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Mechano-activated surface modification of calcium carbonate in wet stirred mill and its properties

DING Hao(丁 浩)[1], LU Shou-ci(卢寿慈)[2], DENG Yan-xi(邓雁希)[1], DU Gao-xiang(杜高翔)[1]

1. School of Materials Science and Engineering, China University of Geosciences(Beijing), Beijing 100083, China;
2. School of Civil and Environmental Engineering, University of Science and Technology Beijing, Beijing 100083, China

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Abstract: Surface modification of calcium carbonate particles using sodium stearate(SDS) as a modification agent incorporated with the simultaneous wet ultra-fine grinding in the laboratory stirred mill was investigated. The physical properties and application properties of modified calcium carbonate were measured and evaluated. The action mechanism between SDS and calcium carbonate in the modification was studied by infrared spectrometry(IR) and X-ray photoelectron energy spectroscopy(XPS). The results indicate that the crushing mechanic force intensity can obviously influence the modification effect of calcium carbonate because of mechano-chemical effect. The hydrophilic surface of calcium carbonate is turned into hydrophobic after modification. The properties of polyethylene(PE) filled by modified calcium carbonate powder is markedly improved. And the adsorption of SDS could occur by chemical reaction with calcium carbonate surface.

Key words: surface modification; calcium carbonate; mechano-chemical effect; action mechanism

1 Introduction

Finely ground calcium carbonate has been widely applied as the filler material[1−4]. However, it is essential to make the hydrophilic calcium carbonate particles compatible with the matrix, such as plastics, rubber and adhesives. Surface modification, a key process in functional powder preparation, is commonly used to achieve this purpose. Surface modification of fillers in plastics, rubber and adhesives can improve their mechanical and physicochemical properties, increase filler loading in the matrix, and lower producing cost.

The conventional surface modification technology, consisting of the heating mix modification and the packing modification method，has been applied widely in treatment of the fillers and pigments. But it has some defects such as weak stirring, low materials mixing degree, uneven dispersion between agent and materials, and especially the lack of reaction foundation. Moreover, the modification effect is weak, and the product quality is unstable. Thus, the improvement of mechanical performance of the product is inconspicuous[5−7]. So, it is necessary to carry out modification with a high effective method.

Mechano-activated surface modification is a modification method of utilizing mechanochemical effect during ultrafine grinding. Mechanochemical effect is a physical and mechanical change on the near surface region, where the solids come into contact with each other under mechanical forces[8−9]. It can lead to particle energy stored on the surface of the minerals in grinding and bring about the surface activity. So, it is thought to be more valuable and effective because the mechanochemical effect resulted from ultra-fine grinding can increase mineral surface activity and enhance reactivity between phases[10−11]. This has been proved by the modification of powder, such as SiO_2[12], α-Al_2O_3[13], SiC[14] and other minerals[15]. But these modification has mainly been carried out in dry grinding system, which needs a very long time and much more energy.

Because many control factors, such as the characteristic of mechanochemical effect, dispersion of the particles, surface modification temperature, content of solid, can be increased in wet grinding system, the

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Corresponding author: DING hao; Tel: +86-10-80685966; E-mail: dinghao@cugb.edu.cn

mechano-activated surface modification in wet grinding system is thought to be one of the best surface modification methods. Moreover, this method combines the surface modification and the ultra-fine grinding technique that is widely used to produce high quality mineral powder, together in one equipment. So, it has optimized potential in industrial application. Nowadays, besides being used to produce high quality mineral powder, the wet ultra-fine grinding by stirred mill is also used to increase modification effect. It has been used in the modification of some minerals, such as wollastonite [16] and tourmaline[17]. In this study, surface modification of calcium carbonate particles with sodium stearate(SDS) incorporated with the simultaneous wet ultra-fine grinding in stirred mill was described, and the influence of varied parameters on the properties of the modified product was discussed. The modification effect was evaluated by the physical properties and application properties of modified calcium carbonate. The action mechanism between SDS and calcium carbonate in the modification was also studied.

2 Experimental

2.1 Samples and reagents

The experimental sample was a finely ground calcium carbonate powder came from Gansu province, China. Its main chemical compositions were as follows (mass fraction, %): CaO 55.20, CO_2 43.20, SiO_2 0.18, Al_2O_3 0.10, Fe_2O_3 0.04, K_2O 0.012, Na_2O 0.018, MgO 0.78. The size distribution of sample was (%): ＜1 μm, 0.7; ＜2 μm, 4.2; ＜5 μm, 13.2; ＜10 μm, 32.7; ＜15 μm, 47.1;＜20 μm, 58.0; ＜30 μm, 80.9; ＜40 μm, 92.9; ＜50 μm, 100. The mean size of the sample was 16.33 μm, the specific surface area 0.275 m^2/g, brightness 91.00, and density 2.70 g/cm^3.

