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NOTE

Saccharides with Different Molecular Weight Affects Crystallization of Calcium Carbonate

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In this work, soluble starch, chitosan, glucose and sucrose were used to induce the formation of calcium carbonate. The $CaCO_3$ crystals were characterized by scanning electron microscope and Fourier transform infrared spectrograph. The results showed saccharides with different molecular weight had significant influence on the morphology of $CaCO_3$.

Key Words: Soluble starch, Chitosan, Glucose, Sucrose, Calcium carbonate, Biomineralization.

Calcium carbonate is the most widely used mineral filler, primarily in the paper, plastics, paints and coatings industries. Industrial applications of calcium carbonate are determined by the control of chemical purity, polymorphism, particle size and morphology. Various controllable syntheses of calcium carbonate have received much research interests[1-3]. Certain additives, such as biopolymers, synthetic polymers, fatty acids and polypeptides containing acidic or basic functional groups, have been shown to influence the growth of calcium carbonate crystal[4]. Depending on the application, a wide variety of soluble organic additives have been examined for their effects on the crystallization of calcium carbonate[5-11]. Saccharides are one of important polymers widely presenting in living organisms. Saccharides are also used as organic matrix to biomimetic crystallization of calcium carbonate. A novel aragonite[12] was synthesized with specific morphology by β-cyclodextrin. Glucan[13] was used as a template to control synthesis of aragonite calcium carbonate. As a derivative of chitin, chitosan is adjustable and frequently employed as an insoluble substrate to mimic biomineralization[14-16]. The study focused on the preparation of calcium carbonate particles in the presence of various organic macromolecules, soluble starch, chitosan, glucose and sucrose, which find a wide spread use in the paper and non-paper industries. The aim of these experiments is to find the effect on the polymorph and morphology of calcium carbonate by organic macromolecules.

The anhydrous calcium chloride, sodium bicarbonate, soluble starch, chitosan, glucose and sucrose were analytically pure. All solutions were prepared with deionized water. The size and morphology of $CaCO_3$ precipitates were characterized by using SEM on a DSM 940 A (Carl Zeiss, Jena) microscope. The specimen powders were prepared for SEM analysis by coating each with a thin gold/palladium layer to prevent specimen charging under the electron beam. Calibration of $CaCO_3$ pellets (in a proportion of 1 % in KBr powder) was performed and recorded with a Niolet 870 Fourier transform infrared spectrometer between 4000 and 400 cm^{-1} with a resolution of 4 cm^{-1}.

The precipitation of calcium carbonate was initiated by pouring 250 mL of sodium bicarbonate solution (C = 0.020 mol dm^{-3}) into the same volume (250 mL) of calcium chloride solution (C = 0.020 mol dm^{-3}). The additive was added to the sodium bicarbonate solution prior to mixing the reactants. The additive final concentration was all 5 wt %. When a large number of crystals were formed in the reaction vessel with 5 wt % soluble starch, 5 wt % chitosan, 5 wt % glucose and 5 wt % sucrose, respectively. The crystalline calcium carbonate was collected and filtered through the solution and rinsed with distilled water and anhydrous alcohol at least five times, then centrifuged, dried and collected.

Fig. 1 shows typical SEM pictures of $CaCO_3$ particles precipitated in both the absence and presence of saccharides. Regular rhombohedral $CaCO_3$ particles were obtained in the distilled water as shown in Fig. 1A. It is surprised to find leaf-like $CaCO_3$ particles (Fig. 1B) precipitated in the presence of soluble starch. There were irregular particles formed which composed of little rhomboidal particles when glucose was presented. At the same time, regular rhombohedral $CaCO_3$ particles were still obtained (Fig. 1C). However, maize cob-pine flower shaped $CaCO_3$ aggregates radially aligned crystals were obtained (Fig. 1D). Fig. 1E showed the $CaCO_3$ particles catkin- like, which formed in sucrose solution.These results indicated that saccharides with different molecular weight had significant influence on the morphology of $CaCO_3$.

