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Dynamic compaction of calcium phosphate biomaterials

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The purpose of this study was to apply the dynamic compaction process to calcium phosphate biomaterials. This new technique is currently used to compact metallic powders at room temperature but has not been previously applied to biomaterials. A detailed study of hydroxyapatite compacts was carried out to determine shock compaction parameters. Low static precompaction (3.1 MPa) resulted in slight peripheral cracks. A compaction degree of about 70% and macrohardness of 51 H_V were achieved for a striker velocity of about 50 m/s. FTIR spectroscopy and X-ray diffraction showed no differences in structure and composition after dynamic compaction. Two other infrequently used biomaterials were also tested: an unstable octacalcium phosphate and β-calcium metaphosphate fibres. Scanning electron microscopy showed that dynamic compaction preserved the initial fibre structure of the material. No major structural or chemical changes were noted after shock consolidation. Our results show that dynamic compaction could extend the range of bioceramics.

1. Introduction

Conventional powder-processing techniques involve consolidation of powder by compaction and heating to achieve sintering of the material. Although dense calcium phosphate ceramics with good mechanical strength [1–3] are produced by this method, sintering has certain limitations: (a) crystallinity and morphological features change with high temperatures [4–7]; (b) unstable materials alter when heated [6]; and (c) biological factors cannot be mixed with calcium phosphate materials during the sintering process. A new process to consolidate powders at room temperature would be useful.

Dynamic compaction is a very promising technique for the production of bulk material from metallic powders [8–16] but has not been used for bioceramic applications. Consolidation is achieved by a shock wave produced by piston impact or explosives placed around the powder. This wave deforms powder particles so quickly that interparticle melting and welding occur without external heating. This feature makes shock compaction an attractive process for the development of new bioceramics, particularly composites associating calcium phosphates and organic compounds (drugs, antibiotics, growth factors, etc.).

The present study determined the quantitative compaction parameters of hydroxyapatite powder and investigated the behaviour of β-calcium metaphosphate fibres and octacalcium phosphate (OCP) during dynamic consolidation.

2. Experimental procedure

2.1. Materials

Experiments were conducted on hydroxyapatite (Merck), OCP (prepared by Dr R. Z. LeGeros, University of New York, USA) and β-calcium metaphosphate fibres (provided by Kasuga *et al.*, Department of Materials Science and Engineering, Nagoya Institute of Technology, Japan). The materials were identified by X-ray powder diffraction (Kristalloflex D5000 diffractometer, Siemens), FTIR spectroscopy (32-scan Nicolet 20 SCX FTIR) and scanning electron microscopy (SEM) (Jeol JSM-6300).

2.2. Static compaction

The shock compaction apparatus was positioned horizontally so that static precompaction of the powder had to be performed before firing. The powder was compacted uniaxially in a 20 mm diameter cylindrical die using a Teswell-type testing machine (see Fig. 1 for a schematic view of the system). Crosshead compression velocity was kept constant at 10 mm/min, and static compaction stress ranged from 3.1 to 310 MPa.

2.3. Dynamic compaction

A schematic view of the dynamic compression system is shown in Fig. 2. The Hopkinson bar apparatus (gas pressure 0 to 2 MPa) fired a 20 mm diameter projectile

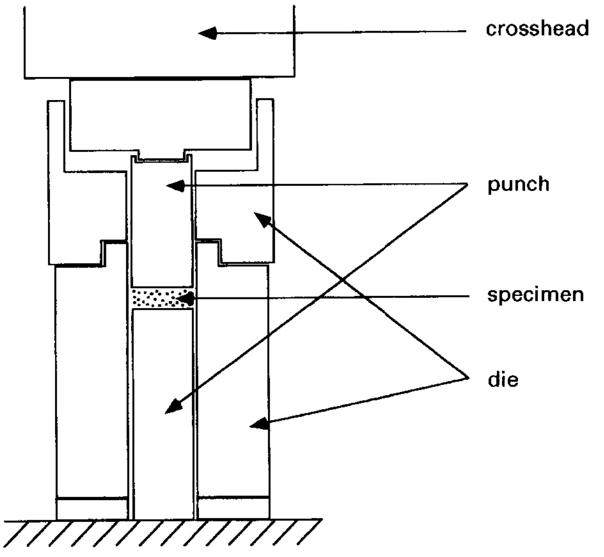

Figure 1 Static compaction system.

