

Effect of succinic acid on the crystal habit of alpha-hemihydrate gypsum prepared from phosphogypsum: Experimental and molecular dynamics simulation study

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ABSTRACT: To efficiently select a reasonable amount of crystal habit modifier to improve the hydration matrix strength of alpha-hemihydrate gypsum (α -HH), this study used phosphogypsum (PG) as the raw material to prepare α -HH using a semi-liquid phase method under high temperature and high pressure. The effects and mechanism of succinic acid on the growth and development of α -HH were investigated by experimental study and molecular dynamics (MD) simulations. The results showed that succinic acid increases the formation time of α -HH. The corresponding bending/compressive strength was adjusted from 3.3/21.1 MPa to 7.0/50.0 MPa. The X-ray photoelectron spectrometer (XPS) further confirmed this finding. The succinic acid carboxyl group reacted with Ca^{2+} ions, and the succinic acid was adsorbed on the surface of α -HH, inhibiting its axial growth, explaining this mechanism. The (002) face had the largest surface energy (55.24 J/m^2) and roughness, fastest growth rate, and the available adsorption sites. The binding energy of succinic acid to the (002) face was the largest at 0.15% concentration. The following sequence was obtained: $E_b(0.15\%) > E_b(0.3\%) > E_b(0.10\%) > E_b(0.06\%)$. Succinic acid significantly inhibited the axial growth of α -HH, which can reasonably explain the experimental results. This guided the preparation of α -HH selective crystallizer with PG.

KEYWORDS: phosphogypsum, alpha-hemihydrate gypsum, succinic acid, molecular simulation, modification mechanism

INTRODUCTION

Phosphogypsum (PG) is a by-product of wet production of phosphoric acid in the phosphate fertilizer industry. It is estimated that for every 1 ton of phosphoric acid produced, 4–6 tons of PG are produced as a waste by-product; the global annual output of PG is about 280 million tons [1, 2]. 85% of PG is discarded into a large number of stocks without pretreatment, resulting in severe pollution of air, soil, and water, which may be harmful to human health [3], thus utilization of PG has become an urgent problem. One promising technology is to convert PG into hemihydrate gypsum [4–6]. Calcium sulfate hemihydrate is divided into alpha-hemihydrate gypsum (α -HH) and beta-hemihydrate gypsum (β -HH) due to the difference in crystal form and dehydration mode. Their chemical compositions are the same [7, 8], but β -HH crystal has poor crystallinity, large specific surface area, and low mechanical strength, while α -HH crystal has stable crystal structures, compact hydration products, and high mechanical strength. Thus, α -HH is a critical phase in hemihydrate gypsum, and also the primary phase in high-strength gypsum, and has good application prospects in precision casting, automobiles, and aircraft, etc. The crystal habit of α -HH crystal has attracted increasing attention [9–13], for example, its

use as a raw material to produce ceramic molds [14], cement [15], fiber self-setting biomaterial [16], and to repair bone defects, etc. [17]. Without adding a crystal habit modifier, α -HH crystal often takes the shape of needles or long rods, which is unfavorable for its fluidity and strength [18]. The organic acid such as succinic acid is commonly used as a α -HH crystal habit modifier, which is characterized by low concentration required and suitable crystal transformation effect. The adsorption characteristics of succinic acid and maleic acid on this crystal have been studied extensively [19, 20], mainly showing that it complexes with Ca^{2+} , inhibiting growth on the C-axis and reducing the aspect ratio of the crystal [21].

