

Surface modification of wollastonite by the mechano-activated method and its properties

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Abstract: Surface modification of wollastonite particles using titanate as a modification agent incorporated by simultaneous wet ultra-fine grinding in a laboratory stirred mill was investigated. The physical, physico-chemical and application properties of the modified wollastonite were measured and evaluated. The results showed that grinding intensity markedly influences the modification effect because of the mechano-chemical effect. The hydrophilic surface of wollastonite was turned into a hydrophobic one after modification. The interaction between titanate and wollastonite under wet grinding circumstances was studied. It was suggested that physical adsorption and chemical adsorption of titanate coexisted on the wollastonite surface. The mechanical properties of polyethylene (PE) filled with the modified wollastonite powder were markedly improved.

Keywords: silicate minerals; modification; surface properties; ball milling; fillers

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1. Introduction

Surface modification, as a key process in functional powder preparation, is an important modern processing technology for non-metallic minerals. The modified wollastonite has been widely applied as a filler material. Surface modification renders hydrophilic wollastonite particles hydrophobic, which makes wollastonite filler particles well coupled with the organic matrix, such as plastics, rubber, and adhesives. The filler particles with modified surfaces markedly improve the mechanical properties of the matrix, increase the loading in the matrix, and lower the production cost.

The conventional surface modification technology, including the heating mixing modification and the packing modification methods, has been widely applied to fillers and pigments treatment. However, it has some defects such as weak stirring strength, low materials mixing degree, uneven

dispersion between agent and materials, and especially, the lack of favorable reaction circumstances. Consequently, the modification effect is poor and the product quality is unstable [1-3]. Thus, it is necessary to search for a highly effective modification method.

Mechano-activated surface modification is a modification method of utilizing the mechanochemical effect. The mechanochemical effect occurs during high intensity grinding, the solid particles collide against each other under instant enormous mechanical forces, causing a series of surface interactions, such as physical, physicochemical, structural, and mechanical changes on the surface as well as in the subsurface region [4-5]. The mechanochemical effect results in energy storage on the surface of minerals and markedly enhances the surface reaction activity [6]. Therefore, mechano-activated surface modification enhances the reactivity between phases due to the increased surface activity of mineral particles [7-8]. The advantage of mech-

ano-activated surface modification has been proved by many surface modification studies on mineral powders, such as SiO_2 [9], $\alpha\text{-Al}_2\text{O}_3$ [10], SiC [11] and others [2]. However, most of these modifications have been carried out in a dry grinding system, which need a very long time and much more energy.

Because many technological factors, such as the suspension of particles and dispersion of agents, the change of modification temperature and solid density of pulp, can be well controlled in a wet grinding system, the mechano-activated surface modification in the wet grinding system is considered to be one of the most efficient and promising surface modification methods. Moreover, this method combines surface modification and ultra-fine grinding together in the grinding equipment, which has already been commercially used to produce fine and ultra-fine mineral powders. Therefore, the wet mechano-activated surface modification is easier to be applied on an industrial scale.

As reported recently wet chemico-mechanical surface modification has been studied and used in the modification of calcium carbonate with sodium stearate [12], titanate [13-14], aluminate [15], alkyl amine dimethyl phosphonic acid [16], and polymer grafting [3] as modifiers respectively, and also in the modification of tourmaline with sodium stearate as the modifier [17].

The surface modification of wollastonite particles with titanate incorporated with simultaneous wet ultra-fine grinding in a stirred mill was described in this paper, and the influence of various technological parameters on the properties of the modified product was discussed. The modification effect was evaluated by the physical and mechanical property tests of polymer materials with modified wollastonite particles as the filler. The mechanism of the interaction between titanate and wollastonite was studied.

