Synthesis and Characterization of Monetite from Calcium Carbonate Recovered from Carpet Waste

Kasidit Janbooranapinij, Arinchai Yimponpipatpol, Narueporn Ngamthanacom, Jularpar Suthiprapar, Gasidit Panomsuwan*

Department of Materials Engineering, Faculty of Engineering, Kasetsart University, Bangkok 10900, Thailand

*E-mail: gasidit.p@ku.ac.th

Abstract. Calcium carbonate (CaCO₃) was recovered from the carpet waste by combustion at 500 °C under an air atmosphere. The CaCO₃ had a pure calcite phase without detection of other crystalline phases, as confirmed by X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) measurements. Dicalcium phosphate (CaHPO₄) or monetite, which is known as a family of calcium phosphate-based biomaterials, was synthesized by mixing the CaCO₃ recovered from the carpet waste with phosphoric acid (H₃PO₄) solution. The reaction was kept at a constant temperature of 80 °C for 24 h. The XRD and FTIR results demonstrated that the pure monetite phase was successfully formed by the reaction between CaCO₃ and H₃PO₄. The energy-dispersive X-ray spectroscopy analysis confirmed that the monetite was composed of calcium, oxygen, and phosphorus. The results obtained in this work revealed that CaCO₃ recovered from carpet waste could potentially be an alternative material for the synthesis of monetite under mild conditions.

1. Introduction
The demand for carpet has been increasing every year due to the growth of populations and economies worldwide. In the manufacturing process, the carpet is eventually cut and trimmed along both edges to obtain specific dimensions, which generates a vast amount of carpet waste [1]. The proper management and utilization of pre-consumer carpet waste have become critical issues for manufacturers from the ecological and environmental viewpoints. Although the carpet industry has put significant efforts into the recycling of carpet waste to reuse as raw materials in the process, it is tough to implement as a practical process owing to the difficulty in separating the fibers and backing, the requirement for a multi-step process, and the high processing cost [2, 3]. Therefore, most of the carpet waste is discarded by either disposal in landfill or incineration, which does not add value and also causes environmental harm [4]. From the incineration process at high temperatures, besides the generation of heat, calcium carbonate (CaCO₃) is obtained as ash, while the fibers and backings are decomposed [5, 6]. CaCO₃ is used as the inorganic fillers (30–35%) in the adhesive for joining the primary and secondary backings of carpets [7]. Therefore, carpet waste is an alternative source for the recovery of CaCO₃, which can be widely used in various applications, such as reinforcement fillers in composites and construction materials [8, 9], adsorbents [10, 11], catalyst supports [12], and precursors in the synthesis of calcium phosphate-based materials [13–17].

Calcium phosphate is a mineral compound that contains calcium ions (Ca²⁺) and phosphate anions (e.g., PO₄³⁻, H₂PO₄⁻, and/or HPO₄²⁻) [18, 19]. Calcium phosphate is recognized as one of the most
promising materials for applications in bone replacement or regeneration due to its similar composition to the bones [19]. Among various types of calcium phosphate, hydroxyapatite (Ca_{10}(PO_{4})_6(OH)_2) has received much attention in the field of bone tissue engineering since it exhibits good biocompatibility, biological activity, and osteoconductivity [20–22]. In addition to hydroxyapatite, dicalcium phosphate (CaHPO₄) or monetite is another type of calcium phosphate that has attracted significant interest over the past years since it can regenerate the bond and also resorb in vivo faster than other calcium phosphates [23–25]. Moreover, monetite in a powder form is used in some toothpastes, chewing gums, and the food processing industries [26]. So far, monetite has successfully been synthesized using CaCO₃ as the starting precursor by several synthesis routes [15–17]. However, to the best of our knowledge, there have been no reports on the utilization of CaCO₃ recovered from carpet waste as a precursor for monetite synthesis.

In this work, the CaCO₃ fillers were recovered from the carpet waste by combustion at 500 °C under an air atmosphere. The monetite was then synthesized by mixing CaCO₃ with a phosphoric acid solution (H₃PO₄). The formation of the CaCO₃ and monetite phases were confirmed by X-ray diffraction (XRD) and Fourier-transform infrared spectroscopy (FTIR) analyses. In addition, the morphology of CaCO₃ and monetite was also examined by scanning electron microscopy (SEM). Furthermore, the formation of monetite from the reaction between CaCO₃ and H₃PO₄ was described and discussed.