With the extensive application of computing technology in chemical simulation, a solution has been proposed to study the macroscopic properties of α -HH crystal and explain the crystal habit associated with its molecular dynamics. Yang et al [22] used molecular dynamics (MD) to study its equilibrium morphology and analyzed the relationship between the distribution of water molecule channels and its elation. The MD method was also used to show that Al^{3+} is preferentially adsorbed on the (002) face at the top of the crystal and significantly inhibits its growth along the C-axis [23]. Tang et al [24] calculated the adsorption energy of dicarboxylate ions on each

face of α -HH crystal using MD and explained the effect of trace amounts of sodium dicarboxylate on its morphology. The use of cetyltrimethylammonium bromide with different mass fractions as an additive was found to regulate the crystal morphology of hemihydrate gypsum by being adsorbed on the (110) and (100) faces [25]. Luan et al [26] studied the effect of different mass fractions of aluminum sulfate solution on phosphorus plaster crystal using MD. They found that the optimal mass fraction of aluminum sulfate solution had an excellent inhibitory effect on the crystal faces with faster crystal growth. Regarding the crystallization mechanism of succinic acid on α -HH crystal, these studies have only considered its effect inhibiting growth in the long-axis direction, but few studies have been conducted on the crystal habit of α -HH crystal and the effect of succinic acid on its crystal habit and mechanical properties.

Unlike other experimental techniques, MD can be used to study the effects of crystal habit modifiers in detail at the atomic level. This paper studies the effect of succinic acid on the formation process, crystal development, and macroscopic mechanical properties of α -HH crystal. Materials Studio is used to establish a surface model of the vital growth surface of α -HH crystal and the adsorption of different concentrations of succinic acid on α -HH crystal was carried out. The model of the crystal surface of gypsum and its interaction energy and surface energy was calculated by MD to further analyze the crystal habit of α -HH crystal surface and the adjustment of α -HH crystal with different succinic acid concentrations, systematically explaining the crystal mechanism and effect of succinic acid on the crystal habit of α -HH crystal.

MATERIALS AND METHODS

Materials

The PG used in the test was obtained from Hubei Yuangu New Building Materials Technology Co., Ltd., China. Fig. 1 is an optical photo of PG, showing that the morphology of PG is mainly rhombus, with a relatively complete crystal shape. The crystal habit modifier was an analytically pure succinic acid chemical reagent produced by Shanghai McLean Biochemical Co., China.

Experimental procedures

The α -HH was prepared by the semi-liquid phase method, the oily organic matter and residual acid was pretreated by washing multiple times in the PG, the suspension was repeatedly washed with water until the pH was 7, and the resulting PG was stored at 45 °C, dried in a blast drying oven, and sieved through a 0.3 mm square-hole sieve for later use. 0.06%, 0.1%, 0.15%, and 0.3% succinate solutions (added according to mass percentage of PG) were mixed with the pretreated PG based on the experimental concentrations,

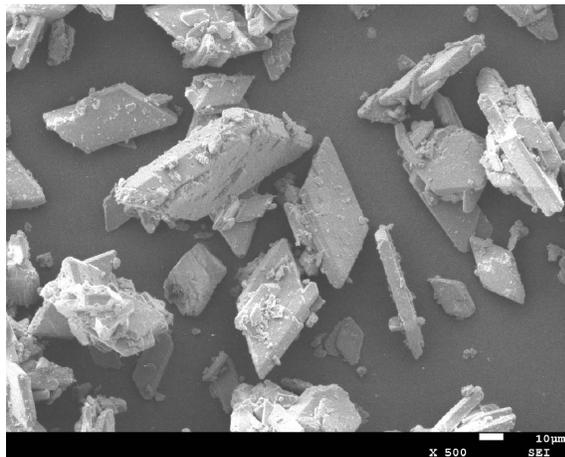


Fig. 1 Microstructure of PG crystal.

and the PG slurry was fully mixed using a net slurry mixer. A mixer thoroughly stirred the PG slurry, and it was placed in an autoclave. After autoclaving at 144 °C for 1–6 h, the reaction product was put into an oven, dried at 110 °C, and ground up for subsequent use.

Characterization

Sample morphology was performed using a Scanning electron microscope (SEM, JSM 7500F, JEOL, Japan) and digital microscope (KH-7700, Takaishi Co., Japan). An X-ray photoelectron spectrometer (XPS, AXIS Supra, Shimadzu Co., Japan) was used to examine the surface of the calcium sulfate hemihydrate. The crystal water content of the above products was analyzed according to GB/T 17669.2-1999. Their compressive strengths were tested according to JC/T2038-2010 “ α -High strength gypsum plaster” (Chinese national standard for high strength gypsum plaster).