2. Experimental

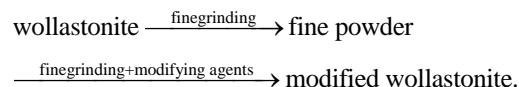
2.1. Samples and modifying agents

The experiment sample was fine wollastonite powder from Jilin Province, China. Its main chemical composition (wt%) was CaO 44.86, SiO_2 50.32, Al_2O_3 0.48, Fe_2O_3 0.31, K_2O 0.064, Na_2O 0.050, and MgO 1.26. The particle size distribution (accumulated percentage, %) of the sample was as follows: $<1\text{ }\mu\text{m}$, 1.6; $<2\text{ }\mu\text{m}$, 4.7; $<5\text{ }\mu\text{m}$, 12.8; $<10\text{ }\mu\text{m}$, 27.5; $<15\text{ }\mu\text{m}$, 45.1; $<20\text{ }\mu\text{m}$, 63.8; $<30\text{ }\mu\text{m}$, 82.4; $<40\text{ }\mu\text{m}$, 91.3; $<50\text{ }\mu\text{m}$, 96.7; $<60\text{ }\mu\text{m}$, 100. The medium size of the sample was $16.31\text{ }\mu\text{m}$, the specific surface area $0.280\text{ m}^2\cdot\text{g}^{-1}$, the brightness 88.40, and the density $2.85\text{ g}\cdot\text{cm}^{-3}$.

The titanate coupling agent (NT2) used in the experiments was chemically pure, and the water used was distilled water.

2.2. Test and evaluation method

Modification experiments were conducted in an ultra-fine stirred mill with a volume of 0.25 L. The process was



The grinding media were glass balls with a tiny diameter. The mineral sample of 20 g was added for each test. The optimized technological parameters were determined through experiments. The samples examined were the products treated under the optimized technological conditions. The modified samples were cleaned by acetone many times for mechanism studying.

The effect of surface modification of the wollastonite sample was evaluated by sedimentation tests in kerosene. The sedimented particle mass on a sedimentation disc from the beginning to the end of sedimentation was recorded by an electronic balance in a self-assembled sedimentation set-up, and the ratio of sediment mass to the total particle mass over the sedimentation disc, namely the sedimentation ratio, was calculated. The lower the sedimentation ratio for a sample, the better the dispersion of particles in kerosene and the more the hydrophobicity of particle surfaces. As a result, the modification effect of particles will be more enhanced.

The particle size distribution of the ground wollastonite was measured by an SA-CP3 type sedimentation particle size distribution analyzer made by Shimadzu Co., Japan. The adsorption form of NT2 on the surface of wollastonite was determined by infrared spectrometry (Bruker IFS-113 infrared spectrometer).

3. Results and discussion

3.1. Influence of the intensity of grinding mechanical force on the surface modification of wollastonite

(1) Particle size

The NT2 agent was used to modify wollastonite after the sample was wet ground to a certain size for a given period. Fig. 1 shows the relationship between grinding time and sedimentation ratio. The influence of grinding time on the medium size (d_{50}) and the specific surface area (S_v) of the ground wollastonite is shown in Fig. 2.

As shown in Fig. 1, the sedimentation ratios of wollas-

tonite modified by NT2 (1wt%) are significantly lower than those of non-modified wollastonite (0wt%). The sedimentation ratios of modified wollastonite by NT2 decrease gradually with the increase in grinding time, and becomes stable (less than 20%) after 1.5 h. It shows that the modification effect of wollastonite ground with modification agent NT2 is remarkable, and grinding time 1.5 h is optimal. Fig. 2 shows that the particle size of wollastonite under optimal modification conditions is $d_{50}=2.58 \mu\text{m}$ and $S_v=1.223 \text{ m}^2\cdot\text{g}^{-1}$.

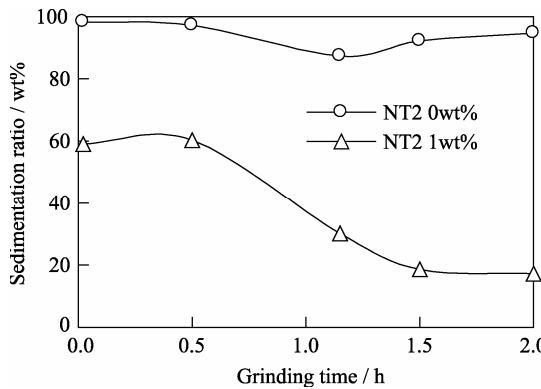


Fig. 1. Influence of grinding time on the modification effect.