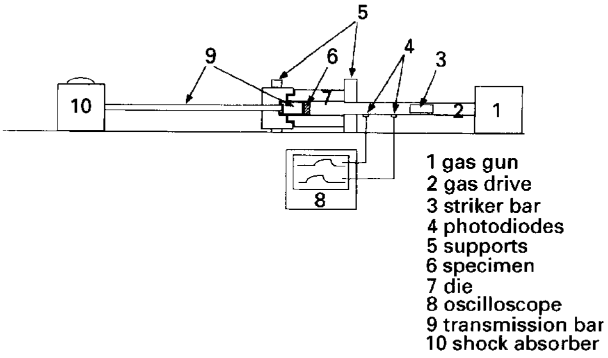

Figure 2 Dynamic compaction system.

into the same lubricated die used for static compaction. Striker velocity was measured by means of two photodiodes positioned 100 mm apart on the gas-drive and connected to a digital oscilloscope (Nicolet Model 206).

2.4. Compact characteristics

FTIR spectroscopy and X-ray diffraction were performed to investigate the chemical and crystallographic characteristics of the material after compaction. Morphological features were examined by SEM. Relative density *D*, i.e. the ratio of the apparent density of compact to the true density of powder, was calculated to express the degree of compaction. Hardness was measured by the Vickers indentation method using an indenting load of 49 N. Specimens were embedded in araldite resin, polished and coated with a 30 to 40 nm layer of chromium. The thickness of this layer, as measured by an alpha-step profiler (Tencor Instruments), was insignificant in comparison with indentation depth (40 μm minimum). Each sample was indented 10 times. As some authors have noted that the shock wave work-hardened metals [15], we also tested conventional sintered compacts of the same density as dynamic compacts. These samples were prepared by static compaction (3.1 MPa and 31 MPa) and sintered at 1100 °C for 2 h in a Vectar MRFS-818P furnace.

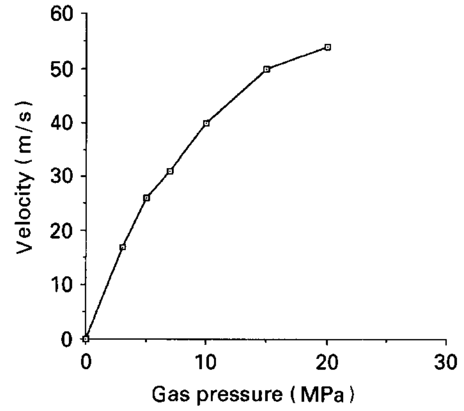

Figure 3 Striker bar velocity as a function of gas pressure.

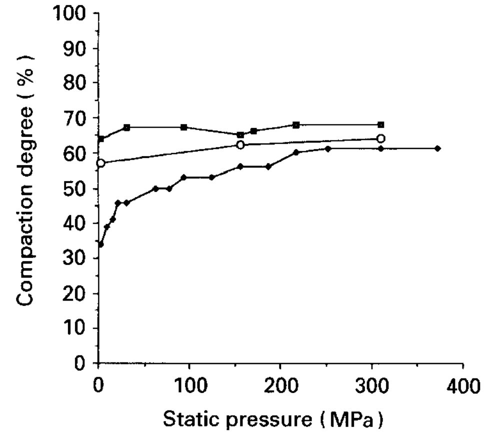

Figure 4 Compaction degree of compacts as a function of compaction pressures (◆ 0; ○ 1 MPa; ■ 2 MPa).

3. Results and discussion

3.1. Compaction parameters evaluated using hydroxyapatite powder

3.1.1. Striker velocity

The effect of gas pressure (0 to 2 MPa) on striker bar velocity was investigated in this experiment (Fig. 3). For subsequent dynamic compaction trials, three gas pressures were compared: 0 (only static compaction), 1 MPa and 2 MPa.