Simulations

The molecular model of a solvent box of succinic is shown in Fig. 2(a). The α -HH crystal structure was obtained from Bezou et al [27] with unit cell dimensions of $a = 12.0317 \text{ \AA}$, $b = 6.9269 \text{ \AA}$, $c = 12.6712 \text{ \AA}$, $\beta = 90.270^\circ$, and $Z = 12$. The crystal system was monoclinic with spatial group I 121 (Fig. 2(b)). The crystal morphology in a vacuum was predicted using attachment energy (AE). Fig. 3(a) illustrates the four dominant faces predicted by AE [(002), (200), (110) and (1–10)]. The interaction of aqueous solvents on the four crystal faces was considered under actual test conditions, and the crystal morphology was modified, as shown in Fig. 3(b). The morphology was rod-like, and the percentage of crystal surface area decreased significantly at the crystal tip (002), consistent with the morphology of naturally growing crystals observed by digital microscope. Simulation of the crystal surface used a sheet (slab) model composed of multiple atomic

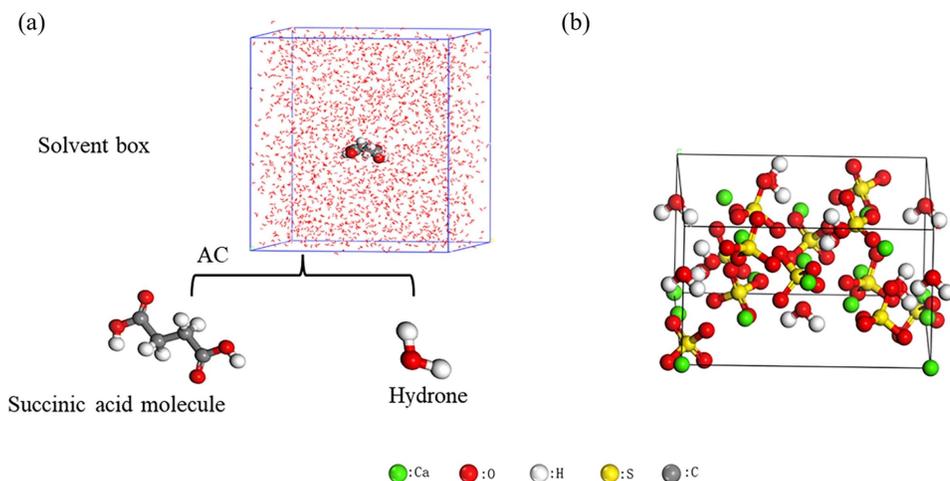


Fig. 2 Schematic diagram of building model. (a) solvent box of succinic, and (b) $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ crystal.

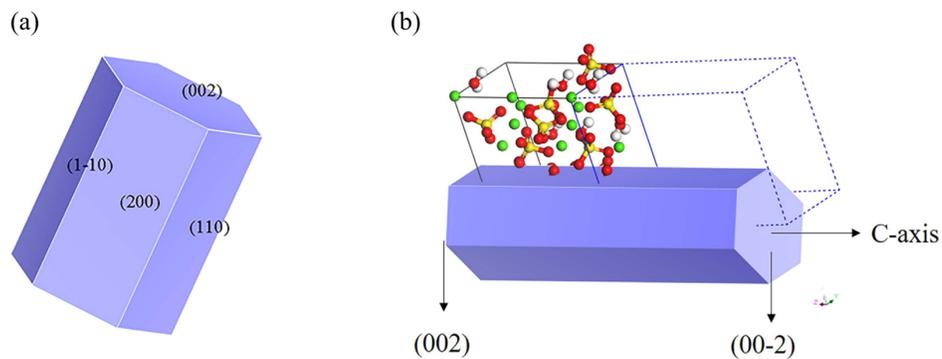


Fig. 3 $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ crystal morphology predicted using AE. (a) in a vacuum, and (b) in an aqueous solution.