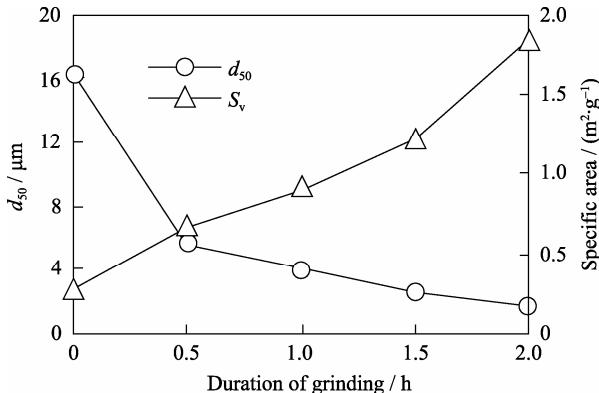


Fig. 2. Fineness of wollastonite at different grinding time.

The influence of NT2 dosage on the modification effect of wollastonite (ground for 1.5 h) is shown in Fig. 3. It can be seen that the modification effect is strengthened until the NT2 dosage reaches 1wt%. Beyond this dosage, the modification effect remains unchanged.

(2) Modification time and mixing speed

The influence of modification time and the rotation speed of the stirred mill on NT2 modification effect is shown in Fig. 4. The fixed conditions are as follows: pH 8.0; pulp temperature, 70°C; pulp density, 40%; the mass ratio of grinding media to mineral feeding, 5; and grinding time be-

fore modification, 1.5 h. It can be found that the optimal values of modification time and mixing speed are 20 min and 1000 r·min⁻¹, respectively.

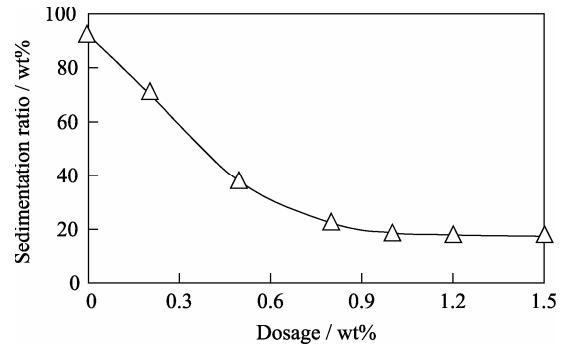


Fig. 3. Effect of the NT2 dosage on modification.

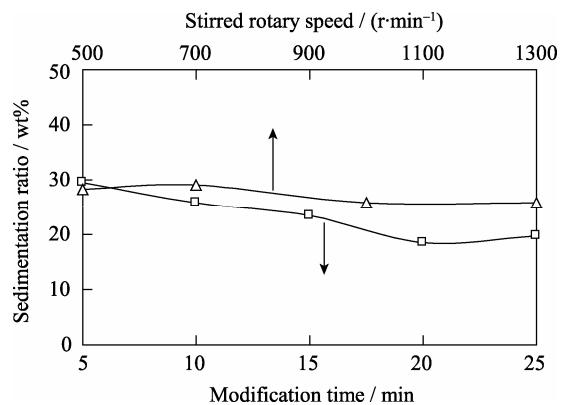


Fig. 4. Influences of modification time and stirred rotary speed on the modification effect.

(3) Mass ratio of grinding media to mineral feeding

The mass ratio of grinding media to mineral feeding is one of the most important technological factors of wet ultra-fine grinding. The influence of different mass ratios of grinding media to mineral feeding on the modification of wollastonite is shown in Fig. 5. Other factors in the experiments are the same as those in the above experiment (Fig. 4) except for modification time (20 min) and mixing speed (1000 r·min⁻¹). It is seen that the modification of wollastonite can be markedly enhanced at the ratio beyond 3, and the optimal value is 5.

3.2. Properties of modified wollastonite

(1) Physical properties

The physical and physic-chemical properties of wollastonite before and after modification are shown in Table 1. Compared with non-modified wollastonite, the contact angle of modified wollastonite increases in water and decreases in

kerosene; the water absorption values for 7, 14, and 21 d decrease greatly; and the water permeating time also increases greatly. This indicates that the hydrophilic surface of wollastonite is rendered hydrophobic after modification. The modification also leads to the increase in brightness.

