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Biphasic products of dicalcium phosphate-rich cement with injectability and nondispersibility

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ABSTRACT

In this study, a calcium phosphate cement was developed using tetracalcium phosphate and surface-modified dicalcium phosphate anhydrous (DCPA). This developed injectable bone graft substitute can be molded to the shape of the bone cavity and set in situ through the piping system that has an adequate mechanical strength, non-dispersibility, and biocompatibility. The materials were based on the modified DCPA compositions of calcium phosphate cement (CPC), where the phase ratio of the surface-modified DCPA is higher than that of the conventional CPC for forming dicalcium phosphate (DCP)-rich cement. The composition and morphology of several calcium phosphate cement specimens during setting were analyzed via X-ray diffractometry and transmission electron microscopy coupled with an energy dispersive spectroscopy system. The compressive strength of DCP-rich CPCs was greater than 30 MPa after 24 h of immersion *in vitro*. The reaction of the CPCs produced steady final biphasic products of DCPs with apatite. The composites of calcium phosphate cements derived from tetracalcium phosphate mixed with surface-modified DCPA exhibited excellent mechanical properties, injectability, and interlocking forces between particles, and they also featured nondispersive behavior when immersed in a physiological solution.

1. Introduction

Calcium phosphate cement (CPC) is widely used as a filling material in dental and orthopedic applications because of its superior biocompatibility and osteoconductivity. CPC presents several advantages because its paste can be easily shaped during operation or injected into cavities by using a syringe without requiring an open portal through the tissues. The viscosity of the cement can be adjusted depending on its applications in orthopedic, craniofacial, and periodontal operations. However, the general paste form of conventional CPC (c-CPC), which comprises an equimolar mixture of tetracalcium [$Ca_4P_2O_9$, TTCP] and dicalcium phosphates (DCPs), monetite [$CaHPO_4$, dicalcium phosphate anhydrous (DCPA)], or brushite [$CaHPO_4 \cdot 2H_2O$, dicalcium phosphate dihydrate (DCPD)], requires almost 60 min to harden [1]. Moreover, c-CPC is characterized by low strength, easy dispersion when in contact with body fluids, and production of hydroxyapatite [$Ca_5(PO_4)_3OH$, HA] as the final product phase after setting. Several strategies are available to overcome these physiochemical shortages, including changing the composition of CPC by mixing reinforcements or binders, such as fibers or biopolymers, into the original calcium phosphate powder [2,3], increasing the ion concentration of the setting solution, supplying fresh sources of reactants to accelerate the reaction rate [4], or creating nanocrystal structured calcium phosphate [5].

When CPC components are primarily inorganic reactants, CPCs generally produce HA as the major product phase. Although HA is the major product of CPC and is a mineral component of cortical bones and enamel, the minerals derived after the reactions are hardly resorbed by bone regeneration after implantation. HA may be fabricated via CPC emulsion in oil, low-temperature settings, and so on [6,7]. These unfavorable conditions limit the applications of CPC in clinical use, especially for the repair of periodontal defects or as scaffolds for the bone in vertebral reconstruction.

To retain the osteoconductivity of CPC and to avoid undesirable bioresorption rates, many studies on the fabrication of biphasic or multi-phasic products after reaction with natural additives of collagens or specific proteins have been conducted [8,9]. Various synthetic calcium phosphate restoration particles have been proposed and applied

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for repairing bone damage by using synthetic methods via high-temperature thermal decomposition and composite additives. These restoration particles include a biphasic compound mainly composed of HA and beta-tricalcium phosphate [$Ca_3(PO_4)_2$, β-TCP] phases [10,11]. The effectiveness of these materials has been proven in various clinical applications [12–15]. The developed specific composition of CPCs, especially those with lower Ca/P atomic ratio phases than c-CPC, has a significant effect on bone growth enhancement [9]. A lower Ca/P atomic ratio would affect the strength of CPC and would also have a negative impact on the anti-dispersive ability of CPC pastes, thereby limiting its clinical applications.

Thus, the aim of this study is to investigate the physiochemical properties of the newly developed DCP-rich CPC composed of surface-modified DCPA powders with nanocrystals and TTCP. We also compared the injectability, dispersibility, strength, working/setting time, and final phases of DCP-rich CPCs with those of conventional c-CPCs.