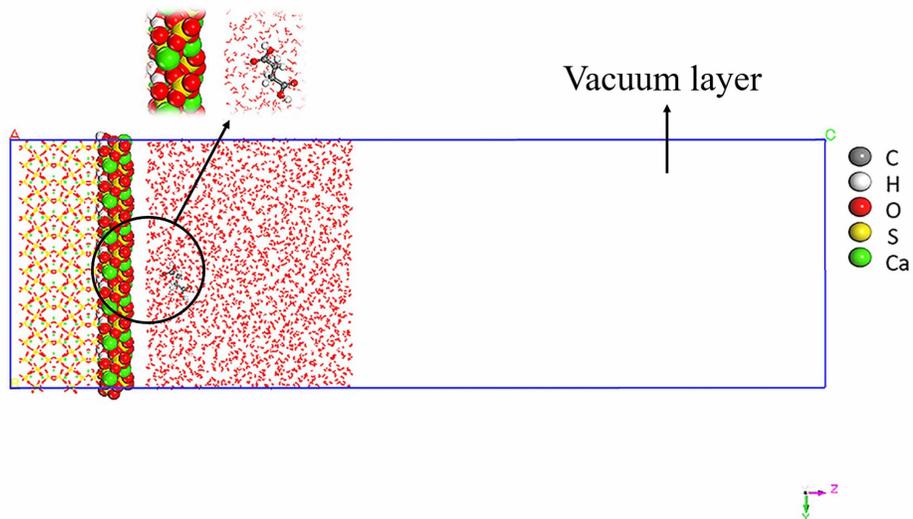


Fig. 4 Interface adsorption model between succinic acid solution and $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$.

layers and a vacuum layer. The α -HH crystal was cut into four important growth surfaces, a 15 Å vacuum layer separated the (1 × 1) surface supercell structure layer crystal, and a vacuum region with a thickness of 15 Å was set between the lamellar layers. In the slab model, the positions of the bottom atoms were fixed.

Fig. 3(b) shows that the model of α -HH crystal in an aqueous solution predicts a shape of a long stick, and the area of the (002) face was the smallest. Therefore, this paper mainly considers the (002) face of α -HH crystal to simulate the effect of the succinic acid solution on α -HH crystal, and the (002) face of α -HH crystal was cut to establish a 4 × 7 supercell. Succinic acid solution layers with respective concentrations of 0.06%, 0.1%, 0.15%, and 0.3% were established, and placed upon the substrate surface model along the Z-axis to form a α -HH growth interface model. As shown in Fig. 4, a vacuum layer of 80 Å was left above the solution layer.

The MD simulation process used the force module in Materials Studio 2017. The simulation condition was a regular system (NVT), leaving the particle number, volume, and temperature of the system unchanged. The temperature was set to 417.15 K (the experimental temperature was 144 °C), the temperature control was velocity scale [28], and the COMPASS force field was used [29]. The van der Waals force and electrostatic force were calculated using atom-based and Ewald summation methods [30], respectively. The potential energy was calculated with a computational accuracy of 1×10^{-5} kcal/mol and a spline intercept of 15.5 Å. MD simulations of the above system were carried out at 200 ps. Finally, the surface energy, interaction energy, and binding energy were calculated using the statistical average of the last 50 ps to ensure that the system is in equilibrium.

Surface energy [23] is an essential physical quantity that determines surface stability. It can be expressed as E_{surf} which was calculated by the following formula:

$$E_{\text{surf}} = \frac{E_{\text{slab}} - \left(\frac{N_{\text{slab}}}{N_{\text{bulk}}}\right)E_{\text{bulk}}}{2A} \quad (1)$$

where E_{slab} refers to the total energy of the slab, E_{bulk} is the energy of the $\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$ unit cell, N_{bulk} represents the energy of the unit cell, N_{slab} is the atom number of the slab, A is the surface area, and N_{bulk} is the atom number of the bulk.

