

Preparation and properties of superfine $Mg(OH)_2$ flame retardant

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Abstract: Preparation of superfine magnesium hydroxide with the bittern and ammonia was studied. The properties of the products were analyzed by laser granularity, X-ray diffraction, scanning electron microscope, the limiting oxygen index and the wetting angle measurements. The results show that the mean particle size of the magnesium hydroxide is about 230 nm with a platelet shape and the specific surface area is about $48 \text{ m}^2/\text{g}$ when the temperature is $55 \text{ }^\circ\text{C}$, and the ammonia and bittern are instilled simultaneously during the reaction process. After the modification, the limiting oxygen index and physical chemistry performance of the magnesium hydroxide were examined. The results show that the contact angle of magnesium hydroxide is 132.5° and the limiting oxygen index is 31.5 %, indicating that the modified magnesium hydroxide is an effective flame retardant and can be applied as flame retardant additives of the macromolecule compounds such as plastic, synthetic rubber and synthetic fibre.

Key words: bittern; ammonia; magnesium hydroxide; $Mg(OH)_2$; flame retardants; limiting oxygen index

1 Introduction

With the fast development of the macromolecule industry, the macromolecule synthetic materials such as plastic, synthetic rubber and synthetic fibre are used in a wide range of fields of building materials, household appliances, plane and automobile manufactures and chemical industry and so on. Now the performance of macromolecule flame retardant material has drawn worldwide attention[1]. In recent years, due to the problems of the increasing number of fire disasters as well as the pollution caused by plastic incineration and the appearance of Dioxin, more and more attention has been paid to the environmental protection. Therefore the application of the organic bromic flame retardant which enjoys a large market share before is restricted in more and more areas[2]. Nevertheless the research on the innocuous, highly efficient and smoke-repressive inorganic flame retardant, especially the magnesium hydroxide flame retardant, is very interest-arousing. Scientists all over the world are now showing great enthusiasm on the magnesium hydroxide flame retardant which is bound to have an optimistic market prospect[3–8].

Magnesium hydroxide is a kind of inorganic flame

retardant additive, and has the following advantages: 1) excellent smoke-repressive property, its smoke-repressive capability is better than aluminum hydroxide[9]; 2) innocuous property, it has no harmful emission during the process of preparation and application (It's a real kind of environmentally friendly material[10]); 3) plentiful resource of raw materials, China has a big province of the salt lake, and the plentiful magnesium resource of the salt lake, the brine emitted from potassium fertilizer plant can also be used as the raw material for magnesium hydroxide manufacture; 4) compared with organic bromic flame retardant, it is more financially competitive due to its low cost[11].

According to the raw materials used, the magnesium hydroxide preparation techniques can be mainly defined into magnesite calcination hydration method, bischofite pyrolysis method, seawater (brine) lime cream magnesium-deposition method, etc[12]. But in the preparation of the superfine magnesium hydroxide these ways are usually not used. The bischofite from Cha'erhan saline(Qinghai Province) was used as a raw material and the high-concentration brine was confected after simple purification pretreatment. The platelet-shaped and superfine magnesium hydroxide sample was prepared through ammonia magnesium-deposition

method. The flame retardant performance was measured by the Limiting Oxygen Index (LOI) method after further surface modification treatment.

2 Experimental

2.1 Preparation of superfine magnesium hydroxide

The bischofite was dissolved in deionized water to produce saturated solution, and was further diluted to a solution with a certain magnesium ion concentration by adding deionized water after removing the suspending impurities by filtering. Ammonia was as precipitator. In the experiment, ammonia and the brine were instilled simultaneously into a reactor which had a stirrer and was filled with the 50 mL substrate liquid. The substrate liquid was a mixed solution of ammonia and ammonium chloride. The pH value of the solution was controlled by means of controlling the instilling speed of ammonia and bittern. A certain temperature and time were controlled during the whole reaction process. The past-filtered $Mg(OH)_2$ precipitate was cleansed for three times respectively by diluted ammonia and anhydrous alcohol. Afterward, $Mg(OH)_2$ precipitate was dried at 110 °C in dehumidifier oven, then the sample was dispersed by the assistance of ultrasonic waves with anhydrous alcohol, and then dried. Finally white loose superfine $Mg(OH)_2$ powder was obtained.

2.2 Surface modification of superfine $Mg(OH)_2$

In the experimental process, the obtained $Mg(OH)_2$ powder and a certain amount of anionic surface modifier and deionized water were added into another reactor, where they reacted for 2-3 h at 60–80 °C with adequate stirring. After completion of filtration, cleaning and then drying at 110 °C, finally the flame retardant standard $Mg(OH)_2$ powder was obtained.