3.1.2. Degree of compaction

Each compact was prepared with 4 g of powder. The true density of hydroxyapatite (2.95 g/cm^3) was measured using an Accupyc 1330 helium–air pycnometer. Powder compressed with a gas pressure of 2 MPa (velocity 54 m/s) showed higher relative density (Fig. 4). Greater static pressure (more than 310 MPa) would have been required to achieve the same degree of compaction (about 70%). These results differ from those of Morimoto *et al.* [12] who found that the relative density of aluminium powder was greater after static than dynamic pressure, but are in agreement with the conclusions of Page and Raybould [14] who demonstrated that dynamic compaction produced higher densities with aluminium, iron and tungsten. Static precompaction had a limited effect on the final density of dynamic compacts.

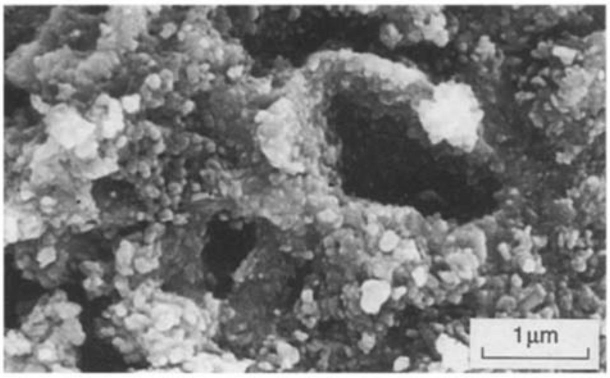

Figure 5 Scanning electron micrograph of a compact (static precompaction 310 MPa, dynamic pressure 2 MPa) showing micropores.

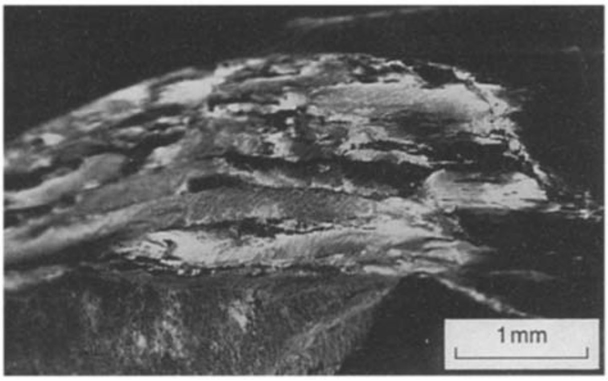

Figure 6 Scanning electron micrograph of a compact (static precompaction 310 MPa, no dynamic compaction) showing large peripheral cracks.

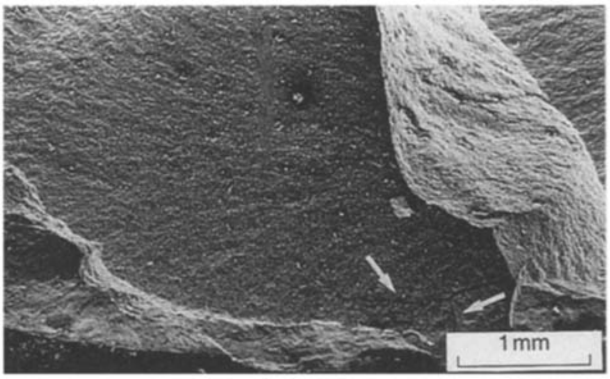

Figure 7 Scanning electron micrograph of a compact (static precompaction 3.1 MPa, dynamic pressure 2 MPa) showing circumferential and transverse cracks.

With the present compaction system, the highest densities were 70%. SEM observations (Fig. 5) showed that the size of the remaining pores was smaller than 10 μm. From the point of view of the powder-compaction industry, this might appear to be a drawback. However, microporosity is an advantage for the production of bioceramic since it allows internal biological fluid circulation, thus promoting bioactivity [18–21] while retaining sufficient mechanical properties [22]. Exchanges can take place, and the biological compound in association with calcium phosphate can be released into the environment.