Sodium stearate(SDS) used in experiments was chemical pure reagent, and the distilled water was used.

2.2 Test and evaluation method

Modification experiments were conducted in an ultra-fine stirred mill, and its volume was 0.25 L. The grinding media were glass balls with tiny diameter. 20 g mineral sample was added for each test. The technological parameters of stirring mill were determined through the experiments.

The effect of surface modification was evaluated by floating test, that was, to measure the ratio of floated product to the overall mass of sample after mixing in water and aeration. The ratio is called active rate, and the higher the active rate, the better the modification effect is.

The adsorption form of SDS on the surface of calcium carbonate was determined by infrared spectrometry(IR) and X-ray photoelectron energy spectroscopy(XPS). The testing equipments were the Bruker IFS−113 infrared spectrometer and the KRTOS XSAM800 multi-purpose surface analyzer. The samples examined were the products under the best technology condition. The samples of IR and XPS test were cleaned by acetone many times.

3 Results and discussion

3.1 Influence of technology conditions on modification of calcium carbonate

3.1.1 Particle size and dosage of SDS

The SDS agent was used to modify calcium carbonate after the sample was wet-ground to a certain size for a given period. The influence of SDS dosage on modification effect under different grinding sizes is shown in Fig.1.

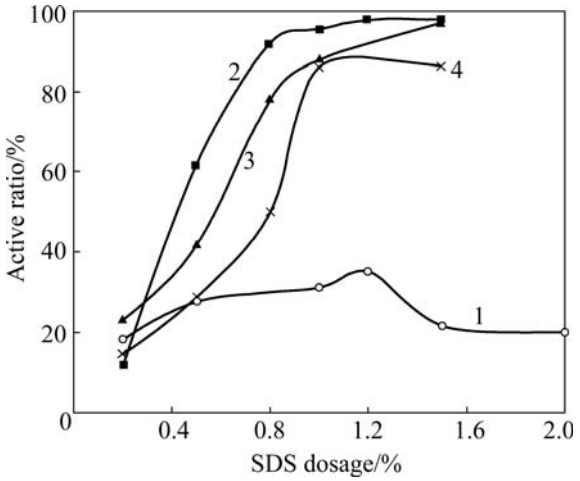

Fig.1 Influence of SDS dosage and particle size on modification effect (Medium size, specific surface area: 1—6.33 μm, 0.275 m^2/g; 2—1.33 μm, 2.315 m^2/g; 3—0.94 μm, 3.133 m^2/g; 4—0.77 μm, 4.021 m^2/g)

The particle size has a great effect on the modification of calcium carbonate. The modification result of non-ground samples (d_{50}=16.33 μm, specific surface area 0.275 m^2/g) is very weak, and the active rate can only reach 35%. If the modification agent is added when the sample is ground to d_{50}=1.33 μm (specific surface area 2.315 m^2/g), its effect increases remarkably, and the active rate can reach 98%. Thus, wet ultra-fine grinding obviously strengthens the modification effect.

The specific surface area of the particles increases with the further grinding. Although the agent coverage on particle surface is decreased and the active rate decreases slightly when the agent dosage remains the same, the modification effect is still much better than that of non-ground samples. The modification effect

reaches its largest when the sample is ground to d_{50}=1.33 μm (specific surface area 2.315 m^2/g) under experimental conditions. And this size is just the optimum filling size (＜10 μm, 100%; d_{50}=1−2 μm) of functional filler for rubber products.

3.1.2 Intensity of crushing mechanical force

The crushing mechanical force exerted on particles is the motivation to produce mechano-chemical effect, so its intensity is an important factor influencing the mechano-activated modification effect. This influence is studied through changing the stirrer rotary speed, the mass ratio of grinding media to mineral feeding and the duration of grinding. The results are shown respectively in Figs.2 and 3.

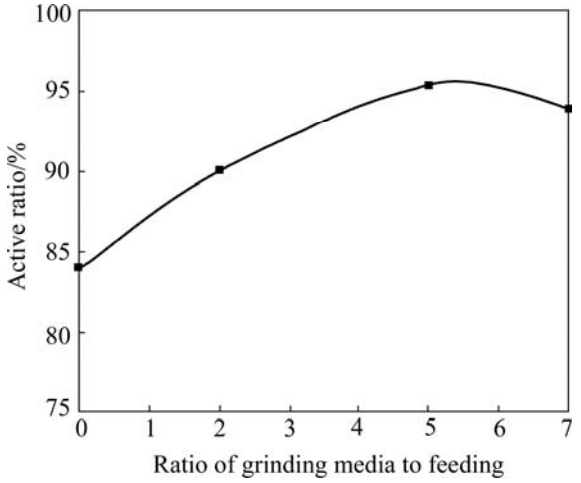

Fig.2 Influence of mass ratio of grinding media to mineral feeding on modification effect (1.2% SDS)

