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Process Amplification and Performance Characterization of Nano-coated Heavy Calcium Carbonate

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Abstract: **The reaction system of Ca(OH)2- calcite -CO2 is different from the carbonation reaction of Ca(OH)2 suspension absorbing CO2 to produce ultrafine calcium carbonate. It not only contains the dissolution process of CO2 and Ca(OH)2 solid particles, the chemical reaction of CO32- and Ca2+, but also accompanied by the nucleation process of newly generated nano calcium carbonate on the surface of calcite particles.In this paper, the effects of calcium hydroxide concentration, ultra-fine calcite powder content and gas stirring form in the process of nano-coating ultra-fine calcite powder were investigated. According to different pilot-scale process conditions, the products were prepared and the SEM morphology, specific surface area and particle size distribution were measured.**

Keywords: **Calcite powder; Calcium hydroxide concentration; Gas stirring; Pre-production test**

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1.Introduction

Mineral powder with high whiteness, as the industrial raw material with the largest consumption in papermaking, plastics, coatings and other industries, plays an important role in reducing product cost and improving performance. With the rapid development of China's economy, the annual consumption of high whiteness minerals has increased dramatically, and a large number of low whiteness resources have been abandoned as tailings, resulting in waste of resources and destruction of ecological environment[1-2]. Taking calcite and marble carbonate minerals as examples, although the reserves in China are large, the reserves of high whiteness resources are limited, and mineral resources with whiteness below 90% are abandoned because they cannot be effectively utilized. Filling non-metallic mineral powder is an important means to reduce the cost and improve the performance of polymer matrix composites such as plastic and rubber. Because there is a great degree of incompatibility between mineral powder and polymer matrix, it is necessary to carry out inorganic coating or organic modification on the surface of mineral powder [3-6].

The study on failure mechanism of plastic polymer matrix composites shows that in the process of crushing nonmetallic minerals into fine powders, the particles break along the cleavage plane of crystals to form sharp edges and flat sections. After being filled into the polymer, the edges and corners and flat sections are difficult to form a close combination with the macromolecule of the polymer, such as winding and adsorption, so as to form the weak point of micro damage of the composite after being subjected to external force. Treating mineral particles with surface modifier or coupling agent can improve the interfacial compatibility between mineral particles and polymer matrix to a certain extent, but it cannot change the inherent morphological defects of the particles, especially the adverse effects of their sharp edges and flat fracture surfaces on the application properties of the composites[7-12].

Calcite is selected as raw material, and a layer of high whiteness nano calcium carbonate is deposited on the particle surface under chemical reaction conditions[13-14]. The coating passivates the edges and corners, and the surface nano-structure strengthened the bonding between polymer and particle interface, which significantly improved the compatibility between mineral particles and polymer, thus improving the strength of the composite [15-21]. This is of great significance for the composite functionalization of non-metallic minerals, the efficient utilization of low whiteness mineral resources and the improvement of the performance of nonmetallic mineral fillers.

2.Experimental preparation

2.1. Materials and Instruments

Ultrafine calcium carbonate (calcite powder), Haicheng Fuhai Co., Ltd., 800 mesh; Industrial calcium oxide, Hebei Lude Group Company, with a purity of 99.5%; Pilot plant for coating nano calcium carbonate, Zibo Qingda Powder Engineering Co., Ltd.; SEM Quanta 200F, FEI company; PSI–4 gas permeation particle size analyzer, Zhang ruifu powder testing technology research institute; ZBD whiteness analyzer, Wenzhou Ludong instrument factory.

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2.2. Technological Process

Adding calcium oxide into the pilot plant, adding water, stirring and dispersing for a certain time, and forming a Ca(OH)2 solution with a certain concentration. According to a certain proportion of the total mass of the system, ultrafine calcite powder is added to stabilize the stirring speed at a certain value. Introducing the mixed gas of CO2