The Interaction energy (ΔE) [23] between α -HH crystal surface and Succinic acid in an aqueous solution can be calculated using the following formula:

$$\Delta E = \frac{E_{A1+B+A2} - E_{A1+B} - E_{A2+B} - E_{A1} - E_{A2} + E_B + E_{A1+A2}}{2} \quad (2)$$

where E_{A1} is the total energy of succinic acid in the solution layer, E_B denotes the total energy of water in the solution layer, E_{A2} represents the energy of the crystal surface layer, $E_{A1+B+A2}$ represents the total

energy of the interface model, E_{A1+B} is the total energy of the solution layer, E_{A2+B} is the total energy of water in crystal surface layer and solution layer, and E_{A1+A2} is the total energy of succinic acid and the crystal surface layer in the solution layer.

The binding energy [23] reflects the interaction between the solution and the crystal layer and is defined as the inverse of the interaction energy:

$$E_b = -\Delta E \quad (3)$$

The larger E_b is, the stronger the interaction between the ion solution and the crystal surface.

RESULTS AND DISCUSSION

Effect of succinic acid on crystal morphology

Fig. 5(a) shows the development process of α -HH crystals without succinic acid. It was observed that after autoclaving for 1 h, a small amount of the PG exists as plate-like crystals which were not dissolved in water, and the number of α -HH crystals was small. After 2 h, the crystals were significantly reduced, and many fine needle-like α -HH crystals were formed. After 4 h, the crystals developed into long rods, demonstrating that α -HH prepared by the PG semi-liquid phase method forms in a dissolution-crystallization process.

Fig. 5(b,c) show the development process of α -HH crystal doped with 0.15% and 0.3% succinic acid, respectively. Fig. 5(b) shows that at a succinic acid concentration of 0.15%, the number of plate-like PG crystals was large after autoclaving for 1 h. After 2 h, the number of rod-shaped α -HH crystals increased significantly. After 4–6 h, the rod-like crystals further developed into short columns, but a small amount of plate-like PG crystals were still not converted into α -HH. Fig. 5(c) shows that at a succinic acid concentration of 0.3%, a small number of needle-shaped α -HH crystals could be observed after autoclaving for 4 h, and longer rod-shaped α -HH crystals appeared after 6 h.

The above analysis shows that the addition of an appropriate amount of succinic acid significantly improves the crystal morphology of α -HH crystals, but delays the dissolution of PG crystals and the crystallization of α -HH crystals. This conclusion is consistent with the conclusion on the effect of succinic acid on the crystallization water content of the autoclaved product.

Previous studies have attributed the inhibitory effect on α -HH crystallization to selective adsorption of the inhibitor on active growth sites on the crystal surface [31], so the experimental method of XPS was used to investigate the detailed mechanism further. XPS spectra of α -HH are shown in Fig. 6(a). The curve-fitting analysis shows that C 1s spectra of α -HH located at 284.8 eV is the standard peak of carbon, arising from carbon contamination or C–C/C–H in the succinic acid. The component at 286.1 eV came from

