Calcium phosphate is known as a major component of biological hard tissues. This study aimed to produce calcium phosphate by recycling kneaded surplus gypsum. β-dihydrate gypsum was derived from commercial dental β-hemihydrate gypsum, which was mechanically powdered and mixed with the liquid component of a commercial zinc phosphate cement. This mixture was fired at 1,200°C and evaluated by XRD analysis, thermal analysis and scanning electron microscopy (SEM). An acceptable ratio of mixing was 4 g of β-dihydrate gypsum powder to 1.5 mL of phosphoric acid liquid. XRD peaks were monotonic below 800°C, but new β-TCP was formed by firing at 900°C or more, although TG-DTA analysis of synthetic β-TCP suggested that some residual dihydrate gypsum remained in the sample. SEM images indicated a fused-block bone-like structure covered with phosphorus and calcium. These results suggest that production of synthetic β-TCP is possible through ecological techniques using recycled materials.

**Keywords:** Recycling, Synthetic β-TCP, Used gypsum, Phosphoric acid

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**INTRODUCTION**

Patients suffering from bone disorders such as fractures and tumors often require surgical management, but the excision of jaw bone can be physically, functionally and mentally distressing. If bone loss is significant, intraoral facial prosthetics are the only realistic option for recovering the facial profile and some degree of oral function, such as speaking, mastication and swallowing. Autogenous bone is the gold-standard material for such reconstruction because it has a high inherent physiological capacity for bone formation and demonstrates similar mechanical properties to those of the excised bone, but also carries the risk of extensive bone resorption at the donor site. A heterograft may be used as an alternative, but is itself complicated by the possibility of cross-infection. Thus, artificial bone substitute products are already commercially available, known as bio-active ceramics and including calcium phosphate (OCP), tri-calcium phosphate (TCP), hydroxyapatite (HAP), dicalcium phosphate dehydrate (DCPD), and tetra-calcium phosphate (Te-CP), are commonly used as bone substitute materials. HAP has been enthusiastically adopted for its superior bone conductivity and rapid osteoinductivity, but its mechanical strength in insufficient to support an artificial root (i.e., an implant) so it is predominantly used as a coating material for titanium surfaces. Furthermore, HAP does not enhance bone remodeling activity and can still harbor some types of infection. In contrast, TCP has outstanding potential as a bone substitute, but current commercial preparations are prohibitively expensive, which has limited its clinical application.

However, many dental products contain calcium and phosphorus. Calcium sulfate dihydrate set by a hydration reaction (Code: dihydrate gypsum, CaSO4·2H2O); calcium sulfate hemihydrate yielding calcining gypsum (Code: hemihydrate gypsum, CaSO4·½H2O); dental gypsum-bonded investment material; alginate impression material; and calcium hydroxide (Ca(OH)2) all contain significant amounts of calcium, while dental investment binder materials, etchands and zinc phosphate cements are well known sources of phosphorus. Dental gypsum is popular in making the dental models used for diagnosis and for the fabrication of dental restorations and prostheses. Then, surplus gypsum would be remaining because everyone weighing gypsum a little too much to avoid lacking gypsum when making models. Hemihydrate gypsum is thus consumed in large quantities for routine dental work, and dihydrate gypsum is produced in large amounts as a waste product of these activities.

Gypsum-bonding dental investment materials decompose to calcium oxide (CaO) when heated at high temperatures (~1,000°C) following the reaction:

\[ \text{CaSO}_4 \rightarrow \text{CaO} + \text{SO}_2 + \text{(O)} \]
Using this decomposition, an elegant method for developing new investment materials for titanium has been already reported\(^{30,31}\). Given that calcium phosphate (Ca\(_6\)(PO\(_4\))\(_2\)) can be easily produced by mixing CaO powder with phosphoric acid, and that CaO can be derived from anhydrous calcium sulfate (CaSO\(_4\), Code: anhydrite), we planned to test the viability of synthesizing artificial calcium phosphate from used dental materials. There are two methods for recycling CaO: 1) extracting it from used gypsum (dihydrate gypsum) by firing and then mixing this extract with phosphoric acid or 2) synthesizing calcium phosphate by high temperature firing after mixing used dental gypsum with phosphoric acid. Because of the instability of calcium oxide, we adopted the latter of these methods in our efforts to recycle dental materials into new materials for use as bone substitutes.

