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Design of Integrated Process of Slacking and Carbonization of Coated Nano-sized Heavy Calcium Carbonate

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Abstract: The preparation of composite mineral filler by nano-coating mineral particles by carbonization reaction is of great significance to the production of polymer composites. Aiming at the problems of unstable calcium hydroxide concentration and low utilization rate in the current nano-coated calcium carbonate process, the nano-coated heavy calcium carbonate pilot plant system is improved by designing the "slacking-carbonization" integrated process, which improves the coating effect and production efficiency, so as to prepare nano-coated composite mineral particles with stable performance.

Keywords: heavy calcium carbonate; nano-coating; calcium oxide slacking; integrated process

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1.Introduction

China is a big plastic country in the world today, and various fillers account for about 10% of the total output of plastic products in that year, that is, at least 2 million tons of various mineral fillers are applied to plastics every year. Mineral filler is cheap and has a reinforcing effect on polymer materials, so mineral powder as filler plays an important role in the production of polymer materials such as plastics. However, inorganic mineral powder fillers are incompatible with organic materials such as rubber and plastics due to the differences of physical and chemical properties. During the preparation process of ultrafine powder, it has many sharp edges and corners (formed by intersection of 2-3 crystal cleavage planes) and smooth surfaces (broken crystal cleavage planes along the particles) [1-5]. The performance of composite products depends on the stress transfer on the two-phase interface between inorganic filler and organic matrix material. The research of micro fracture mechanics shows that these sharp edges and corners will become the internal stress concentration point of the material, and then produce cracks in the process of use. Moreover, in plastic production, the sharp edges and corners of mineral particles have great wear on the screw of plastic extruder. The cleavage surface of mineral particles is very smooth, which is difficult to form an effective combination with the polymer chain segment. Improving the adhesion between interfaces is the key to improve the strength of composites. Therefore, surface modification is usually required before inorganic mineral powder is added to polymer materials as filler[6-8].

There are a large number of reports on the research of nanoparticles as fillers of polymer composites[9-14]. The research shows that the structure of nanoparticles is rough, its surface morphology is atomic steps, the atomic energy at the edges and corners of the steps is high, the activity is large, and it is easy to have physical and chemical interaction with polymer chains[15-17]. Taking advantage of the high surface activity of nanoparticles and good compatibility with polymers, the method of using nano fillers to enhance polymers has been proved, and has gradually attracted the attention of industrial enterprises. However, the production cost of nano powder is high, the dispersion is poor, and it is easy to agglomerate. It is difficult to achieve uniform dispersion when mixing with the matrix material, and it is difficult to give full play to the excellent characteristics of nano powder itself. To solve these problems, according to the “particle design” theory, the surface of micron particles grows nanoparticles through chemical or physical action, which can not only effectively utilize the excellent characteristics of nanoparticles, but also change the surface properties of micron powders. The surface of mineral particles is nano-coated by carbonization reaction method, that is, through chemical reaction in uniformly dispersed mineral powder slurry, the newly generated substances can grow on the surface of non-mineral powder in the form of nanoparticles [18-23]. By improving the process of nano-coated heavy calcium carbonate, it is of great significance to improve the coating effect and production efficiency and prepare nano-coated composite mineral particles with stable properties.

2.Rxperimental part

2.1. Experimental Method

At first, a certain amount of heavy calcium carbonate powder is added into a calcium hydroxide solution with a certain concentration, and is uniformly mixed by mechanical stirring or gas stirring to form a suspension. Then a

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mixed gas of carbon dioxide and air is introduced for carbonization reaction. In the reaction process, the gas-solid-liquid three phases are uniformly mixed through the material circulation system outside the system.In a certain period of time, the nanoparticles generated by the reaction between the reaction substance and the reaction gas nucleate and grow on the surface of ultrafine calcium carbonate powder. And finally, filtering, drying and dispersing to prepare the calcium carbonate composite particles with nanometer coating on the surface [5-6,24].