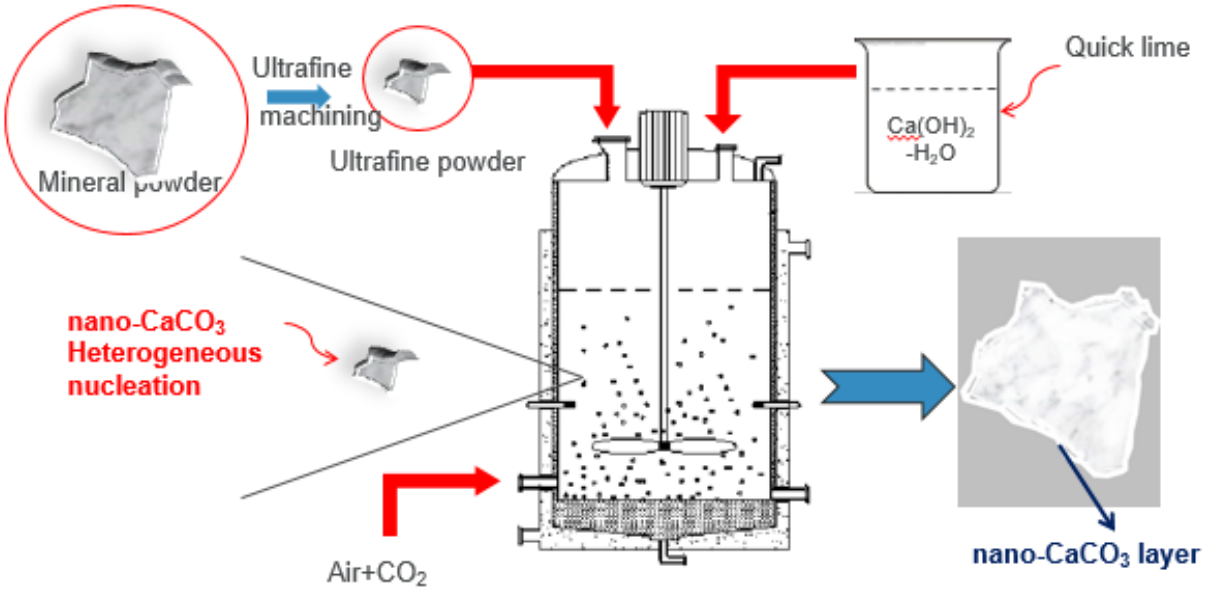

Figure 1 Schematic diagram of coating composite powder reaction system

and air into the reactor at a certain volume flow rate. The reaction solution is continuously stirred so that the gas, liquid and solid phases are uniformly mixed. Stop the reaction when the pH is determined to be neutral after a certain reaction time. Filtering and drying to obtain the nano-coated composite calcium carbonate product[3,22-26].

2.3. Testing and Characterization

2.3.1. Morphology

The surface morphology of composite carbonate was observed by field emission scanning electron microscope. The main technical indexes are as follows. Resolution: 1.5nm at 30KV and 3nm at 1 KV. X-ray energy spectrum analysis: energy resolution is 150eV. Element range B-U. High performance cathode fluorescence has the ability to analyze and image specific wavelength spectrum (specify wavelength spectrum surface distribution).The wavelength range with resolution better than 30nm is 200nm~900nm.

2.3.2. Specific surface area

The specific surface area of composite carbonate is measured by gas permeation method. The main technical indicators are as follows. The design accuracy of the instrument is 0.01, Particle size measurement accuracy is 0.02. The envelope specific surface particle size Dk of the measurement range is 0.02~120μm, Specific surface particle size Dv is 0.002~0.5μm. Specific surface area measurement as follows. Total specific surface area of powder Sk is 0.05~300 (m2/g), total specific surface area of powder Sv is 12~3000 (m2/g), total specific surface area of powder Sw is 0.2~1.5×103(m2/g).The environment temperature is 25±12℃, and the relative humidity is less than 80%.

2.3.3. Whiteness

The measurement range: 0~100. Measuring aperture: a round hole with a diameter of 32mm. Linear deviation of whiteness ≤ 0.5. Reading convergence ≤ 0.2.Thickness of sample ≤20mm.

3.Result and discussions

3.1. Influence of Calcium Hydroxide Concentration

Calcium hydroxide reacts with carbon dioxide to generate calcium carbonate, so as to prepare composite particles

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coated with composite nanoparticles on the surface of ultrafine calcite powder particles. The concentration of calcium hydroxide in the solution will significantly affect the surface morphology of the final nano-coated composite calcium carbonate powder particles. Tests were carried out at different concentrations, and the test results are shown in Figure 2. The results show that when the concentration of calcium hydroxide is lower than a certain value, the supersaturation in the solution is not enough to uniformly nucleate, and few coated particles are formed on the surface of ultrafine calcite powder particles, which are mainly film-forming coating caused by non-uniform nucleation, as shown in Figure 2(a). When that concentration of calcium hydroxide is relatively high, uniform nucleation can occur in the solution, Then the surface particle coating of ultrafine calcite powder particles can be formed, as shown in Figure 2(b) and Figure 2(c). With the increase of calcium hydroxide concentration, the particle size of coated particles on the surface of ultrafine calcite powder decreases. This is because when the concentration of calcium hydroxide is higher, the saturation of reactants in the solution is larger, and a large number of calcium carbonate crystal nuclei can be formed by uniform nucleation in the reaction process. So that the particle size of the coating layer on the surface of the final superfine calcite powder is smaller.