2. Materials and Method

2.1. Preparation of CaCO₃ from carpet waste

The carpet waste, which was chopped and shredded into small pieces, was obtained from InterfaceFlor (Thailand) Co., Ltd. A total of 5 g of carpet waste was loaded into a ceramic boat and placed in a Vecstar tube furnace (model: VCTF4). The combustion process was performed at 500 °C with a heating rate of 10 °C/min for 1 h under an air atmosphere. After naturally cooling to room temperature, the product (1.98 g) was collected and then ground into fine powders using agate and mortar to further the synthesis of monetite.

2.2. Synthesis of monetite from CaCO₃ and H₃PO₄

One gram of CaCO₃ (10 mmol) was introduced into a glass beaker containing 40 mL of deionized water and then stirred at 400 rpm until the pH was stable. The pH was measured using FiveGo pH meter F2 (Mettler Toledo). Ten milliliters of H₃PO₄ solution (6 mmol) was slowly added into the suspension at the rate of 1 mL/min. The reaction was then kept at a constant temperature of 80 °C for 24 h. After that, the solid product was collected by vacuum filtration through a filter paper (Whatman no. 1). The solid product was repeatedly washed with deionized water and dried at 100 °C for 24 h.

2.3. Characterization

XRD patterns were recorded on a Bruker 8D Max diffractometer with Cu Kα radiation (λ = 0.15406 nm) at 40 kV and 40 mA. FTIR spectra were collected with a Bruker Alpha-E in the range of 500–4000 cm⁻¹, using the potassium bromide (KBr) method. SEM and energy-dispersive X-ray spectroscopy (EDS) mapping images were taken on a SU3500 Hitachi scanning electron microscope equipped with an Ametek EDAX, which were operated at an accelerating voltage of 5–15 kV. The specific surface area was measured on a Micromeritics 3Flex surface characterization analyzer at a liquid N₂ temperature (−196 °C). Prior to the measurement, the samples were heated at 150 °C for 12 h under vacuum conditions.

3. Results and Discussion

The phase structure of carpet waste after combustion at 500 °C was investigated by XRD. As depicted in figure 1a, the XRD pattern in the 20 range from 20° to 70° showed strong and sharp diffraction peaks, which are all assigned to the calcite phase of CaCO₃ (ICSD no. 37241). There was no detection of diffraction peaks of other phases, indicating the single calcite phase of CaCO₃.
The FTIR spectrum of the carpet waste after combustion was recorded in the wavenumber range of 500–4000 cm\(^{-1}\) and is demonstrated in figure 1b. The broad absorption peak at 3425 cm\(^{-1}\) corresponded to the bending mode of the O–H bond. A major absorption peak at 1428 cm\(^{-1}\) along with four minor peaks at 2500, 1800, 875 and 710 cm\(^{-1}\) can be attributed to the different vibration modes of the C–O bending in the carbonate group (CO\(_3^{2-}\)), which are the characteristics of CaCO\(_3\) [27, 28]. Besides, the small absorption peak of the C=C stretching was also observed at 1630 cm\(^{-1}\), which implied the presence of organic residue in the sample due to the incomplete decomposition of the polymeric materials (i.e., fiber, backing, and adhesive). Both the XRD and FTIR results confirmed that CaCO\(_3\) with a calcite phase was successfully recovered from the waste carpet by combustion at 500 °C under an air atmosphere.

![Figure 1](image1.png)

**Figure 1.** (a) XRD pattern and (b) FTIR spectrum of CaCO\(_3\) recovered from the carpet waste.

![Figure 2](image2.png)

**Figure 2.** SEM images of CaCO\(_3\) recovered from the carpet waste.

The SEM images in figure 2 show the large agglomeration of irregular-shaped CaCO\(_3\) particles with a dense surface. The agglomerate size was about 20–30 μm. The average particle size of CaCO\(_3\) (\(D\)) can be estimated from the Brunauer–Emmett–Teller (BET) surface area (\(S_{BET}\)) according to the following formula [29]:

\[
D = \frac{6}{\rho_b S_{BET}}
\]

where \(\rho_b\) is the density of CaCO\(_3\) (2.71 g/cm\(^3\)) [2]. The \(S_{BET}\) value was quite low at 1.94 m\(^2\)/g. The average particle size estimated using Eq. (1) was about 1.14 μm. The N\(_2\) adsorption-desorption isotherm of CaCO\(_3\) in figure 3 revealed low quantity adsorbed with a hysteresis loop corresponding to a type IV isotherm according to the International Union of Pure and Applied Chemistry (IUPAC). This characteristic feature of isotherm indicates non-porous or mesoporous structure of CaCO\(_3\) [30].
Figure 3. N$_2$ adsorption-desorption isotherm of CaCO$_3$ recovered from the carpet waste.