3.1.3. Compact morphology

Different types of macrofractures were noted in SEM observations. Cracking occurred at the periphery of the compact (Fig. 6) and, circumferential and transverse cracks appeared when shock compaction was performed (Fig. 7). High static precompaction resulted in larger peripheral fissures, indicating inhomogenous densification. Capping, i.e. lamination of the compact upon ejection from the die, made it difficult to cut the sample. Fracture during load removal is a well-known problem in the industry, and an effort has been made to identify the parameters governing powder behaviour during compaction. For example, Es-Saheb [8] has shown that relaxation of axial pressure is faster than that of radial pressure, thus producing lamination of the compact. The second group of fractures was observed when dynamic compaction was performed. Transverse cracks appear regardless of the type of static precompaction used. These kinds of cracks have also been observed by other authors [9–11] using different firing configurations.

Our experiments indicate that low static precompaction resulted in more uniform density compacts with smaller peripheral cracks. The dynamic effect appeared to be greater when the powder particles moved with shock wave propagation, i.e. when precompaction was low. The similar degree of compaction achieved (Fig. 4), regardless of the type of precompaction used before firing (64% with 3.1 MPa versus 68% with 310 MPa precompaction), confirms that shock consolidation has a limited effect on dense materials.

3.1.4. Hardness

Samples compacted at 3.1 MPa and not subjected to shock consolidation could not be tested by this technique since indentation was too large. Hardness measurements were performed approximately in the middle of compacts. Fig. 8 shows that the highest hardness was obtained with 2 MPa gas pressure. The variation in compact hardness as a function of compaction degree is shown in Fig. 9, which indicates that

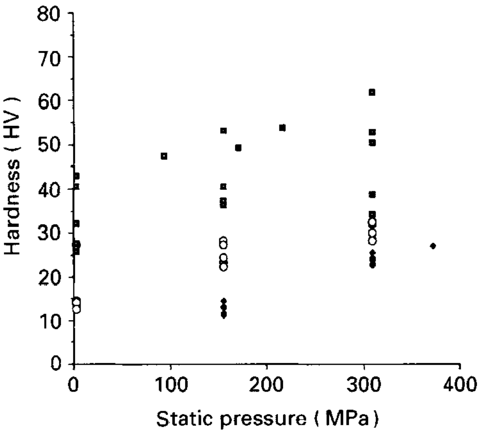

Figure 8 Hardness of compacts as a function of compaction pressures (◆ 0; ○ 1 MPa; ■ 2 MPa).

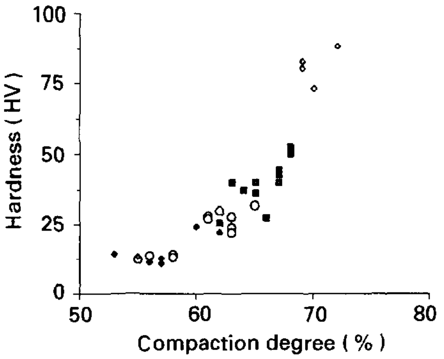

Figure 9 Hardness of compacts as a function of compaction degrees (◆ 0; ○ 1 MPa; ■ 2 MPa; ◇ sintering).