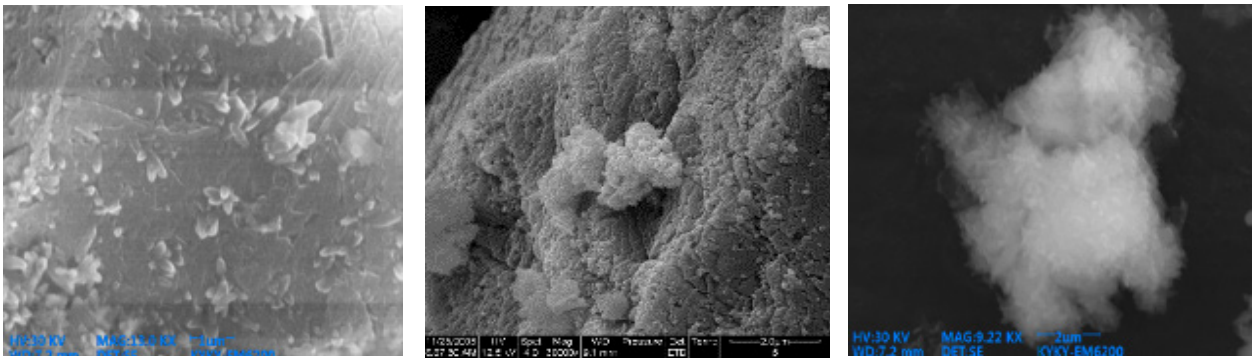

Figure 2 Composite ultrafine calcite powder SEM of calcium hydroxide concentration (a) 0.1mol/L, (b) 0.3mol/L and (c) 0.5mol/L

3.2. Effect of Heavy Calcium Carbonate Addition

Adding different amounts of ultrafine calcite powder particles into calcium hydroxide solution for surface nano-modification test (the amount of ultrafine calcite powder is calculated as the percentage of slurry mass), and the results are shown in Figure 3. It can be seen from Figure 3 that when the amount of ultrafine calcite powder is small,

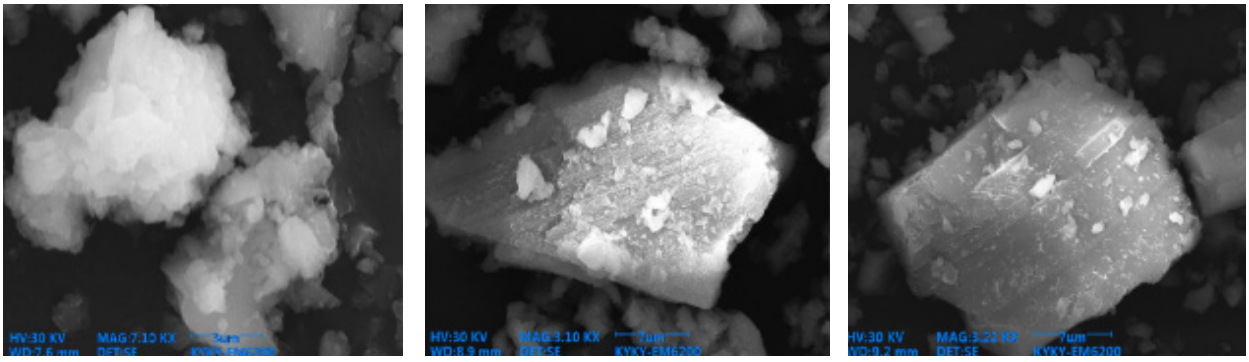

Figure 3 Composite ultrafine calcite powder SEM of (a) 10%, (b) 20% and (c) 30% addition amount of ultrafine calcite powder

the surface of ultrafine calcite is coated with particles, and the particle size of the coated particles is small. However, when the amount of ultra-fine calcite powder increases, the surface of ultra-fine calcite powder presents incomplete particle coating and transits to film coating. When the content of ultrafine calcite powder reaches 30%, it is basically coated with film. Therefore, in order to form ultrafine calcite composite particles coated with nanoparticles, the addition amount of parent particle ultrafine calcite powder must be strictly controlled.

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3.3. Effects of Different Gas Distribution Modes and Gas Flow of Gas Stirring

Gas stirring is widely used in the actual production process, which is determined by two factors. First, it is difficult to use mechanical stirring in the actual production process, and it is difficult to obtain higher intensity stirring. Second, because kiln gas resources are abundant in the actual production process, a large amount of kiln gas will be used in the production process, and the expenses can be saved by mixing kiln gas. However, the traditional gas distribution method has a low utilization rate of kiln gas, which will not only cause waste of energy and resources, but also cause pollution to the environment. Therefore, it is a very realistic problem for the design in production to make rational use of gas stirring and make carbon dioxide and slurry fully contact and react. During the experiment, the influence of different gas flow rates on the coating effect was tested by controlling the gas flow rate of the mixed gas under different stirring conditions (Table 1).