2.2. Process Principle

In this study, the system includes CaO slacking reaction and Ca(OH)2-H2O-CO2 carbonization reaction. At first, the Ca(OH)2 suspension is prepared by CaO slacking reaction, and then CO2 is introduced into the mineral powder and the Ca(OH)2 suspension, and nano-scale CaCO3 particles are generated and coated on the surface of mineral powder particles. There are six main chemical reactions in the liquid phase of this system.

① CaO(s) + H2O (aq) = Ca(OH)2 (s)
② Ca(OH)2 (s) $\rightleftharpoons$ Ca2+(aq)+2OH- (aq)
③ CO2 (g) $\rightleftharpoons$ CO2 (aq)
④ CO2 (aq) + OH- (aq) → HCO3- (aq)
⑤ HCO3- (aq) + OH- (aq) = CO32- (aq) + H2O (aq)
⑥ Ca2+ (aq) + CO32- (aq) = CaCO3 (s)

2.3. Experimental Materials and Equipments

Quicklime, Qingzhou Yuxin Calcium Industry Co., Ltd., purity 95%.CO2, Qingzhou Yuxin Calcium Industry Co., Ltd., purity 99.8%. Ultrafine ground calcium carbonate (800 mesh), Hebei Huabo fine chemical co., Ltd. Water (H2O), self-made.

Reaction kettle (equipped with stirring device), self-made. Slaking tank (equipped with stirring device), self-made. ZL112 pH meter, Guangdong zhengliang instrument technology co., Ltd. Model 390 plate and frame filter press, Donglong chemical machinery co., Ltd. 200 mesh screen, Anping Sheng Bang Screen Factory. DGG-9003 air blast drying cabinet, Shanghai senxin experimental instrument co., Ltd.

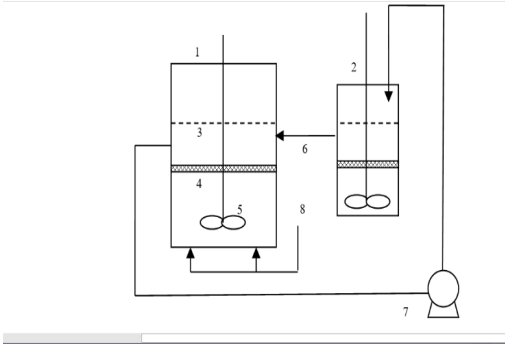

Figure 1 Process flow chart of "slacking-carbonization" integrated nano-coating (1. Reaction kettle 2. Calcium oxide slaking tank 3. Liquid surface 4. Screen mesh 5. Mixing device 6. Overflow 7. Pump 8. Mixed CO2 and Air)

3.Results and discussions

3.1. Process Calculation

The reactor in the pilot-scale reaction system has a diameter of 0.54m and a height of 1m. The digester is 0.3m in diameter and 0.8m in height, and the total volume of materials in the reaction system is 0.285m3.

Different from Ca(OH)2 chemicals added in laboratory research, Ca(OH)2 produced in the digestion process of CaO added in industrial production can not completely form a transparent solution, but will form a suspension of Ca(OH)2. Considering the poor fluidity of the suspension, diaphragm pump was chosen to realize the material circulation of the two reactors. The reaction time is 4h, and all materials are circulated for 200 times. Then the design flow of diaphragm pump should be greater than 14.25m3/h.

In order to prevent larger particles from entering the material circulation systems of the two reactors and causing

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pump damage or blockage, 200 mesh filtration systems are set at both ends of the circulation system to effectively separate the reaction system from the material circulation system.

3.2. Process Steps

① Adding CaO into slacking tank. According to the Ca(OH)2 content in the Ca(OH)2 suspension is 0.3mol/L, the input amount of quicklime (CaO content is 95%) is 5.04kg.

② Quicklime slacking. Add 285L water to slack quicklime, start the mixing device, and set the speed of the mixer to 90 rpm. Open the diaphragm pump to establish the circulation system between the reaction kettle and the digestion tank.

③ Adding superfine heavy calcium carbonate. According to the ratio of coated substance to coated substance (1:5), 42.8kg superfine heavy calcium carbonate is added.

④ Circulate the slurry in the circulation device for about 10 minutes to fully mix the solid and liquid.