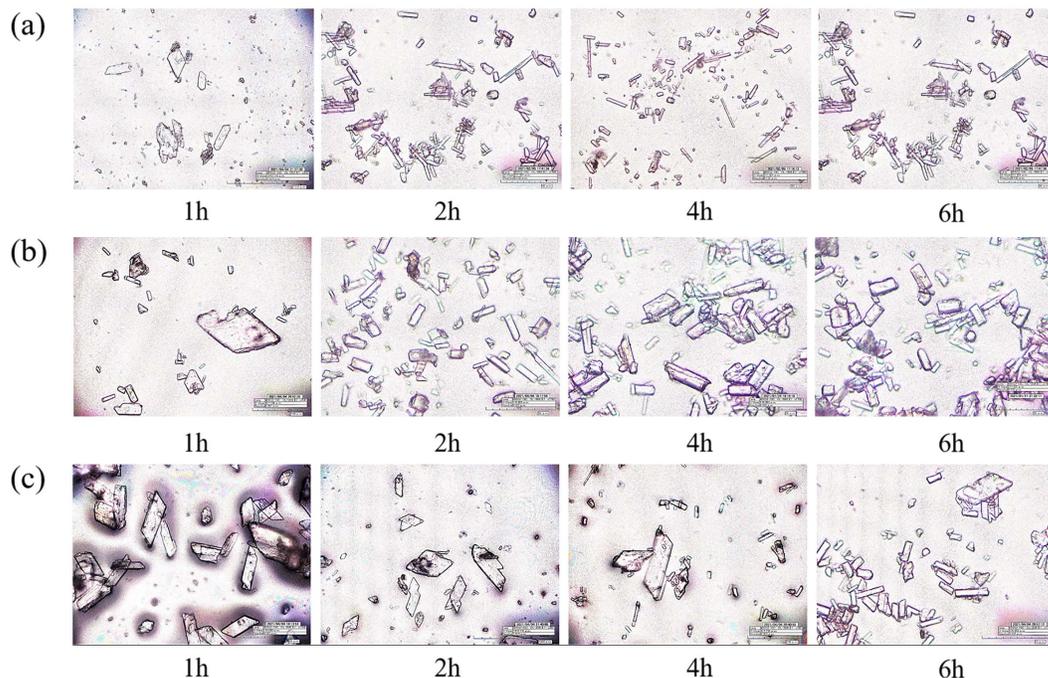


Fig. 5 Development of α -HH crystals over time at varying succinic acid concentrations, (a) 0%, (b) 0.15%, and (c) 0.3%.

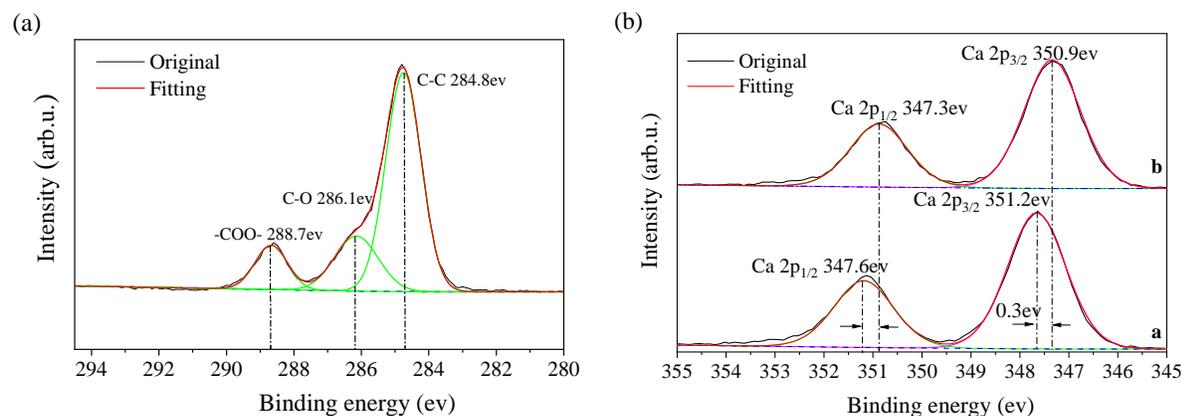


Fig. 6 High-resolution XPS of (a) C 1s peak in α -HH at 0.15% succinic acid concentration, and (b) Ca 2ps peaks in α -HH at 0% and 0.15% succinic acid concentrations, respectively.

C—O in the residual organic matter in the raw PG. A new signal appeared at 288.7 eV, which explains the appearance of —COO on the crystal surface, indicating the adsorption of succinic acid. For Fig. 6(b), Ca 2p had two peaks at 347.6 eV and 351.2 eV. After succinic acid modification, however, the binding energy of Ca 2p appeared at 347.3 eV and 350.9 eV. The binding energy of Ca 2p decreased by 0.3 eV, which may be due to the carboxyl group of succinic acid. When the carboxyl group reacts with the Ca^{2+} of the α -HH surface, the negatively charged carboxyl group contributes electrons, reducing the binding energy. Based on these results, it can be inferred that succinic

acid reacts with the Ca^{2+} , leading to the adsorption of succinic acid.

