Dry surface modification of heavy calcium carbonate powder with two modifiers

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Abstract. In this work, The modification of heavy calcium carbonate powder was studied by dry surface modification with stearic acid and anhydrous citric acid. we have developed a facile and inexpensive dry surface method to fabricate a lower oil absorption value of calcium carbonate surface. The modification process was analyzed by modifying temperature, modifying time, modifiers percentage. Infrared spectral and TG showed that stearic acid modifier was mainly reducing oil absorption value of CaCO₃ powder from 33.9 ml/100 g to 19.0 ml/100 g.

1. Introduction
Fillers are used in the industries of plastics, rubber, paint, fibers, and so on. One of the most challenging issues for the use of calcium carbonate(CaCO₃) is the hydrophilic property.

The successful surface modification of CaCO₃ with a hydrophobic species would widen the range of potential applications. Dry surface modification method is cheaper than wet surface modification method. In general, stearic acid[1], KR-TTS titanate coupling agents[2], aluminate coupling agent (ACA)[3], oleic acid [4,5] are often present as modifiers. The hydrophobic characters of modified calcium carbonate powder contain water contact angle, activity index, oil absorption value. Oil absorption value is seldom evaluated the modified calcium carbonate powder.

In this paper, stearic acid and anhydrous citric acid were used to modify heavy calcium carbonate. Oil absorption value is evaluated the modified calcium carbonate powder. The surface modification processes are carefully studied, at the same time, the mechanism of surface modification was analyzed.

2. Experimental
1500 mesh calcium carbonate (CaCO₃), stearic acid and anhydrous citric acid were used as starting materials. In typical procedure, firstly, CaCO₃ and certain content anhydrous citric acid were put into mental jar by use of QM-2L ball mill equipment at 100r/min about 1h. After, stearic acid was put into the same jar milled 1h at the condition. Then, the 50g of mixture CaCO₃ was placed in culture dish and it was heated at certain certain period of time at some constant temperature in drying oven to modification. After the reaction was completed, as a primary criterion the oil absorption value of sample was employed to evaluate the surface modification effect. The oil absorption value is quantity of Diocyl-Phthalate/5.00. The quantity of Diocyl-Phthalate is determined by titrating the modified powder(5g) until it becoming a group. The dispersity of modified calcium carbonate powder was also evaluated by sedimentation. Firstly, modified CaCO₃ powder(5g) and absolute ethyl alcohol
solvent(50mL) are added into beaker. Then the beaker was place on the 78-1 magnetic stirring apparatus and stirred 30 min. At last, suspension with modified CaCO₃ powder was put into graduated cylinder(50mL), and the sedimentation height of suspension changes according to sedimentation time. Fourier transform infrared (FTIR) spectra were recorded with a Nicolet Is10 spectrometer at room temperature. TG and DTA was tested by use of Netzsch 214.

3. Results and discussion

3.1 The analysis of modification condition

Oil absorption value of unmodified CaCO₃ powder is 33.9 mL/100 g through testing. Many factors can impact the modification effect. These parameters are modification temperature, anhydrous citric acid percentage, stearic acid percentage, and modification time. The oil absorption value was employed as reference standard.

3.1.1 The effect of modification temperature

Fig. 1 shows the oil absorption value of the modified powder with different modification temperature. The anhydrous citric acid and stearic acid is respectively at 5wt%. It can be seen that with the increasing modification temperature, the oil absorption value first goes down, then it stays flat, at last it goes up. It is thought that increasing temperature enhances the reaction activity between the modifier and CaCO₃ surface. While the high temperature decomposes the modifiers. This is because that the anhydrous citric acid is resolved according to its nature. A kind of burnt smelled up during modification when the temperature above 175℃. Thus, the optimum modification temperature is at 125~150℃.

3.1.2 The effect of anhydrous citric acid percentage

Fig. 2 is the oil absorption value of the modified powder with different anhydrous citric acid percentage, when the stearic acid percentage is at 5wt%. It is contributed to physical or chemical reaction between CaCO₃ powder and the modifier. It can be seen that anhydrous citric acid has an obvious influence on modification effects. The oil absorption value increases along with the increase of anhydrous citric acid percentage. The reason is that more anhydrous citric acid first coated CaCO₃ surface, which hinders stearic acid modification effects.