2. Materials and methods

2.1. Preparation of powders

TTCP powder was prepared from the reaction of dicalcium pyrophosphate ($Ca_2P_2O_7$; Alfa Aesar, Johnson Matthey Company, MA, USA) and calcium carbonate ($CaCO_3$; Shimakyu's Pure Chemicals, Osaka, Japan) and was used as an ion supplement for the surface modification of DCPA particles. This sintering method for TTCP preparation was

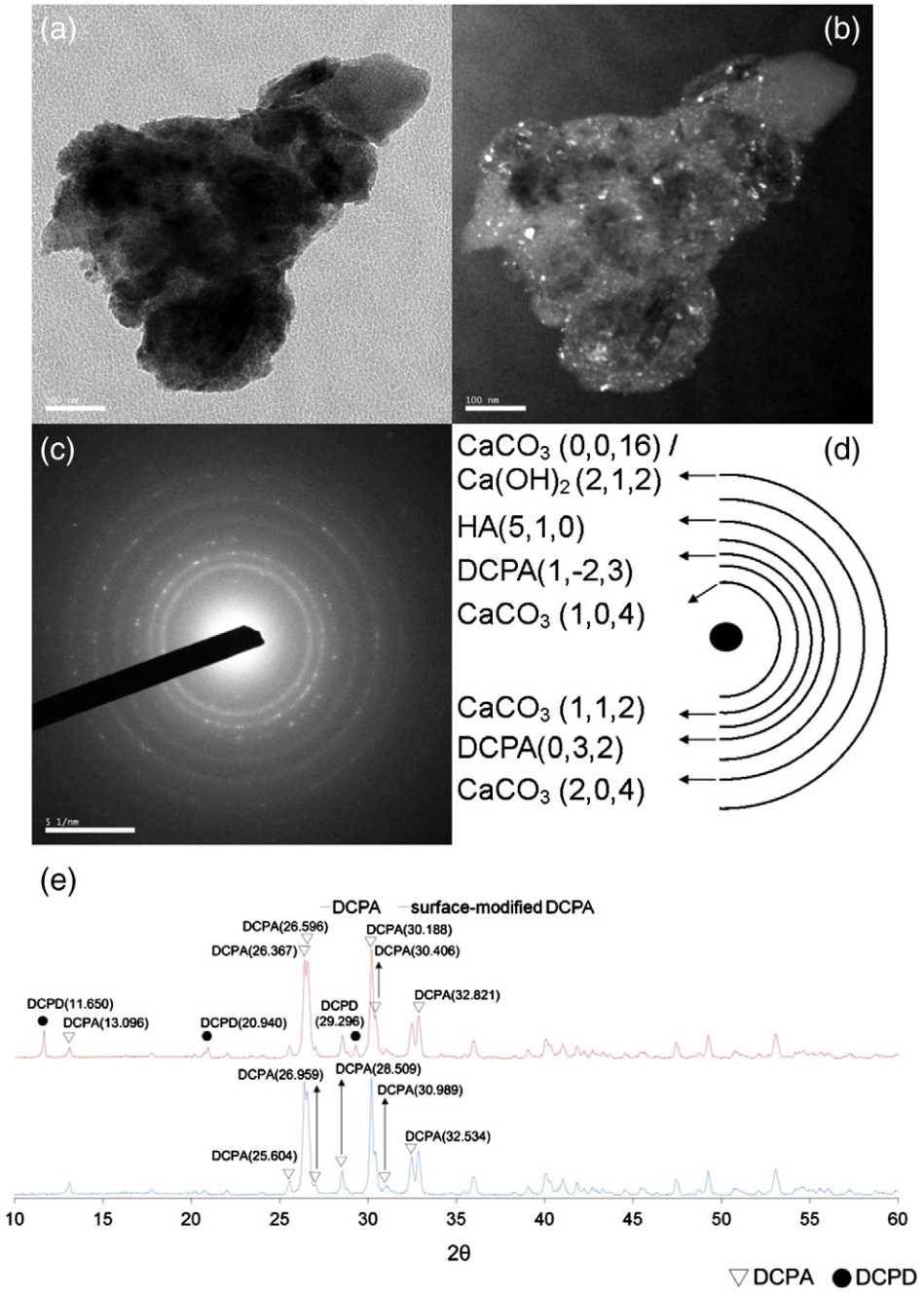

Fig. 1. BF (a) and DF (b) images of the same particle as well as the SAD pattern (c) with its index (d) of surface fine crystals of DCPA particles treated for 20 min. (e). XRD pattern of DCPA and fine surface crystals of DCPA particles treated for 20 min.