Effects of Aragonite & Calcite Precipitated Calcium Carbonate on the Synthesis of Calcium Lactate

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Introduction

Calcium carbonate (CaCO₃), natural occurring and abundant mineral comprising approximately 4% of the earth crust, has three crystal phases – calcite, aragonite and vaterite[1,2]. The calcium carbonate used in industries could be classified into limestone powder, ground calcium carbonate, and PCC by their shape, particle size and preparation method. The ability to manufacture PCC with specific morphology, structure, and particle size is invaluable due to its wide application as plastics, rubbers, paper, paints, food, medical supplies, etc[3]. However, PCC is not commonly used as calcium source in food and medical industry owing to little absorption rate in the body. Therefore, hybrid compounds used to be made by reacting PCC with various organic acids, such as lactic acid, citric acid, gluconic acid, and pantothenic acid, for high absorption.

In general, calcium lactate is the most widely used as a calcium fortification with high absorption rate and for the food and drug industry as various foods. Also, it is commonly used as tissue reinforcing agents in various processed agricultural products and pickled foods[4].

The objective of this study was preparing calcium lactate using PCC by the solution process. Also, experiments were conducted to investigate the effect of calcite and aragonite PCC on the yield of calcium lactate in the solution process.

Experimental

By investigating effects of PCC morphologies on lactic acid solution under experimental conditions in the solution process, the calcium lactate was synthesized in 2.0 mol % lactic acid solutions. Also, calcium lactate was synthesized at various temperatures (20~80 °C). For each experiment, the solution of 100ml was prepared in the Pyrex reactor (Φ=80mm; h=95mm) as shown in Fig. 1.

In this reaction, a stirrer was operated at a rotation rate of 600rpm. The reaction temperature was kept at 20~80 °C by circulating water through an outer jacket on the reactor. To monitor the variation of the pH continuously and temperature during the reaction in solution, a digital pH meter and a thermometer, were used, respectively. Before the PCC was carried into the reactor, the lactic acid in each solution was sufficiently mixed for 10 min by stirring to ensure that the lactic acid sufficiently
dissolved. The reaction was stopped until there were no variations of pH in suspension. After the reaction stopped, the products were filtered, dried and analyzed. The yield of calcium lactate was quantitatively calculated and the characterization of calcium lactate was investigated by FT-IR and SEM.

Results and discussion

1. Effects of reaction temperatures on the synthesis of calcium lactate

The solution process, which synthesizes calcium lactate using aragonite and calcite, in lactic acid-water solution was carried out at 20~80℃. At this condition, the concentration of lactic acid solution was fixed as 2.0 mol%, and the amount of PCC (either aragonite or calcite) was 1.0 g. Its yield of calcium lactate variation was shown in Fig.2.
Fig. 2 showed that the yields of calcium lactate increased with temperature up to 60°C. However, yields of calcium lactate decreased at higher temperatures (70~80°C). At that time, the maximum yield of calcium lactate using aragonite was 85.0% and that using calcite was 88.7%, respectively. For both cases, the optimum temperature for the preparation appeared at around 60°C. Also, the variation of pH and yields of calcium lactate in the solution of lactic acid-water at 60°C were shown in Fig. 3. During the period without aragonite and calcite (from the start to the position (1) in Fig. 3) the initial pH of lactic acid solution (2.0 mol%) was 2.38. By adding the aragonite and calcite, the protruding peak of pH was shown immediately (the position (2), 10 seconds after PCC addition in Fig. 3). At position (2), the yields of calcium lactate were 77.0% (using aragonite) and 75.7% (using calcite), respectively. Also, the pH increased rapidly from 2.38 to 4.87 and 4.10 during the period. From position (3) to position (4) in Fig. 3, despite the slow forming rate at the initial stage, the final yield of calcium lactate appeared higher when calcite was used. At same time during the period, pH and yield of calcium lactate, in case of using aragonite, were kept constant at the end of the reaction. But, the yield of calcium lactate increased to position (5) when calcite was added. Those results were considered to be due to different solubilities of aragonite (1.5 mg/100cm³ H₂O at 20°C) and calcite (1.4 mg/100cm³ H₂O at 20°C). At that time, final yield of calcium lactate appeared 85.0% (using aragonite) and 88.7% (using calcite), respectively.

2. Characterization of calcium lactate using PCC

Characteristic alterations are observed in the FT-IR spectrum of calcium lactate using aragonite and calcite (Fig. 4). The strong OH valence band of calcium lactates appeared in the region of 3000~3500cm⁻¹ of FT-IR spectra only with very low intensity. In this study, the FT-IR spectra of calcium lactate (lactic acid : PCC = 2 : 1), shows the characteristic carbonyl band at 1500~1750 cm⁻¹, however with very low intensity. In these results, characteristic signals found at approximately 3000~3500 cm⁻¹ (O-H stretching), 1500~1750 cm⁻¹ (C=O stretching), as well as 1300~1400 cm⁻¹ (C-H bending) identified calcium lactate. Also, graph (1) and graph (2) were very similar. This means that calcium lactates, obtained by reaction of lactic acid and PCC, were same compound, irrespective of PCC morphologies.

Fig. 5 shows SEM images of crystal of calcium lactate and un-reacted PCC (aragonite and calcite). Calcium lactate using PCC exists as plate-like crystals with smooth surface. This result indicates that the particles of calcium lactate using PCC fused together and formed large aggregated particles. Also, SEM analyses showed that prepared calcium lactate appeared as same crystal form, irrespective of PCC morphologies, reaction temperatures and concentrations of lactic acid.

![Fig. 4. FT-IR spectra of calcium lactate using PCC: (1) Calcium lactate using aragonite; (2) Calcium lactate using calcite](image)
Conclusion

The yields of calcium lactate, synthesized by reaction using lactic acid and PCC, increased when reaction temperature increased up to 60°C. At that time, the maximum yield of calcium lactate using aragonite was 85.0% and that using calcite was 88.7%, respectively. Despite the slow forming rate at the initial stage, the final yield of calcium lactate appeared higher when calcite was used. Compared to the FT-IR spectrum of calcium lactate using aragonite and calcium lactate using aragonite shows characteristic signals at approximately 3000–3500 cm\(^{-1}\) (C-H stretching), 1500–1750 cm\(^{-1}\) (C=O stretching), as well as 1300–1400 cm\(^{-1}\) (C-H bending). Also, SEM analyses showed that the prepared calcium lactate appeared as plate-like crystal form, irrespective of PCC morphologies, reaction temperatures and concentrations of lactic acid.

References

3) H. Konno, Y. Nanri, “Effect of NaOH on aragonite precipitation in bath and continuous crystallization in causticizing reaction”, Powder Technology, 129 (2003), 15-21
5) K. S. Seo, C. Han et al., “Synthesis of calcium carbonate in a pure ethanol and aqueous ethanol solution as the solvent”, J. of Crystal Growth, 276 (2005), 680–687