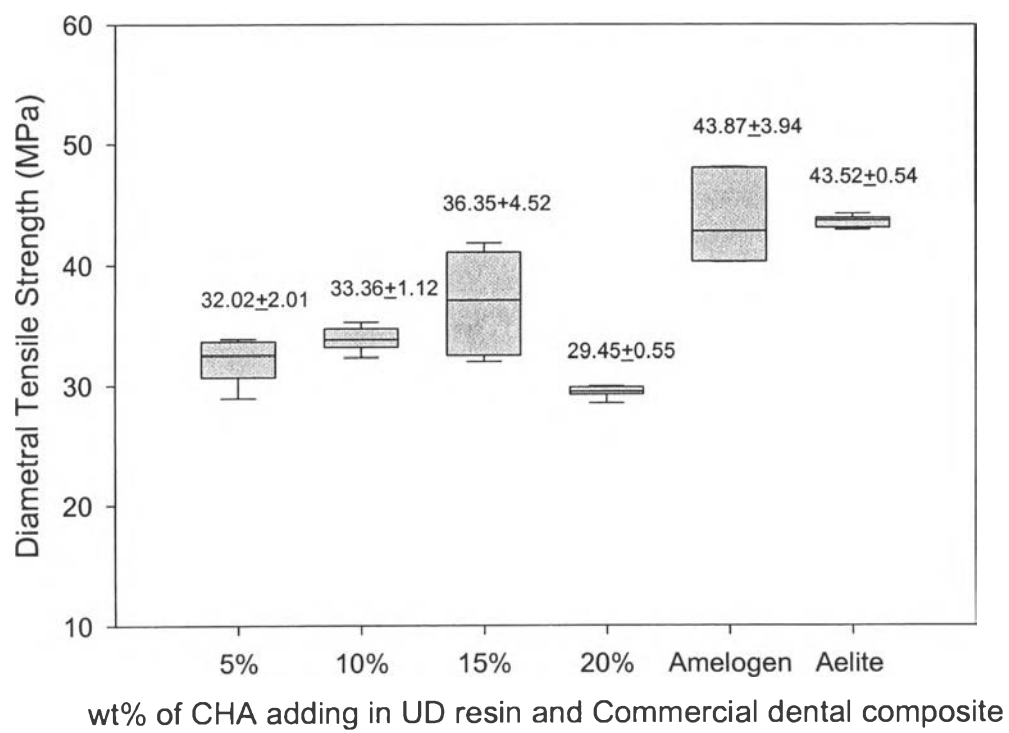
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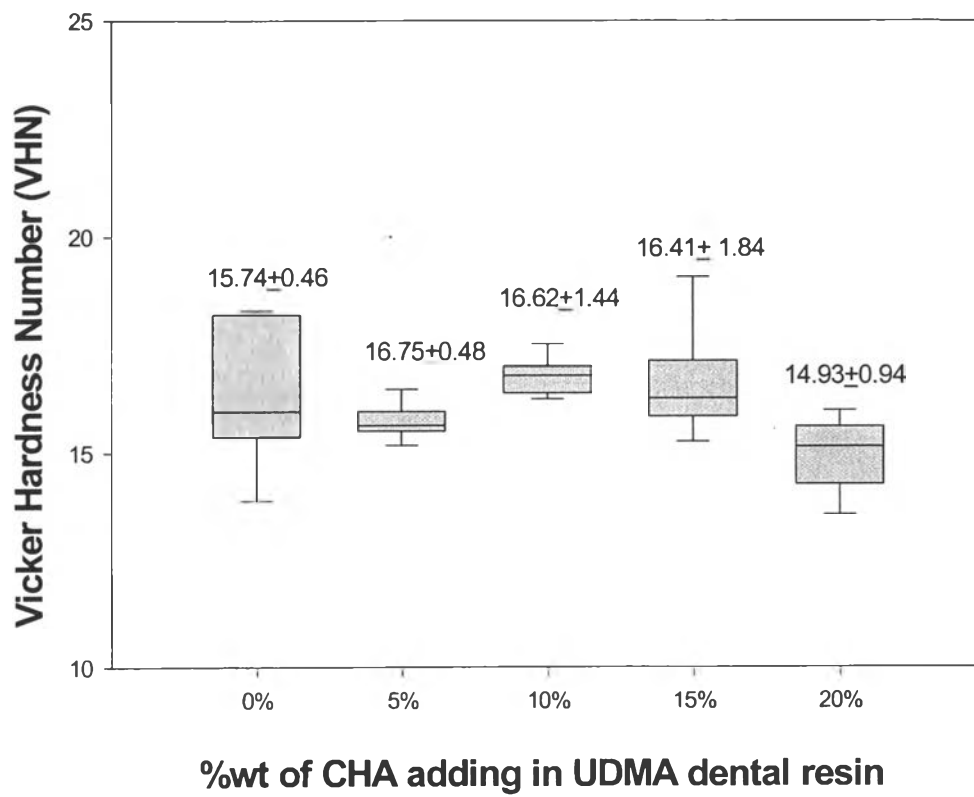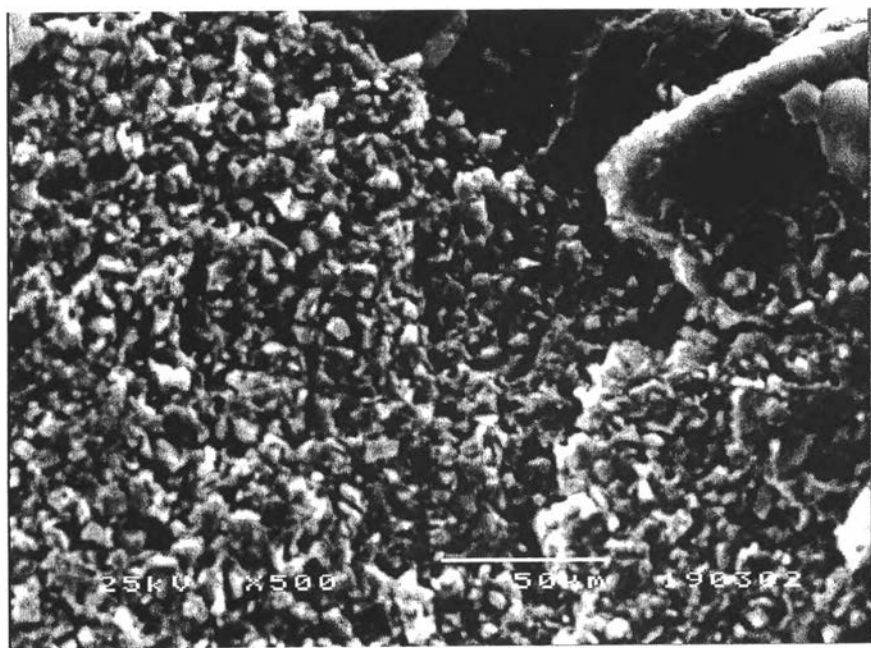