**MATERIALS AND METHODS**

**Gypsum powder preparation**
Commercial dental β-hemihydrate gypsum (Dental plaster D•L-S; Yoshino Gypsum Co., Ltd, Tokyo, Japan) was mixed at the manufacturer-recommended powder:water ratio for 30 s by hand, mechanically mixed for a further 30 s under a vacuum using a rotational mixing machine (V-mix; Yoshida Dental Mfg., Co., Ltd., Tokyo, Japan) and then set into gypsum models. These were allowed to fully set over 24 h and then powdered using a ball-mill apparatus (Pulverisette-6; Fritsch Japan Co., Ltd, Yokohama, Japan) at 360 rpm for 2–3 min. The resultant powder was sieved and particles of 150 µm or less were prepared as a test sample. For comparison, we also prepared a sample from pure gypsum powder (α-hemihydrate gypsum; Kuraray Noritake Dental Inc., Osaka, Japan).

**Optimization of powder:liquid ratio for synthetic TCP formation**
To derive calcium phosphate from our β-dihydrate gypsum powder, we used the liquid component of a commercial dental zinc phosphate cement (Elite cement; GC Co., Ltd, Tokyo, Japan) as a mixing liquid. The chemical reaction between the β-dihydrate gypsum and the phosphoric acid is as follows:

\[
2\text{H}_3\text{PO}_4 + 3\text{CaSO}_4 \cdot 2\text{H}_2\text{O} \rightarrow 3\text{H}_2\text{SO}_4 + \text{Ca}_6(\text{PO}_4)_2 + 6\text{H}_2\text{O}
\]

However, we found that there were discrepancies between the theoretical and practical values when trying to calculate the optimal powder:liquid ratios, so performed a validation experiment that indicated an optimal ratio of 4 g of prepared powder to 1.5 mL of liquid, which gave suitable fluidity and paste-like handling properties.

For comparison, a combination of pure α-hemihydrate gypsum powder and reagent-grade phosphoric acid (Wako Pure Chemical Industries, Ltd., Osaka, Japan) was used, at the same powder:liquid ratio.

**Thermal analysis**
Thermo-decomposition of the β-dihydrate gypsum is important because the calcium oxide within it needs to react easily with phosphoric acid during firing. We therefore investigated the thermal behaviors of both β-dihydrate gypsum and the mixture kneaded with phosphoric acid. Thermogravimetric/differential thermal analysis (TG-DTA) was performed on each of the prepared powders using thermo-mechanical analysis equipment (ThermoPlus TG 8120; Rigaku Co., Ltd., Tokyo, Japan). Around 30 mg of sample was placed in a platinum pan, heated to 1,500°C at 10°C/min, then heat-soaked for 10 min. The samples were monitored for weight loss and for the exothermic or endothermic nature of the reaction. Commercial reagent-grade β-TCP was also examined as a control.

**Firing procedure and sample preparations**
Samples powdered after uniform mixing and sufficient drying under each test condition were placed in a heat-resistant alumina dish in a commercial electric furnace (SINTRA; Argofile Japan Co. Ltd., Tokyo, Japan) and heated to the temperatures specified by the results of the thermal analyses described above. After firing at set temperature for 1 h, the dried or sintered compound was crushed and milled using a pestle and mortar and/or the ball-mill apparatus.

**X-ray diffraction (XRD) analysis**
Powder composition after mixing and firing was examined at each stage using XRD apparatus (LabX; Shimadzu Corp., Kyoto, Japan). Powder was placed in the designated glass holder and analyzed using Cu-K\(_\alpha\) radiation, at 40 kV and 30 mA, with a scanning speed of 2°/min and a scanning range of 10–70°. The XRD analyses were conducted for the following:

1) Gypsum powder: pure α-hemihydrate gypsum and commercial β-hemihydrate gypsum before and after mixing with acceptable water.
2) Samples: β-dihydrate gypsum (4 g) mixed with phosphoric acid (1.0, 1.5 or 2.0 mL) with no heating
3) Sample (4 g β-dihydrate gypsum) with 1.5 mL phosphoric acid fired at the temperatures determined by the TG-DTA analysis.
4) β-TCP (reagent-grade)
5) Pure α-hemihydrate gypsum powder kneaded with reagent-grade phosphoric acid

**Scanning electron microscopy (SEM) and Energy dispersive X-ray spectroscopy (EDX)**
The morphology of the calcium phosphate-like ceramics obtained by our process was observed using SEM (SEM 8000; Hitachi Co., Ltd., Tokyo, Japan) and compared between samples. Each sample was first coated in gold before placing in the metallic holder. Standard SEM procedures were used for the imaging of these samples. The same equipment was used to perform energy-dispersive X-ray spectroscopy on the sample fired at 800°C.
RESULTS