(2) Mechanical properties of polyethylene (PE) filled with wollastonite

The mechanical properties of polyethylene filled with non-modified and mechano-activated modified wollastonite powders at the same filling percentage are listed in Table 2. The melt flow rate reflects the dispersion extent of the filler in the PE matrix, while the tensile strength, critical stretching elongation, and winding yield strength manifest the coupling state between filler particles and the matrix. Table 2 shows that, compared to the non-modified filler, all the me-

Table 1. Physical properties of wollastonite before and after modification

Sample	Contact angle / (°) (in water / in kerosene)	Water absorption value / % (7 d / 14 d / 21 d)	Permeating time of water / s	Brightness
Before modification	48.9 / 110.8	5.56 / 11.11 / 11.11	3	88.4
After modification	78.8 / 70.5	1.96 / 3.92 / 3.92	550	91.2

Table 2. Properties of polyethylene (PE) filled with wollastonite

Sample	Melt flow rate / (0.1 g·min ⁻¹)	Tensile strength / MPa	Critical stretching elongation / %	Winding yield strength / MPa
Non-modified wollastonite	1.12	8.76	140	10.5
Modified wollastonite	1.74	9.09	110	12.0

3.3. Mechanism of the interaction between NT2 and wollastonite

(1) Examination of IR spectra

The IR spectra of wollastonite, NT2, and wollastonite modified by NT2 are shown in Fig. 6. It can be seen from Fig. 6(a) that the characteristic absorption peaks of wollastonite appear between 1086 and 903 cm^{-1} [18]. The absorption peak of NT2 at 3200-3500 cm^{-1} in Fig. 6(b) is caused by the OH^- flex vibration and movement because of the formation of hydrogen bonds, and the absorption peak at 1000-1300 cm^{-1} is formed by $\text{P}-\text{O}-\text{H}$, $\text{P}-\text{O}-\text{P}$, and $\text{P}=\text{O}$, as well as the reaction among them. In the infrared spectrogram of NT2, the flex absorption peaks of CH_3- and CH_2- appear at 2984 and 2934 cm^{-1} , respectively [19]. In Fig. 6(c), very weak characteristic absorption peaks of CH_3- and CH_2- are observed at a wavenumber slightly lower than 3000 cm^{-1} , indicating that NT2 is adsorbed on the surface of wollastonite. Because the infrared sample is cleaned by acetone many times, it is reasonable to suggest that this adsorption may be chemisorption.

chanical properties of PE with the mechano-activated modified filler are markedly improved, except for stretching elongation.

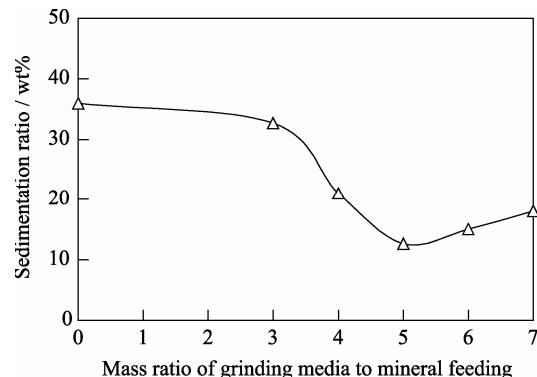


Fig. 5. Influence of the mass ratio of grinding media to mineral feeding on the modification effect.

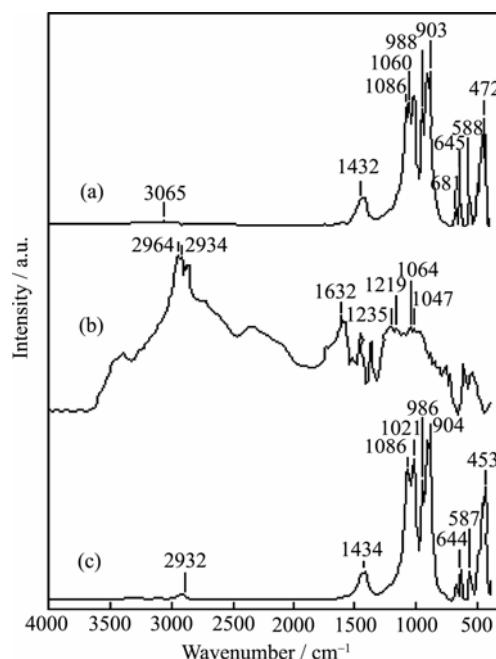


Fig. 6. IR spectra of wollastonite (a), NT2 (b), and wollastonite modified by NT2 (c).

(2) Adsorption strength experiment

The adsorption strength of NT2 on the surface of modified wollastonite (pH 6) was studied by applying stirring and water washing. The results are shown in Fig. 7.