It can be seen from figure 4 that the coating effect under eccentric stirring is better than that under central stirring. However, different flow rates of carbon dioxide or different mixed gases have little influence on the coating effect, and the reaction rates are not much different.

3.4. Analysis of Particle Size Composition during Surface Nano-crystallizationThe particle size distribution of ultrafine calcite powder raw materials, the particle size distribution of nanocomposite calcium carbonate with short coating time and the particle size distribution of nanocomposite calcium carbonate with long coating time were measured. The results show that with the development of nano-coating process, the small particles in the reactant system are decreasing, and the mineral powder particles are growing and increasing.

The fine particles have larger specific surface area and higher surface energy, which is more conducive to become the active area of heterogeneous nucleation. The nano-coating and compounding process is mainly completed on

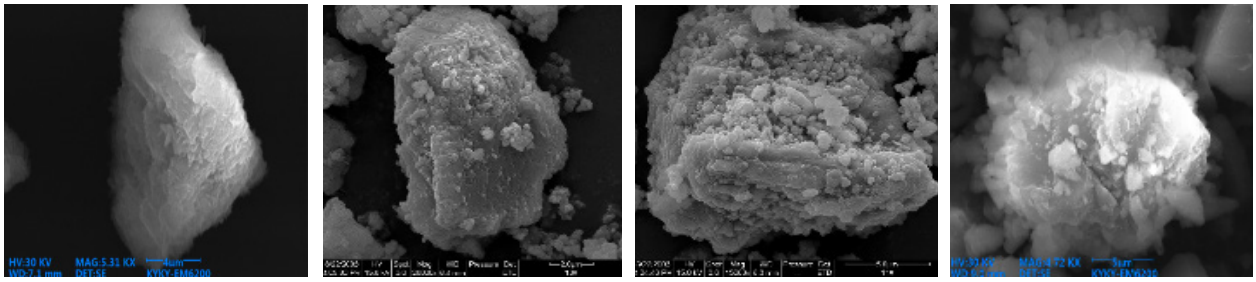

Figure 4 Composite ultrafine calcite powder SEM of different gas flow rates

Table 1 Reaction time of different gas flows

No.	Carbon dioxide flow rate (m^3/h)	Compressed air flow (m^3/h)	Stirring form	Time(min)
a	1.8	4.2	Central stirring	90
b	4.2	1.8	Central stirring	85
c	2.3	5.4	Eccentric stirring	47
d	5.4	2.3	Eccentric stirring	45

the surface of ultrafine calcite powder particles with smaller particle size, so at the beginning of the reaction, the small particles keep growing and the overall proportion of large particles is reduced. With the extension of reaction time, the active regions such as crystal plane junction and surface defects of more large particles also become the active regions of heterogeneous nucleation, and the surface nano modification is gradually completed. After that, the particle size composition of composite calcium carbonate powder will gradually increase.

3.5. Specific Surface Area Test

In order to evaluate the surface condition of ultrafine calcite powder particles treated by surface

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nanocrystallization, the specific surface area of ultrafine calcite powder composite particles was measured. Nitrogen adsorption method (BET) is to adsorb adsorbent molecules with known cross-sectional area on the surface of sample particles, and calculate the specific surface area of the sample according to the adsorption amount of adsorbent, which is used to measure the sample in this pilot test.

The test results show that the specific surface area of ultra-fine calcite powder increases from 1.39 m2/g before surface modification to 3.18 m2/g after surface coating, and the increase range is more than twice. The surface area test results show that the nano modification process makes the flat and smooth dissociation surface of ultrafine calcite powder rough, and the overall sphericity of particles increases. Therefore, nano-coated composite calcium carbonate products have better fluidity. When they are used as fillers in plastics, rubber, papermaking and other industries, their phase interface combination is more firm.

4.Conclusion

The concentration of calcium hydroxide and the amount of ultrafine calcite powder directly affect the production efficiency and product performance. Gas stirring has a great impact on the coating effect, especially through gas stirring, the gas-liquid contact time can be improved and the uniformity of the reaction can be promoted. However, in a certain range, the effect of simply changing the gas composition or flow rate on the reaction is not obvious. The results of specific surface area and particle size distribution showed that the product performance was improved.

Through the experiments in the pilot stage of coated composite calcium carbonate, a large number of studies were carried out on the possible effects of material ratio and different stirring methods and strength on the reaction in the actual production process, the finished products with nano modification on the surface of ultrafine calcite powder were obtained, the necessary technical preparations before industrial production were completed, and some important production parameters were obtained.

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