2.3 Characterization and analysis of products

The crystallography of the magnesium hydroxide was analyzed by X-ray diffraction(XRD) with $Cu K_{\alpha}$ radiation and operated at a tube voltage of 40 kV and a current of 20 mA. The surface morphology of the samples was observed by scanning electron microscope(SEM, KYKY-2800). The particle size and the limiting oxygen index of the samples were carried out on laser granularity apparatus (Ms-2000) and the limiting oxygen index apparatus (HC-2). The contact angle was measured by the wetting angle measurement apparatus (JJC-I).

3 Results and discussion

3.1 Main influence of magnesium hydroxide on particle size during reaction process

The main factors such as the supersaturation degree

and the temperature are studied in the experiment process. The influence of supersaturation degree of magnesium hydroxide on particle size is shown in Table 1. The calculation of $Mg(OH)_2$'s supersaturation degree depends on the following equation[13]:

$$Q = \sqrt[3]{[Mg^{2+}][OH^{-}]^2} \quad (1)$$

In the equation, $[Mg^{2+}]$ and $[OH^{-}]$ are the moment concentration of the structure crystal ion in the deposition process of $Mg(OH)_2$, and they have a direct effect on the values of Q . Therefore, in order to prepare superfine $Mg(OH)_2$ particles, the pH of the solution and Mg^{2+} ion concentration are studied. Table 1 lists the mean particle size of the difference of the pH value and Mg^{2+} ion concentration under a certain experimental condition with 30 °C.

Table 1 Influence of particle size with different pH values and Mg^{2+} concentration

Experiment No.	pH value of solution	Mg^{2+} concentration/(mol·L ⁻¹)	Mean particle size of magnesium hydroxide/nm
1	7.0	0.5	2000
2	9.0	1.3	791
3	10.0	2.0	487
4	10.5	3.0	401
5	11.0	4.0	375

Table 1 shows that the mean particle size of magnesium hydroxide apparently decreases with the increasing of the pH value of the solution and Mg^{2+} concentration under a certain experimental condition. This means that the supersaturation degree of the reaction is important to the particle size of magnesium hydroxide[14].

While considering the crystallization kinetics properties of $Mg(OH)_2$, precipitate formation chemistry is a branch of crystal chemistry. As for crystal precipitate, the particle formation has a course as follows[15]:

Structure crystal ions → (nucleation) → crystal nucleus → (growth) → precipitate particles.

A few structure crystal ions firstly accumulated to form a small particle called crystal nucleus. This process is called nucleating process, and the nucleation rate is used to scale the speed of nucleating process. Then the structure crystal ions will be directionally distributed around the crystal nucleus, and gradually form the precipitate particles. This is the growth process, and the speed is measured by the growth rate. The particle size of $Mg(OH)_2$ is determined by the ratio of nucleation rate and growth rate.

Hence, in order to prepare superfine $Mg(OH)_2$ particles, it is essential to keep enough concentrations of

the Mg^{2+} and OH^- . In the experiment, ammonia and the bittern were instilled simultaneously in the preparation, and controlled by high concentration. The magnesium hydroxide of the mean particle size of 300–400 nm is obtained when the pH value is 11.0 and the Mg^{2+} ion concentration is 4.0 mol/L.

Fig.1 shows the change tendency of magnesium hydroxide of the mean particle size at different temperatures. When the pH value of solution is 11.0 and the concentration of Mg^{2+} is 4.0 mol/L, it can be seen that the particle size of magnesium hydroxide firstly ascends, then descends, and then ascends with temperature. When the temperature is 55 °C, the mean particle size of magnesium hydroxide is about 230 nm. The reason maybe is when the experiment condition is certain, the temperature exerts a strong influence on the aggregation behaviour of the magnesium hydroxide particles and changes the magnesium hydroxide particles, and the mechanism is complicated[16]. It is maybe suggested that at 50 °C, the system was not given enough time to reach its equilibrium state and therefore, the growing particles have not reached less size. The data for over 60 °C cannot be interpreted in the same way due to the difficulty to distinguish single platelets diameter in the morphology and the easiness of aggregation.

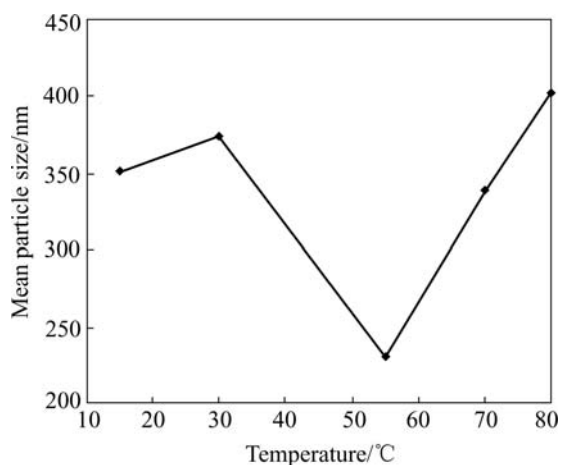


Fig.1 Particle size at different temperatures

The granularity analysis of superfine $Mg(OH)_2$ prepared under the same conditions is shown in Fig.2. It is displayed that the distribution of the particle size is in a narrow range, indicating the material has a very uniform particle size around 230 nm, the specific surface area is about 48 m^2/g , and 98 % of the $Mg(OH)_2$ powders has a particle size smaller than 1 μm , and the powder is fit for the standard of superfine $Mg(OH)_2$. The particle size of the samples is smaller than that of Amerbrom's (0.55 μm), which is the best in America.