The phase structure of CaCO$_3$ after mixing with H$_3$PO$_4$ solution at 80 °C for 24 h was examined by XRD in the 2θ range of 20°–60°, as shown in figure 4a. Clearly, all diffraction peaks could be identified as dicalcium phosphate (CaHPO$_4$) or monetite phase (ICSD no. 917) with the absence of CaCO$_3$ and other phases. The FTIR was also employed to confirm the formation of the monetite phase. The FTIR spectrum in figure 4b shows the characteristic absorption peaks of different P–O stretching at 1130, 1067, and 998 cm$^{-1}$. Besides, the absorption peaks at 1376 and 897 cm$^{-1}$ are associated with the in-plane O–H bending and the P–OH stretching, respectively. The FTIR spectrum feature obtained in this work was similar to several previous reports [15–17]. The lack of appearance of the absorption peaks from the CO$_3^{2−}$ group indicated a complete transformation of CaCO$_3$ into monetite. With a combination of XRD and FTIR results, it confirmed that monetite was successfully formed by the reaction between CaCO$_3$ and H$_3$PO$_4$ at 80 °C, which can be explained as two-step reactions as follows:

\[
\text{CaCO}_3 (s) + 2\text{H}_3\text{PO}_4 (aq) \rightarrow \text{Ca} (\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} (s) + \text{CO}_2 (g) \quad (2)
\]

\[
\text{Ca} (\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} (s) \rightarrow \text{CaHPO}_4 (s) + \text{HPO}_4^{2−} (aq) + 3\text{H}^+ (aq) + \text{OH}^- (aq) \quad (3)
\]

Figure 4. (a) XRD pattern and (b) FTIR spectrum of monetite.

Figures 5a and 5b display the SEM images of monetite. It is seen that there is an agglomeration of irregular-shaped particles with a loose surface. The EDS mapping was also carried out to investigate the
elemental composition and distribution in the monetite samples. The EDS mapping images (figures 5d–5f) and the corresponding spectrum reveal the presence of Ca, P, and O elements with uniform distribution. The Ca, P and O content was 17.5, 18.8, and 63.7 wt%, respectively.

It should be noted that, in fact, the mixture of CaCO$_3$ and H$_3$PO$_4$ with the specific Ca/P ratio of 1.67 used for the synthesis in this work should give rise to the formation of the hydroxyapatite phase. However, the monetite phase was obtained rather than hydroxyapatite. Such an unexpected formation of monetite should be likely due to the deviation of the Ca/P ratio of the mixture to a value lower than 1.67. The deviation of the Ca/P ratio was caused by the residual organic compounds contained in the CaCO$_3$ product after combustion, which led to the lower Ca content than should have been the case. Therefore, the Ca/P ratio deviation to a value lower than 1.67 could result in the formation of monetite. The higher purity of CaCO$_3$ without residual organic compounds can be achieved by increasing the temperature or the time in the combustion process. This would result in the correct Ca/P ratio and precisely controllable formation of monetite and hydroxyapatite phases.

![Figure 5](image_url)

**Figure 5.** (a, b) SEM images of monetite. EDS mapping analysis: (c) the area investigated, (d, e, and f) the distribution of carbon, oxygen, and phosphorus, and (g) the corresponding EDS spectrum.

### 4. Conclusions
CaCO$_3$ was recovered from the carpet waste by direct combustion at 500 °C under an air atmosphere. The XRD and FTIR results confirmed the formation of a single calcite phase without other crystalline phases. The morphology of CaCO$_3$ showed a large agglomeration of irregular particles. By reacting CaCO$_3$ with H$_3$PO$_4$ solution at 80 °C for 24 h, the monetite phase was successfully formed, as evidenced by the XRD and FTIR results. The results obtained in this work showed the potential utilization of CaCO$_3$ recovered from the carpet waste as a precursor for the synthesis of monetite via a simple method.
under mild condition. In addition to monetite, we anticipate that other calcium phosphate materials, such as hydroxyapatite, tricalcium phosphate, etc., could also be synthesized by adjusting the Ca/P ratio and synthesis conditions.

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