The effect of succinic acid concentration on PG dehydration rate

When α -HH was prepared by the PG semi-liquid phase method, the reaction product was a mixed α -HH, dihydrate gypsum, PG, and anhydrite phase. Due to the difference in crystal water content between dihydrate gypsum and α -HH, the closer the crystal water content of the reaction product was to 6.21%, the greater the amount of α -HH produced. Experiments demonstrated that when succinic acid was not

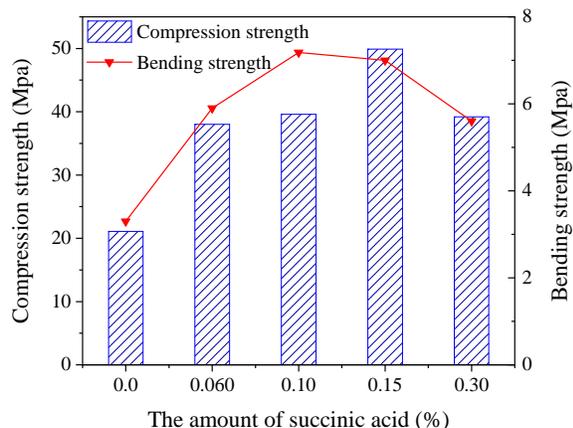


Fig. 7 Effect of succinic acid on compressive and bending strength of α -HH.

added, the crystalline water content of the reaction products decreased significantly with longer steaming time. After 4 h, the decrease slowed down significantly. After adding succinic acid, the crystalline water content changed little for the first 1 h. After 1 h, it began to decrease significantly with longer autoclaving time. When the succinic acid concentration increased to 0.3%, the crystal water content began to decrease significantly after 4 h, but the concentration of the 6 h reaction product was only 11.3%, so the α -HH concentration in the product was low.

The above analysis shows that the addition of succinic acid significantly delays the formation of α -HH. To maximize the conversion of PG into α -HH crystal within 6 h, the succinic acid content should be kept below 0.15%.

The effect of succinic acid on mechanical properties

Fig. 7 shows the effects of different amounts of succinic acid on the mechanical properties of the α -HH crystal. At concentrations within the range of 0.06%–0.15%, the mechanical properties of α -HH were significantly enhanced with increasing concentrations. The bending/compressive strength of α -HH reached a maximum of 7.0/50.0 MPa at 0.15% concentration. Thus, the succinic acid concentration has a significant influence on the mechanical properties of α -HH. As the concentration continued to increase to 0.3%, the bending/compressive strength was greatly reduced, indicating that excessive succinic acid content is not conducive to the growth of α -HH crystals.

Simulation of α -HH crystal habit and interaction

Surface energy is an important parameter to characterize the surface activity of crystals. It roughly reflects the stability of different α -HH crystal surfaces, and therefore how strongly or weakly it interacts with

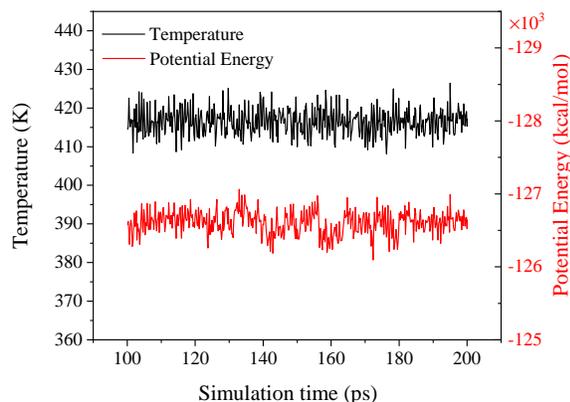


Fig. 8 Potential energy and temperature over simulation time.

the surrounding environment. The higher the crystal surface energy (Eq. (1)), the more easily the crystal face adsorbs substances to reduce its surface energy, causing the crystal surface energy to decrease and tend to be stable.