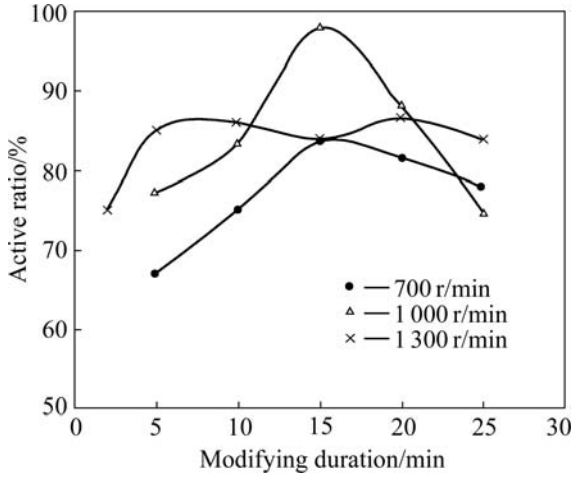

Fig.3 Influence of duration of modification and stirrer rotary speed on modification effect (1.2% SDS)

The influence of the mass ratio of grinding media to mineral on modification is very obvious. Under the SDS dosage of 1.2%, the active rate is less than 85% when the ratio of grinding media to mineral is 0, but the active rate reaches more than 90% when the ratio increases up to 2. Apparently, the mechano-activated effect produced during grinding improves the modification effect. The best result could be attained at the ratio of 5.

Duration of modification could be shortened by raising stirrer rotary speed. For example, the modification effect at 1 300 r/min for 5 min is just equal to that at 1 000 r/min for 10 min or at 700 r/min for 15 min. But the best effect could not be attained at too high or too low rotary speed. The active rate of the product at 1 000 r/min is better than that of the product at 700 r/min or 1 300 r/min under experimental conditions.

It could be seen from the experiment results and corresponding analysis that, there exists a suitable range for the intensity of crushing mechanic force during ultra-fine grinding and simultaneous surface modification of calcium carbonate by SDS addition. If the intensity is too weak, or there is no grinding action, the modification effect would be poor because the mineral surface could not be effectively activated; if the intensity is too high, the modification effect would drop again as the finer particles need more agent. In addition, the reacted product on the particle surface would be lashed and peeled off.

The active rate of the ultra-fine active calcium carbonate filler could reach 98% by optimizing various experimental conditions, and the modification agent SDS dosage is fairly low (the dosage is 1.2%, which is equal to $5.18\times10^{-3}g/m^2$ surface area), and it is even better than that used in the conventional modification technology.

3.2 Properties of modified calcium carbonate

3.2.1 Physical property

The physical properties of calcium carbonate before and after modification are listed in Table 1.

Compared with common calcium carbonate, contact angle of modified calcium carbonate increases much in water, but lowers in kerosene, the 7, 14 and 21 day's water absorption value greatly decreases, and the permeating time of water also decreases greatly. This indicates that the hydrophilic surface of calcium carbonate is turned into hydrophobic after modification. The modification also leads to increase of the brightness of calcium carbonate.

3.2.2 Properties of polyethylene(PE) filled by calcium carbonate

Properties of polyethylene(PE) filled by non-modified or mechano-activated modified calcium carbonate powders at the same filling percentage are listed in Table 2. The melt flow rate reflects the dispersion extent of filler in PE matrix, while the tensile strength, critical stretching elongation and winding yield strength manifest the couching state between the filler

Table 1 Physical properties of calcium carbonate before and after modification

Sample	Contact angle (in water/ in kerosene)/(°)	Water adsorption value (7d/14d/21d)/%	Permeating time of water/s	Brightness
Calcium carbonate	5.0/75.8	6.67/13.33/13.33	4	90.20
Modified calcium carbonate	125.0/65.5	1.96/3.92/5.88	600	91.00

Table 2 Properties of polyethylene(PE) filled with calcium carbonate

Sample	Melt flow rate/ ($g \cdot min^{-1}$)	Tensile strength/ MPa	Critical stretching elongation/%	Winding yield strength/ MPa
Calcium carbonate	0.158	8.08	170	10.2
Modified calcium carbonate	0.192	9.73	165	12.8

particles and matrix.

Table 2 shows that except the stretching elongation, all the other properties of PE product are markedly improved by the mechano-actively modified filler, compared with the non-modified filler.

3.3 Action mechanism between SDS and calcium carbonate

3.3.1 Examination of IR spectra

IR spectra of calcium carbonate, SDS and calcium carbonate modified by SDS are shown in Fig.4.