3.1.3 The effect of stearic acid percentage

Fig. 3 is the oil absorption value of the modified powder with different stearic acid percentage. It can be seen that with the increase stearic acid percentage from 0.3wt% to 0.4wt%, the oil absorption value reduces in a directly and then it keep at 19.0 mL/100 g when the stearic acid percentage is from 0.4wt% to 0.7wt%. We considered that optimum 0.4 wt% content of stearic acid may lead to full
surface coverage. In order to ensure modification stability, 0.5wt% content of stearic acid could be used.

3.1.4 The effect of modification time

Sufficient modification time must be met in order to reach good modification performances. Fig. 4 is the oil absorption value of the modified powder at different modification time. When modification time rises from 1h to 2h, the oil absorption value just lowers from 20.0 mL/100 g to 19.0 mL/100g. The modification time is determined as 2h in this test.

3.2 The analysis dispersity of modified powder

The results show that the stearic acid percentage is the major influencing factor to reduce oil absorption value. At the same time, considering the dispersity of modified powder filled in the industries of plastics, rubber and so on, a further experiment was developed. Fig. 5 shows sedimentation height of power in suspension with sedimentation time. It can be seen that the settling velocity of stearic acid modified powder in absolute ethyl alcohol solvent is faster than the anhydrous citric acid and stearic acid modified powder. We thought that surface of two agents modified powder maybe covered a part of anhydrous citric acid, which created a bigger repulsive force hindering particle agglomeration. And small particles can be dispersed, which caused powder slowing settlement. The phenomenon shows that dispersity of stearic acid modified powder is inferior than two agents.

3.3 TG and DTA analysis

Fig. 6 is TG and DTA of 0.5wt% anhydrous citric acid and 0.5% stearic acid modified CaCO₃ powder. It can be seen that decalescence point appears in the DSC curve of modified powder is about 160.0°C, which is due to that the decomposition of anhydrous citric acid is at 175°C. Then exothermic process with temperature rising above 200°C, which is because stearic acid chains were ruptured releasing heat. When the temperature up to about 350°C, all modifiers are decomposed and volatiled. The process proves anhydrous citric acid and stearic acid are all covered on surface of calcium carbonate power.
3.4 Infrared spectral analysis

The formation mechanism between CaCO$_3$ powder and the substrate can be identified with FTIR. FTIR spectra (Fig. 7.) of anhydrous citric acid (line a), stearic acid (line b), and the modified anhydrous citric acid and stearic acid modified CaCO$_3$ powder (line c). Compared to the spectrum of line b, the asymmetric [vas(CH$_2$)] and symmetric [vs(CH$_2$)] methylene vibration peaks appear clearly at 2918 and 2846 cm$^{-1}$ of line c, which indicates the existence of the stearic acid on the surface. The modified CaCO$_3$ powder was washed with n-propyl alcohol before FTIR test. So it can be considered that stearic acid has bound onto the surface of the CaCO$_3$ powder to achieve modification, while anhydrous citric acid was washed away owing to weak action between it and CaCO$_3$ powder.

![FTIR spectra](image)

Fig. 7. FTIR spectra of (a) anhydrous citric acid, (b) stearic acid, (c) 0.5wt% anhydrous citric acid and 0.5wt% stearic acid modified CaCO$_3$ powder.

4. Conclusion

In this work, we have developed a facile modification method. The optimum technological parameters were the following: modification temperature was at 125-150$^\circ$C, anhydrous citric acid percentage was 0.2wt% and stearic acid percent was 0.4wt%, modification time was 2h.

The oil absorption value of modified CaCO$_3$ have been reduced greatly from 33.9 ml/100 g to 19.0 ml/100 g, the reason was that stearic acid modifier was bound onto the surface of CaCO$_3$ powder. The input of anhydrous citric acid can improve dispersity of modified CaCO$_3$ powder in absolute ethyl alcohol solvent.
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