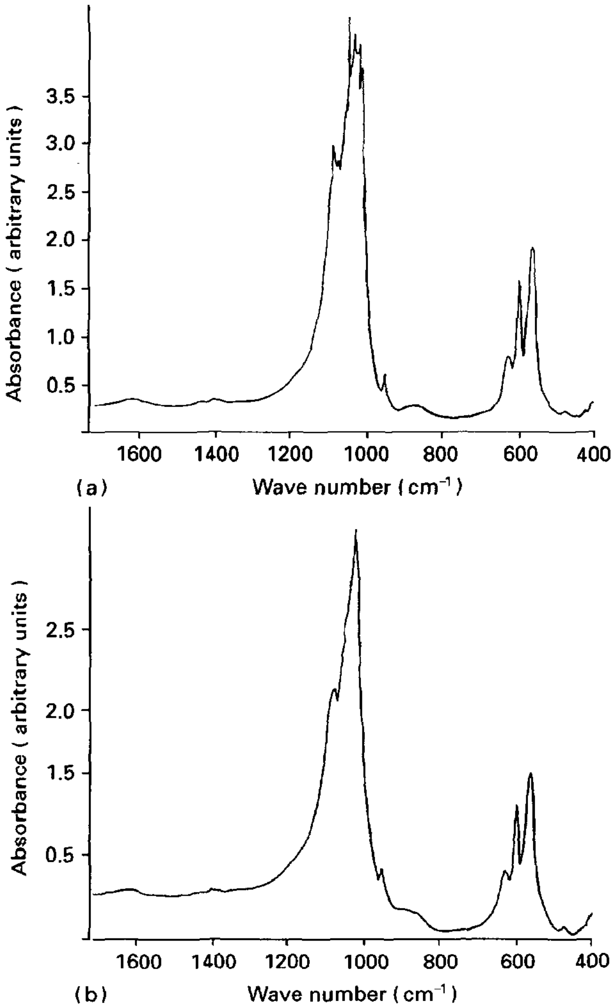

Figure 10 FTIR spectra of the initial hydroxyapatite powder (a) and of the powder after 310 MPa static precompaction and 2 MPa dynamic compaction (b).

increased compaction resulted in greater hardness. The difference in hardness between hydroxyapatite compacts prepared by sintering at 1100 °C and shock-consolidated compacts may be largely due to the difference in compaction degree. The resulting work-hardened structure observed in metals such as stainless steel [15] was not apparent in hydroxyapatite compacts in the compaction conditions used in this experiment (particle velocity of about 50 m/s). However, specimens with a compaction degree of 70% (as hard as conventionally sintered compacts) can be produced by the shock-consolidation technique.

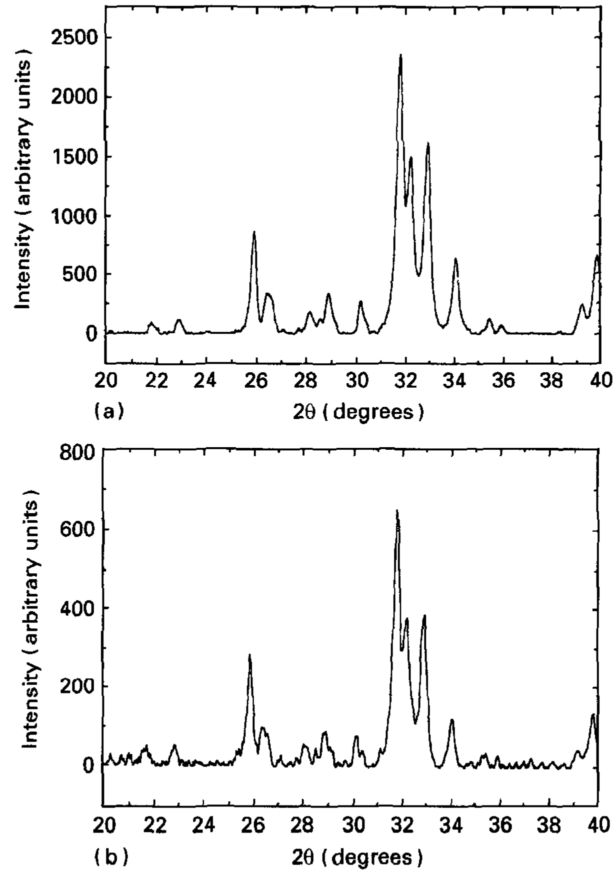

Figure 11 X-ray diffraction spectra of the initial hydroxyapatite powder (a) and the powder after 310 MPa static precompaction and 2 MPa dynamic compaction (b).