The thermal analysis of β-dihydrate gypsum is shown in Fig. 1. Two marked weight losses on the line of TG can be observed at 100°C and 1,200°C, indicated by arrows. The first rapid decrease coincided with exothermic reaction on DTA line, and resulted in the formation of hexagonal anhydrite from β-dihydrate gypsum, while the second represents the decomposition of anhydrite.\(^{20}\)

Figure 2 shows the thermal analysis of the mixtures at different powder:liquid ratios. There was little difference between them, although the sample with 4 g powder:1.0 mL liquid underwent a small initial weight loss at ~200°C that was not evident in the other samples. Since the liquid volume had no effect on thermal behavior, the sample with 4 g powder:1.5 mL liquid was chosen for subsequent experiments because of its preferable handling properties. In addition, the firing temperatures at which to analyze the crystal morphology of each mixture were extrapolated from this TG-DTA curve, and defined as 200, 650, 800, 900, 1,200°C, which were starting and ending points in three plateaus, shown by three arrows in Fig. 2.

The XRD analysis is shown in Fig. 3. The untreated gypsum sample (‘As set’) gave strong peaks of β-dihydrate gypsum and no evidence of the new compound formed by the reaction with phosphoric acid. With increased temperature, there appeared anhydrous crystals (see arrows in Fig.), but there were no further differences between 200°C and 650°C. Peak intensity varied with continuous firing and the fluctuating peaks are shown in the same graph. The anhydrite peak diminishes after firing at 800°C, and a small peak at 31–32 degrees,

Calcium phosphate was not detected in either ‘As set’ samples or those fired below 600°C. However, new peaks were observed after firing at either 900°C or 1,200°C. When reagent-grade β-TCP was compared with the sample after fired at 900°C and 1,200°C, they were totally equivalent.

![Fig. 1 TG-DTA curve of β-dihydrate gypsum.](image1)

![Fig. 2 TG-DTA curves of samples at different dihydrate gypsum/phosphoric acid ratios.](image2)

![Fig. 3 XRD analysis of reagent-grade β-TCP and β-dihydrate gypsum (4 g) mixed with phosphoric acid (1.5 mL) at each experimental stage.](image3)

![Fig. 4 XRD analysis of samples containing different dihydrate gypsum/phosphoric acid ratios after firing at 1,200°C.](image4)
which may represent calcium phosphate, became more prominent. After firing at 900°C, several peaks were formed, giving a similar profile to that produced by firing at 1,200°C. The comparison of pure β-TCP and the gypsum samples after firing at 900°C and 1,200°C reveals peak profiles of similar intensity and distribution. Figure 4 shows the comparison of the three samples prepared at different powder:liquid ratios, after firing at 1,200°C. A small difference was apparent at liquid volumes of 1.5 mL or greater, but this was considered insignificant.

The comparison of the calcium phosphates synthesized from β-hemihydrate gypsum and from β-dihydrate gypsum is shown in Fig. 5. Although the behavior of ‘As set’ β-hemihydrate gypsum was different to that of β-dihydrate gypsum before firing, these differences were no longer apparent after firing.

A similar examination was made using pure α-hemihydrate gypsum and reagent-grade phosphoric acid. In contrast to the recycled gypsum, 7.5 g of pure gypsum was required to react with 1.5 mL of liquid. Furthermore, the anhydrite peaks persisted after firing at 900°C and no crystal-like calcium phosphate was produced (Fig. 6).

Figure 7 shows the results of firing the reagent-grade β-TCP and the samples at 1,200°C. The pure β-TCP had little weight loss except a small decrease at temperatures over 1,000°C. Figure 8 shows an SEM image of the same sample tested in Fig. 9. Newly-produced calcium phosphate crystals are clearly observed in the image. The elemental distribution for this same sample is given in Fig. 9, which in addition to oxygen and carbon shows the obvious presence of phosphorus, calcium and sulfur.
DISCUSSION