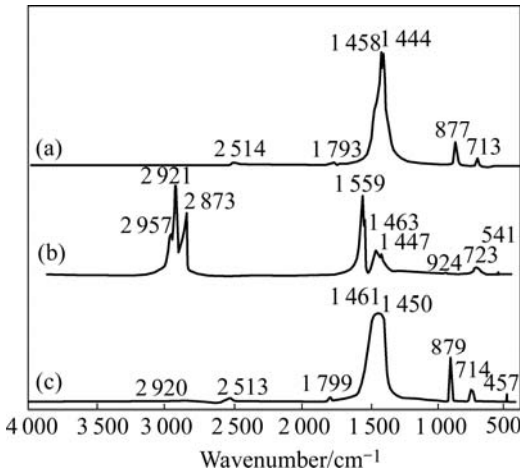

Fig.4 IR spectra of calcium carbonate and SDS: (a) Calcium carbonate; (b) SDS; (c) Calcium carbonate modified by SDS

The characteristics of calcite can be seen obviously from Fig.4(a). The characteristic adsorption peaks of CO_3^{2-} of calcite mineral appear at 1 444 cm^{-1} and 877 cm^{-1}[18]. IR spectrum of SDS is shown in Fig.4(b). The absorbing one at 1 559 cm^{-1} is dissymmetric flex absorbing peak of carboxyl COO^-, and the two peaks at 1 463 cm^{-1} and 1 447 cm^{-1} are its symmetric flex absorbing peaks. The above three peaks constitute the characteristic absorbing of carboxylic acid[18]. Dissymmetric flex absorbing peaks of —CH_3 and —CH_2 appear at 2 921 cm^{-1} and 2 873 cm^{-1}, respectively. It can be seen that characteristic absorbing peaks of —CH_3 and —CH_2 also appear at wavenumbers lower than 3 000 cm^{-1} in Fig.4(c), indicating that SDS has been absorbed on the surface of calcium carbonate. Because the infrared sample is cleaned by the acetone many times, the adsorption includes the chemical action.

3.3.2 Examination of XPS

The XPS of calcium carbonate before and after action with SDS is shown in Fig.5 (Ca 2p and its binding energy). The binding energy of Ca $2p_{3/2}$ on the surface of modified calcium carbonate is 346.30 eV, compared with 346.75 eV before modification. Obviously, the chemistry environment of Ca has changed. Therefore, the chemical adsorption of SDS is thought to happen on the surface of calcium carbonate.

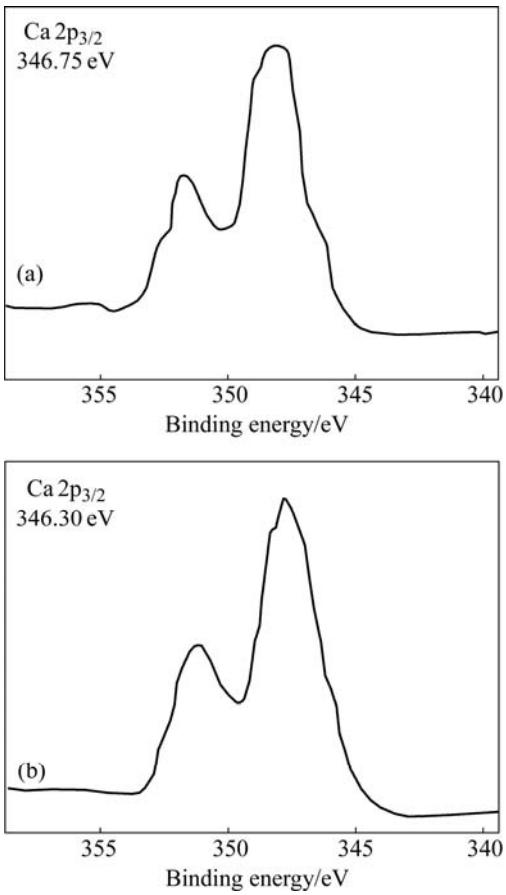

Fig.5 XPS spectra of calcium carbonate before and after action with SDS: (a) Before action; (b) After action

4 Conclusions

1) Mechano-activated surface modification incorporated with the simultaneous wet ultra-fine grinding can intensify the modification process, improve the quality of modified product, simplify the production technique and lower the production cost.

2) The grinding fineness, modification agent dosage and the intensity of crushing mechanic force are the important factors of mechano-activated surface modification. Modified calcium carbonate powder of active rate 98%, mean size 1.33 μm, specific surface area 2.315 m^2/g can be attained by mechano-activated surface modification method under optimized experiment parameters. The necessary dosage of sodium stearate (SDS) in wet mechano-activated modification is lower than that needed for dry modification of ordinary size particles.

3) Modification renders the surface of calcium carbonate hydrophobic. Mechano-actively modified $CaCO_3$ filler can markedly improve the mechanical and physic-chemical properties of PE.

4) Chemistry environment of Ca on the surface of calcium carbonate is changed after being modified by SDS. The chemical adsorption of SDS is thought to happen on the surface of calcium carbonate.

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