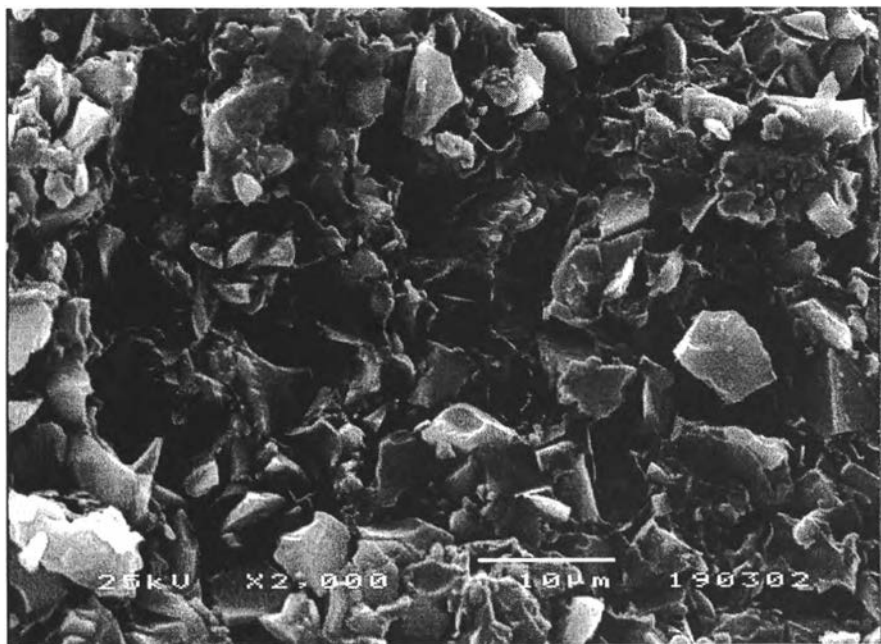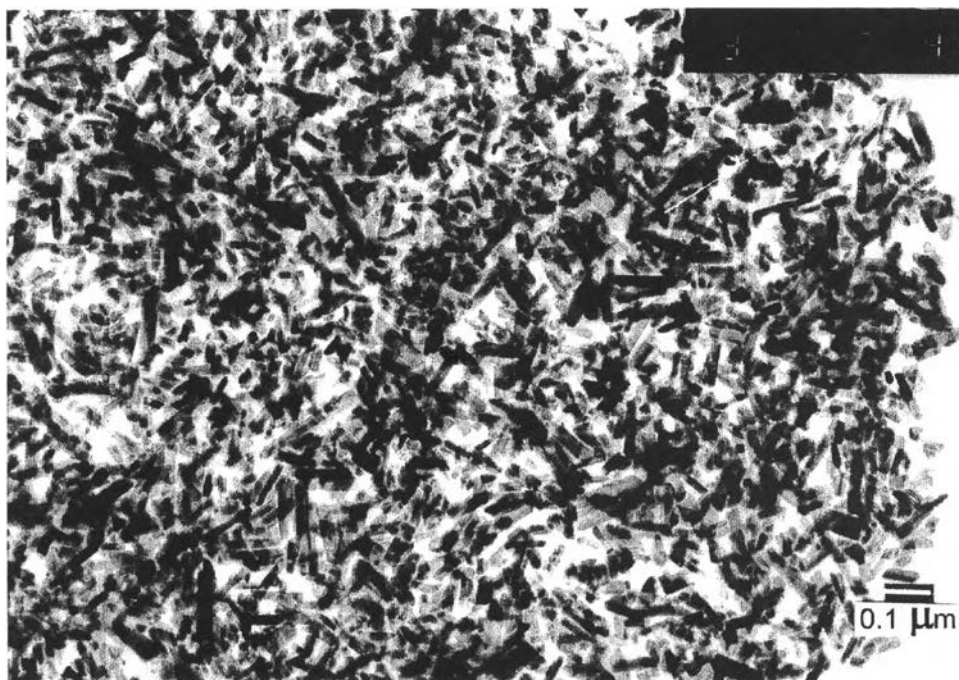
Figure 5

Figure 6a

25kU   X2,000   10μm   190302

Figure 6b

Figure 6c