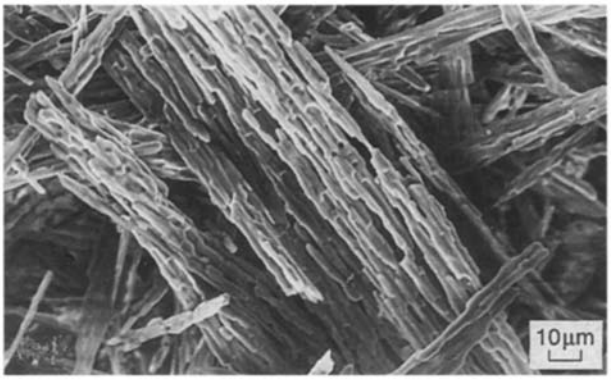

Figure 12 Scanning electron micrograph of β-calcium metaphosphate fibres.

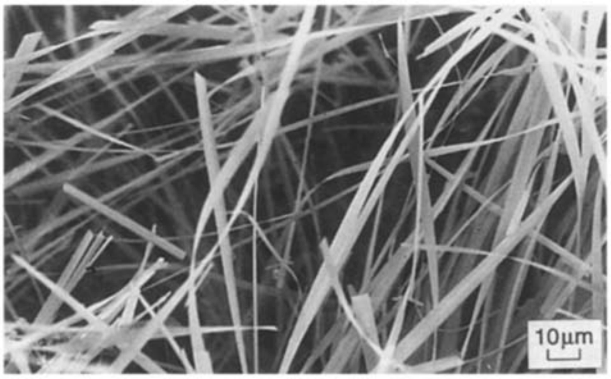

Figure 13 Scanning electron micrograph of octacalcium phosphate.

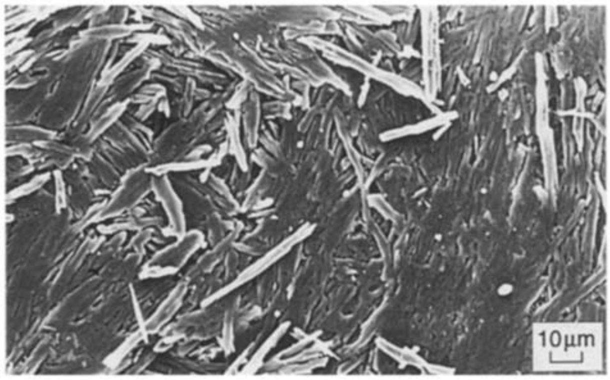

Figure 14 Scanning electron micrograph of β-calcium metaphosphate after dynamic compaction showing the preservation of the initial crystal shape.

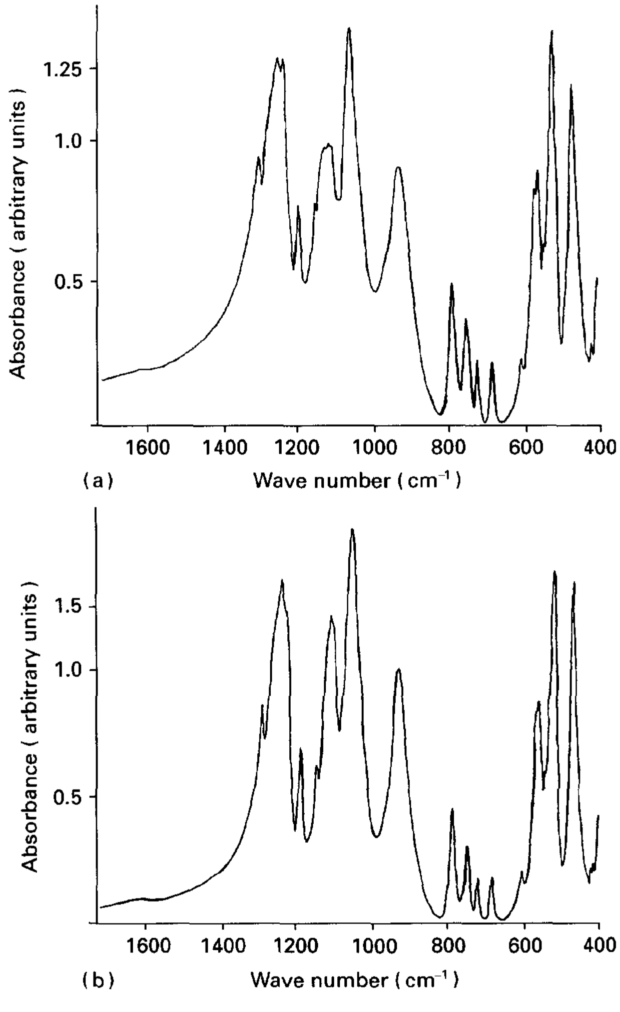

Figure 15 FTIR spectra of β-calcium metaphosphate before (a) and after (b) dynamic compaction.