⑤ Open the outlet valve of the air compressor and the outlet valve of the CO2 storage tank, so that the two gases enter the mixing valve. Adjust the air flowmeter and the CO2 flowmeter, and the ratio of air to CO2 is 2:1 (This is related to the reaction rate, whether the coating layer is formed quickly or slowly, which affects the compactness of the coating layer). Introduce the mixed gas of CO2 and air from the bottom of the reaction kettle (According to the content of Ca(OH)2 in the system, set the air flow rate as 4m3/h and the CO2 flow rate as 2 m3/h).

⑥ Measure the pH value in the reaction kettle every 10 minutes, and stop aeration when the pH of the system is 7.

⑦ Filter the materials from the reaction kettle with a plate and frame filter press.

⑧ The filter cake is dried, crushed and stored.

3.3. Influence of Process on Coating Effect

The original production process route is to digest quicklime with 5-6 times of water to prepare calcium hydroxide solution. In order to ensure that CaO in quicklime is completely converted into Ca(OH)2, the slacking time is set at more than 4 hours. In order to prevent coarse particles in quicklime from mixing with superfine heavy calcium carbonate, the supernatant of calcium hydroxide solution is filtered by filtration and added into the reaction system. Therefore, the actual utilization of Ca(OH)2 is greatly reduced, which leads to low coating rate of heavy calcium carbonate and low production efficiency. The comparison between the original process (Process I) and the current process (Process II) is shown in Table 1.

The total content of Ca(OH)2 lime slurry prepared after quicklime slacking reaction is 2.22%, that is, there is 2.22g Ca(OH)2 lime slurry per 100g water. However, Ca(OH)2 is slightly soluble, and its solubility in water at 80 ℃ is

Table 1 The data comparison between different process

Process type	Quicklime input(kg)	$Ca(OH)_2$ content in the system(kg)	Nano calcium carbonate produced(kg)	Utilization rate of $Ca(OH)_2$	Coating effect	Production time(h)
Process I	5.04	0.27	0.36	4.2%	Incomplete coating	＞8
Process II	5.04	6.33	8.55	100%	Completely coated	4

0.094g per 100g water, so the actual utilization rate of Ca(OH)2 in the original process is only 4.2%.

The reaction coating system is batch production, and with the introduction of CO2, CO2 reacts with Ca(OH)2 in solution continuously to generate nano calcium carbonate, thus promoting the continuous dissolution of supersaturated Ca(OH)2 into the system. The following reaction occurs.

Ca(OH)2 (s) $\rightleftharpoons$ Ca2+(aq)+2OH- (aq)

With the continuous formation and coating of nano calcium carbonate on the surface of heavy calcium carbonate, the full utilization of Ca(OH)2 was realized in the new process. The coating effects of different processes are shown in Figure 2.

In laboratory tests, Ca(OH)2 reagent is often directly used instead of quicklime digestion step, and Ca(OH)2 solution with corresponding concentration is directly prepared. In this case, although the solubility of Ca(OH)2 is low, the solid of Ca(OH)2 is not completely dissolved in water, but Ca(OH)2 is still added into the carbonization reaction system, and with the continuous introduction of CO2, Ca(OH)2 will eventually be fully utilized.

In actual production, Ca(OH)2 lime slurry prepared by slaking quicklime contains dissolved Ca(OH)2,