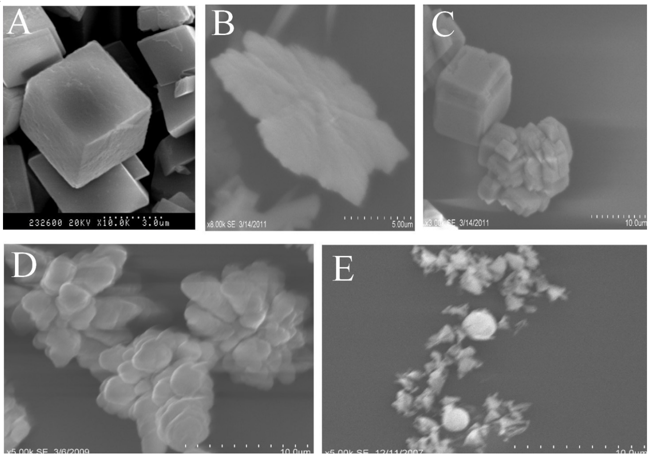

Fig. 1. SEM of $CaCO_3$ crystal obtained from the absence and presence of saccharides solution; A-E: only water, soluble starch, glucose, chitosan, sucrose

Infrared spectra of $CaCO_3$ crystals produced saccharides solution were shown in Fig. 2. While in Fig. 2A, 2B, 2C and 2E, simultaneous occurrence of absorption peaks at 874 cm^{-1} and 708 cm^{-1} or 874 cm^{-1} and 706 cm^{-1} or 870 cm^{-1} and 706 cm^{-1} indicated that the presence of crystalline was calcite. The slight discrepancy between experimental and published IR values could be attributed to the required grinding of a $CaCO_3$ sample with KBr to produce pellets. There was little difference among those four curves. It was not difficult to find there an absorption peaks at 874 cm^{-1} and 744 cm^{-1} in Fig. 2D, which indicated the crystalline vaterite.

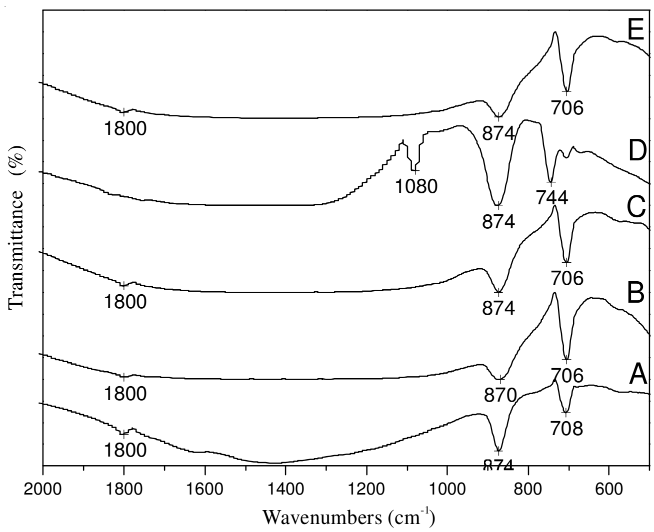

Fig. 2. FT-IR spectra of $CaCO_3$ obtained from the absence and presence of saccharides solution; A-E: only water, soluble starch, glucose, chitosan, sucrose

As we know, soluble starch is traditionally thought to be completely unbranched, it is now known that some of its molecules contain a few branch points. Apart from its influence on the vaterite nucleation, the soluble starch also affects the size of the calcite crystals by adsorbing at their surfaces. Maybe through the branch points, soluble starch induced the leaf-like $CaCO_3$ particles. Although differental morphology of $CaCO_3$ were obtained from the other saccharides solution, they were all calcite just as in water. According to literatures,we know that Ca^{2+} ions would be attracted by the oxygen of hydroxyl from all directions in the system. Through electrostatic matching, structural and interfacial molecular recognition, will lead to the local high supersaturation with $CaCO_3$ around the nucleation site. So the different molecular structure of saccharides will lead to the differental morphology of $CaCO_3$.

Conclusion

The results show that the soluble starch, glucose, chitosan and sucrose can influence precipitation of $CaCO_3$ from solution. It suggests that saccharides with different molecular weight play an important role in the regulation of precipitation of calcium salts during the process of biomineralization. This research may provide new insights into the control of morphologies of $CaCO_3$ and the controllable synthesis of novel inorganic materials.

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