3.1.5. Physicochemical characterization

FTIR spectroscopy and X-ray diffraction spectra of the original powders and typical compacts (static precompaction 310 MPa, dynamic pressure 2 MPa) revealed no major structural or chemical differences (Figs 10 and 11).

3.2. Trials with other calcium phosphate materials

Two unusual materials, β-calcium metaphosphate fibres (Fig. 12) and an unstable OCP (Fig. 13), were used to test the dynamic compaction process. Compacts of OCP and β-calcium metaphosphate fibres showed that fibre structure was retained after dynamic compaction (Fig. 14). The fibres were organized in layers, which is of particular interest since ceramic with high mechanical properties (great bending strength) could be prepared with this technique.

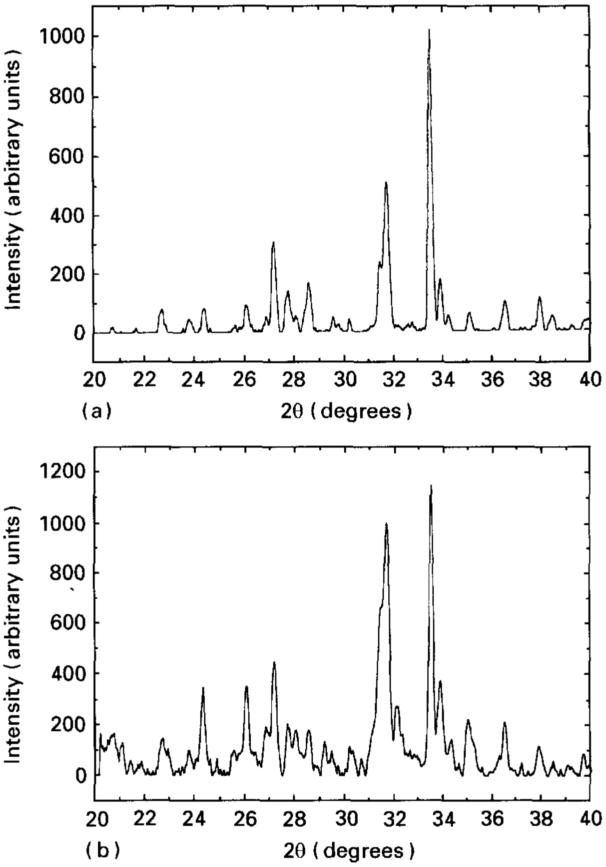

Figure 16 X-ray diffraction spectra of initial β-calcium metaphosphate (a) and after dynamic compaction (b).

FTIR and X-ray diffraction spectra (Figs 15–18) showed no major changes in the materials, even in unstable OCP, during dynamic compaction. As shown by Raybould [15] in dynamic compaction of stainless steel, high temperatures exist for extremely short periods. This makes shock compaction a particularly interesting process for materials which would degenerate or react chemically when exposed to the high temperatures involved in conventional techniques.

4. Conclusions

Dynamic compaction of hydroxyapatite powder at particle velocities of about 50 m/s produced compacts with about a 70% degree of compaction and a hardness similar to that of sintered compacts with the same compaction degree. Physicochemical analyses performed on several materials showed no differences in structure and composition after shock consolidation. These results indicate that dynamic consolidation allows the compaction of powders which are unstable during heating and cannot be produced by sintering. The microporosity remaining in materials after dynamic compaction is an advantage for biomedical