Comparison of the surface energy for the critical growth surfaces of α -HH crystal, shows that the crystal face with the highest surface energy was the (002) face at 55.24 J/m², followed by the (200) face, whose surface energy is 46.94 J/m²; the face with the most negligible surface energy was (110), with a surface energy of 39.31 J/m². The results show that the surface energy of the (002) face is the largest, making this face less stable than the others. This leads to faster growth of the (002) face during crystal growth, which directly affects the final morphology of the crystals, a finding consistent with previous report [32].

The roughness of the crystal face affects its growth rate. Rough faces have more growth steps and kink points, making it easy for them to adsorb solute molecules in the solution. The (1-10) face is the flattest and had the least number of cavities, and therefore the smallest number of available adsorption sites, whereas the (002) face was the roughest and had the most cavities, and therefore the most available adsorption sites. This results in adsorption of the most solvent molecules in the cavity and, ultimately the strongest adsorption affinity. At the same time, the respectively roughness of the (002), (110), (1-10), and (200) critical growth α -HH crystal faces were 1.61, 1.49, 1.27, and 1.48. The results show that the rougher the surface, the more atoms are exposed and the larger the surface energy.

As the succinic acid concentration increased from 0.06% to 0.3%, its binding energy with the (002) crystal surface gradually increased, with respective values of 12.26 kcal/mol, 23.89 kcal/mol, 39.65 kcal/mol, and 38.96 kcal/mol. The interaction with the (002) face was the strongest at 0.15% concentration,

resulting in strong growth retardation in the axial direction, and the crystal changed from a long rod shape to a short column shape, which improved the mechanical properties of α -HH. As the concentration continued to increase to 0.3%, the binding energy decreased, which can help explain the experimental results (Fig. 7). The binding energy of succinic acid on the surface of α -HH (002) showed the sequence $E_b(0.15\%) > E_b(0.3\%) > E_b(0.10\%) > E_b(0.06\%)$ at different concentration levels.

The above analysis shows that 0.15% succinic acid concentration, the (002) face with a faster growth rate was inhibited the most, and the crystal morphology developed to a short column shape. When the content of succinic acid continued to increase to 0.3%, the crystal growth inhibition in the C-axis direction would be weakened.

This simulation study judged, molecular dynamics calculations to have reached equilibrium by observing whether temperature and energy fluctuations were maintained within reasonable intervals and remained relatively stable. Fig. 8 shows typical potential energy and temperature fluctuation curves in the MD simulation of succinic acid solution on the (002) surface for the last 100 ps. The potential energy fluctuated from -126094 to -126992 kcal/mol, with an absolute difference of 898 kcal/mol and a relative difference of less than 5%. The temperature fluctuated from 407 to 427 K, so the simulation reached a relatively balanced state. These data show the calculated simulation, and the results were reliable.

CONCLUSION

This work has found that adjusting the succinic acid concentration delays the dissolution time of PG and significantly delays the formation of α -HH. A 0.15% concentration converts PG to short columnar α -HH to the greatest extent, and the corresponding bending/compressive strength of the α -HH was adjusted from 3.3/21.1 MPa to 7.0/50.0 MPa. According to the XPS experimental results, the succinic acid carboxyl group reacts with Ca^{2+} , resulting in the adsorption of succinic acid on the surface of the α -HH, verifying that succinic acid inhibits the axial growth of α -HH. MD simulation was used to investigate the intermolecular interactions on the α -HH surface and the effect of succinic acid on the α -HH crystal surface. The results show that the (002) surface has the largest surface energy (55.24 J/m^2) and roughness, fastest growth rate, and most available adsorption sites. The binding energy of succinic acid to the surface of α -HH (002) was the largest at 0.15% concentration, inhibiting the growth of α -HH along the C-axis to the greatest extent, and resulting in the formation of short columnar α -HH in the experiment. Through experiments and MD simulations, a new and meaningful method is provided for the selection of α -HH crystallizer types

and concentrations.

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