Fig. 7 shows that the sedimentation ratio of modified wollastonite is much lower than that of wollastonite without modification, and the sedimentation ratio of the washed product is higher than that of the non-washed one. It is evident that washing can remove some weakly adsorbed NT2, but is not able to remove the strongly adsorbed NT2, which means that the chemical adsorption and the physical adsorption of NT2 on the surface of wollastonite coexist at the same time.

(3) Adsorption model of NT2 on the surface of wollastonite

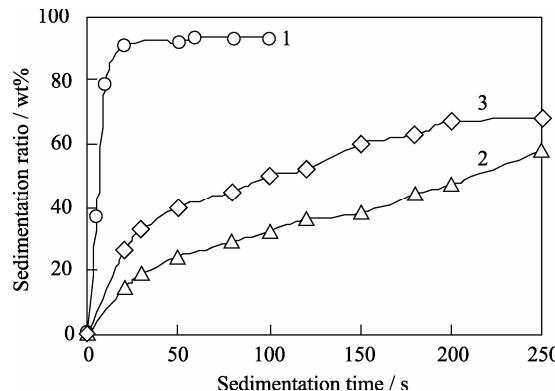
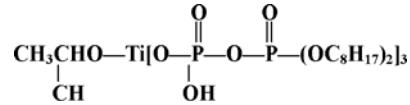


Fig. 7. Sedimentation ratios of different wollastonite products: (1) wollastonite; (2) wollastonite modified by NT2; (3) wollastonite modified by NT2 with water washing 4 times.

The chemical formula of NT2 (single alkoxy pyrophosphate titanate) is shown as the following [1]. NT2 does not dissolve in water and also not react with water. Therefore, NT2 is stable in the modification process.



The chemical formula of wollastonite is CaSiO_3 or $\text{Ca}_3[\text{Si}_3\text{O}_9]$. The unsaturated bonds of $\text{Ca}-\text{O}$ and $\text{Si}-\text{O}$ exposed on the cleavage plane of wollastonite may hydrate to produce some surface OH^- groups [20], as shown in Fig. 8. Therefore, the surface interactions between wollastonite and NT2 during the modification process are suggested as follows: (1) NT2 (without hydrolysis) directly participates in the reaction, after that, the chemical environment of Ti and P changes; (2) surface OH^- groups of wollastonite participate in the reaction with NT2.

The proposed adsorption model of NT2 on the surface of wollastonite is shown in Fig. 9.

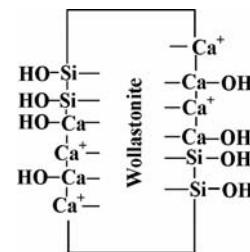


Fig. 8. Surface structure of wollastonite.

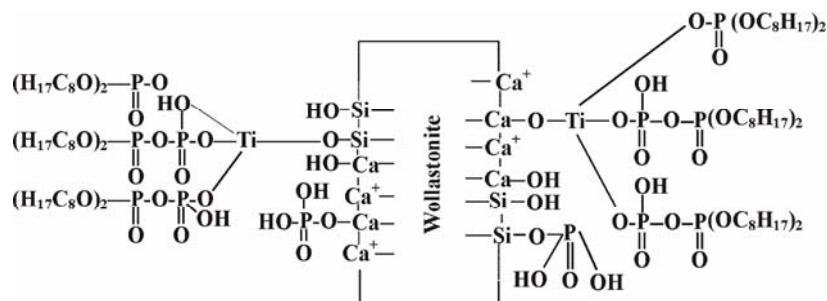


Fig. 9. Adsorption model of NT2 on the surface of wollastonite.

4. Conclusions

(1) Mechano-activated surface modification with wet ultra-fine grinding can intensify the modification process, improve the filling quality of modified products, simplify the production technology, and lower the production cost.

(2) The grinding fineness and the intensity of fine grinding mechanic force, reflected by modification time, the rotation speed of the stirred mill, and the mass ratio of grinding media to mineral feeding, are the important factors of mechano-activated surface modification. Modified wollastonite powder with a medium size of $2.58 \mu\text{m}$ and a specific

surface area of $1.223 \text{ m}^2 \cdot \text{g}^{-1}$ can be obtained by the mechano-activated surface modification method under optimized experiment parameters.

(3) The hydrophilic surface of wollastonite is rendered hydrophobic after modification, and the mechanical properties of polyethylene (PE) filled with the modified wollastonite powder can be markedly improved.

(4) The mechanism of the chemical adsorption of NT2 on the surface of wollastonite and the adsorption model are proposed.

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