Gypsum is mined in its natural form in several areas of the world, or can be produced industrially by a chemical reaction between powdery phosphorite and sulfuric acid. In reference to this manufacturing process, we investigated the viability of synthesizing calcium phosphate from the large volumes of used gypsum originating from the daily activities of dental laboratories. Gypsum is widely used in models for pretreatment diagnostics, orthodontics and in the fabrication of restorative prostheses and artificial dentures, but is also recognized as a bone filling material.33,34) In reference to this manufacturing process, we investigated the viability of synthesizing calcium phosphate from the large volumes of used gypsum. We calculated that 2 mol of phosphoric acid is required to react with 3 mol of β-dihydrate gypsum powder. Phosphoric acid has a greater specific gravity than water (1.67 g/mL), so the calculated ratio of phosphoric acid to β-dihydrate gypsum (liquid:powder) is 4.4:1. However, at this ratio, the mixture had unfavorable handling properties, so we increased the phosphoric acid content until an acceptable consistency was achieved at 4 g of β-dihydrate gypsum mixed with 1.5 mL of phosphoric acid. This ratio did not affect its thermal behavior while firing (Fig. 2), so crystal structures were determined by XRD at various temperatures (200, 650, 800, 900, and 1,200°C) as extrapolated from the thermal analysis (Fig. 2). XRD results of samples after firing at each temperature showed actually other compound formation or crystallinity.

Peaks of β-dihydrate gypsum were detected in the hardened sample (As set) at 24 h after mixing, which then changed to orthorhombic anhydrite after firing. Although the orthorhombic anhydrite peak was detected up to 800°C, its intensity weakened as firing temperature increased. After firing at 900°C, the diffraction pattern had undergone a drastic transformation. The robust peak at 26 degrees was markedly reduced, and new peaks had appeared, notably calcium phosphate peaks at 28 degrees and 35 degrees. There were no differences between the XRD patterns at 900°C and 1,200°C, or between those of reagent-grade β-TCP and the 900°C-fired samples, confirming the feasibility of producing artificial β-TCP from used gypsum.

Because dihydrate gypsum was stable to ~1,200°C (Fig. 1), it may seem counter-intuitive to decompose the gypsum at a lower temperature (900°C). Previous papers on dental gypsum-bonded investment materials50,31) have reported that gypsum disintegrates at lower temperatures in the presence of silicate dioxide. We hypothesized that the phosphorus used in this study would perform a similar role in the decomposition of our gypsum samples.

Our used material was dihydrate gypsum, which has low water solubility, and mixing dihydrate gypsum with phosphoric acid did not produce distinct hardening under normal conditions. Hemihydrate gypsum, however, was four times more soluble in water than dihydrate gypsum and gave improved manipulation and early hardening so was used instead of dihydrate gypsum. Although this is slightly less relevant to the recycling of the most widely used form of gypsum (the dihydrate form), we continued with the hemihydrate as a proof of concept. It is possible that further additives may be included in the process to increase the recovery of calcium phosphate from dihydrate gypsum. We found that phosphoric acid does not contribute to the hardening of gypsum, a finding that should be further explored in the future.
The phosphoric acid and gypsum tested in this study were commercial products, so some impurity is inevitable. We thus compared our study samples against pure α-hemihydrate gypsum and reagent-grade phosphoric acid to determine the effects of these trace impurities. β-TCP was not formed from these pure reagents even if fired at 900°C (Fig. 6), which may be due to α-hemihydrate gypsum decomposing at a higher temperature than β-dihydrate gypsum, or to the high powder:liquid ratio required to achieve suitable handling properties. α-hemihydrate gypsum powder is extremely fine compared with that of β-gypsum, so more is required to make a comparable slurry. The optimal weight for mixing with 1.5 mL of phosphoric acid was ~7.5 g, compared with only 4 g for β-gypsum. Despite these differences at high temperatures, both samples gave identical crystallization profiles after firing at 800°C (Figs. 3 and 6), so crystal alteration by higher firing temperatures seems to be necessary to produce the intended products.

Within the limitations of the current study, we successfully synthesized β-TCP using dihydrate gypsum powder and phosphoric acid. A fused-block exposed a coral-like structure after firing at 1,200°C. Novel compounds were formed by binding calcium ions (released from the gypsum) with phosphoric acid, as shown by the peak distribution on the mapping analysis. However, these data were not consistent with the thermal analysis results of synthetic and reagent-grade β-TCP, in which only the synthetic sample experienced a loss of mass after firing at 1,100°C, whereas the pure gypsum sample remained in the fused-block, perhaps due to insufficient firing. The firing conditions (e.g., firing temperature and holding time) remain to be optimized, as does the powder:liquid ratio. In addition, biological investigations will be needed to validate the use of these materials as bone substitutes.

We conclude that it is possible to produce synthetic β-TCP for use in bone reconstruction procedures using ecological techniques to use dihydrate gypsum obtained from hemihydrate gypsum.

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