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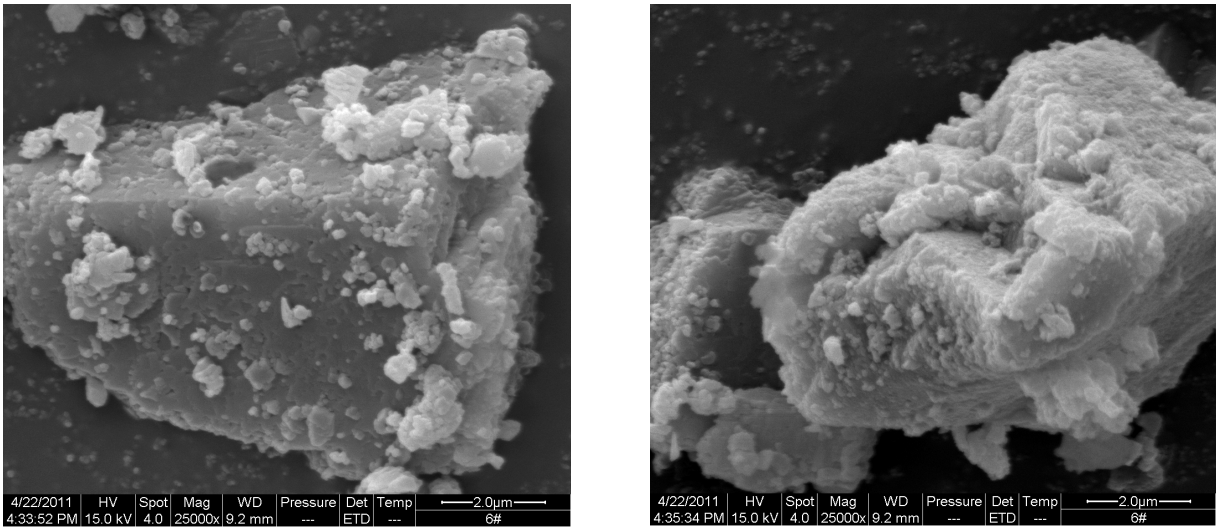

Figure 2 SEM picture of coating effect of original process (a) and new process (b)

undissolved Ca(OH)2 and other large-particle impurities. If all of them are added into the carbonization reaction system, impurities with different particle sizes will be introduced, which will cause abrupt changes in the particle size distribution of ultrafine heavy calcium powder and affect its service performance. Because the solubility of Ca(OH)2 in water is 0.185g/100g-0.085g/100g at 0℃ -90℃ , far less than the concentration of Ca(OH)2 required for coating with nano calcium carbonate. Therefore, if large particles of impurities are filtered out by filtration, a large amount of undissolved Ca(OH)2 will be filtered out together, and the utilization rate is very low. Actually, the Ca(OH)2 added to the carbonization system is only its saturated solution, and the concentration of Ca(OH)2 after being added into the system is not stable, but decreases continuously as the reaction proceeds. Therefore, the coating effect cannot be effectively controlled.

In the new process, all Ca(OH)2 is put into the reaction system, and the material circulation system can keep the concentration balance of Ca(OH)2 between the two reactors. With the continuous introduction of CO2 in the carbonization reactor and the growth of nano-CaCO3 on the surface of heavy calcium particles, Ca(OH)2 is consumed continuously. According to the dissolution kinetics of Ca(OH)2, Ca(OH)2 in the digestion reactor is continuously dissolved in the system. Therefore, the concentration of Ca(OH)2 in the system is always stable at the saturation concentration until all Ca(OH)2 is consumed, which ensures the stable carbonization reaction and nano-coating behavior.

3.4. Reaction Time of Different Processes

The slacking reaction of quicklime in the original process is carried out independently. Firstly, the quicklime is put into a quicklime slacking tank and slacked for 4-6 hours. Secondly, filtering the aged Ca(OH)2 solution with a 200 mesh sieve. Then, the concentration of Ca(OH)2 solution was measured by Baume scale meter, and added into the carbonization reaction system.

The new process circulates through two reactors, which is beneficial to the dissipation of heat generated by quicklime slacking, and improves the slacking effect by stirring. It is determined that the required concentration of Ca(OH)2 solution can be achieved by circulating the system liquid within 10-20 minutes before adding the heavy calcium.

4. Conclusion

The ultra-fine ground calcium carbonate is carbonized and coated with nano-CaCO3, which eliminates the inherent morphological defects of the ground calcium particles, especially their sharp edges and flat cleavage surfaces. With the design of “slacking-carbonization” integrated nano-coating process, the full utilization of Ca(OH)2 resources is realized, the reaction time is shortened, and the coating efficiency is significantly improved. The new process ensures that the concentration of Ca(OH)2 in the reaction system is always in a saturated state, thus making the heterogeneous nucleation process proceed stably.

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