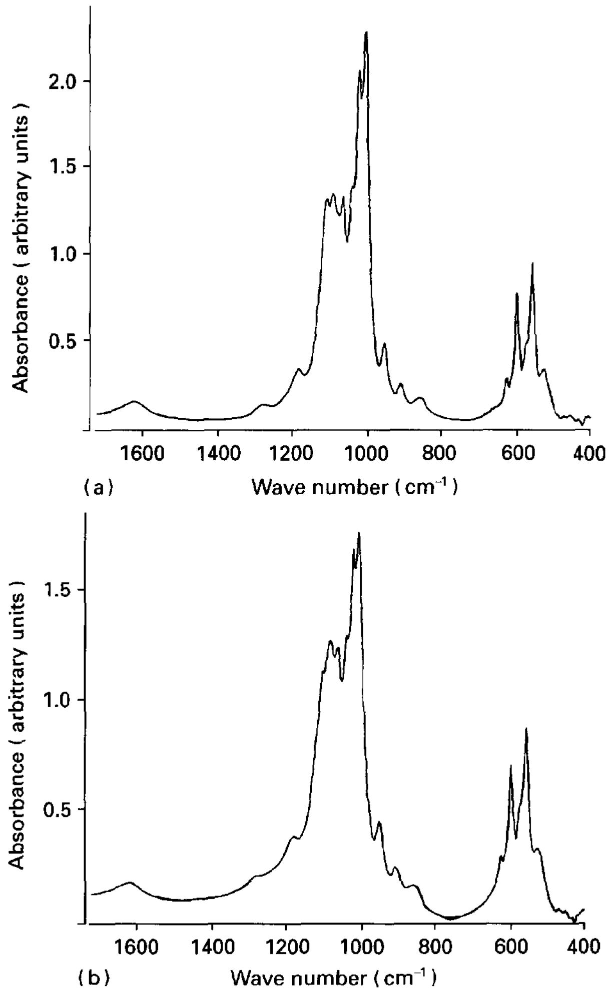

Figure 17 FTIR spectra of octacalcium phosphate before (a) and after (b) dynamic compaction.

applications since biological fluids can circulate inside the ceramic, thus promoting bioactivity. This technique might also be used to produce composite ceramics (associating a biological factor with calcium phosphate powders). Such an association seems possible since no external heating is involved and no changes appear to occur during the compaction process. The resulting circulation of biological fluids would allow the progressive release of the biological compound.

Acknowledgements

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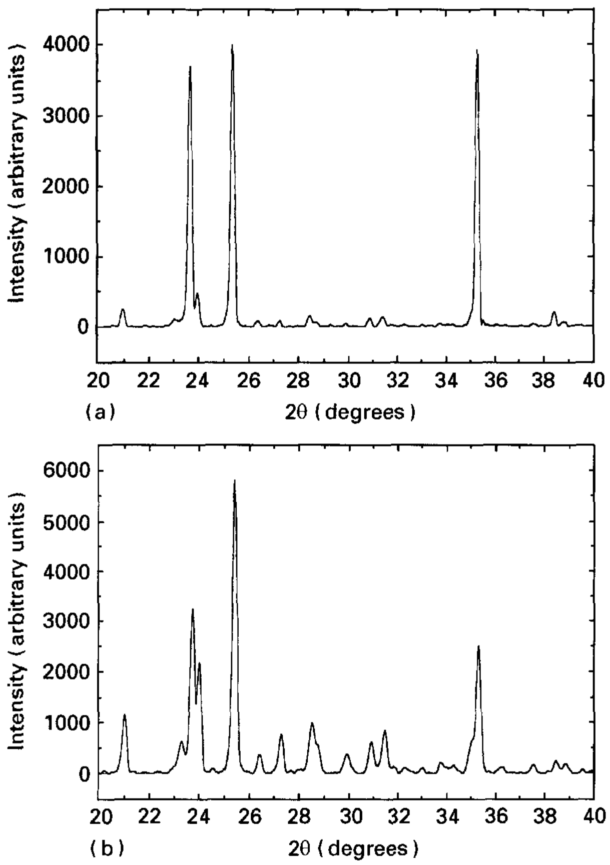

Figure 18 X-ray diffraction spectra of octacalcium phosphate before (a) and after (b) dynamic compaction.

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