3.2 Analysis of SEM and XRD before modification

The scanning electron microscope(SEM) analysis of

superfine $Mg(OH)_2$ is shown in Fig.3. The superfine $Mg(OH)_2$ is platelet-shaped and has a good dispersion.

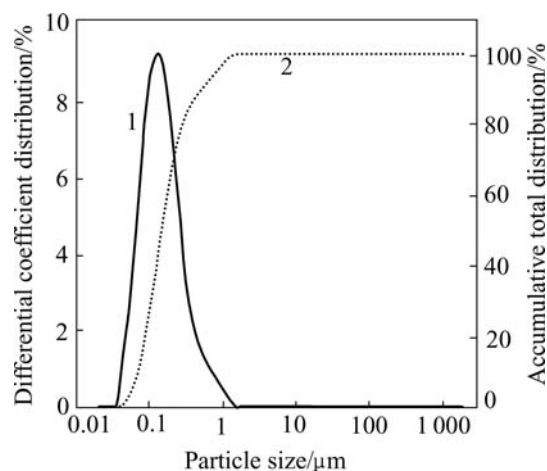


Fig.2 Laser granularity photo of magnesium hydroxide: 1) Frequency curve; 2) Undersize curve

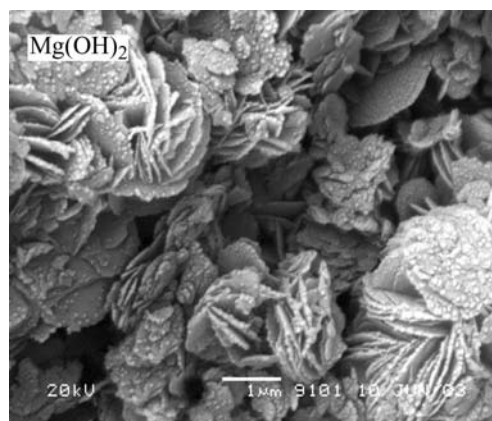


Fig.3 SEM image of magnesium hydroxide

The result of superfine $Mg(OH)_2$ X-ray diffraction analysis is shown in Fig.4. As shown in the figure, there are no curve peaks of impurities besides the curve peak of $Mg(OH)_2$, and the high purity of $Mg(OH)_2$ is undoubtedly proved. The XRD spectra of the samples illustrate that all samples possess the cubic crystalline structure. (Powder Diffraction File JCPDS No.7-239 International Centre for Diffraction Data, Swarthmore, 1989). The XRD curves registered for all investigated samples show that particles have a good crystallinity of magnesium hydroxide.

3.3 Physical and chemical performance of magnesium hydroxide after modification

When $Mg(OH)_2$ was added to polymeric material, the working and mechanical ability got worse because of the bad tolerance of $Mg(OH)_2$ and polymeric material. The worst consequence is that the material would not suit any more. The main reason was that $Mg(OH)_2$ was an inorganic material whose polarization was very large,

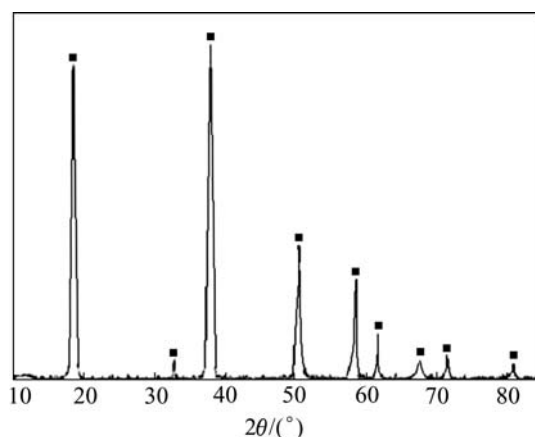


Fig.4 XRD pattern for magnesium hydroxide sample

and the crystal surface possessed positive electricity, it also possessed hydrophilic, while the polymer possessed non-hydrophilic, so the affinity of $Mg(OH)_2$ with the polymer was bad. At the same time, there were gaps in the interface between the $Mg(OH)_2$ and the polymeric material. It shows a bad dispersion. So we should modify the $Mg(OH)_2$ surface to change the hydrophilic, improve its tolerance with polymeric material and to reduce the effects for the working and mechanics ability of polymeric products. For those, we studied the effects of specific surface area and contact angle of modified $Mg(OH)_2$, and the results are shown in Table 2.

Table 2 Effects of specific surface area and contact angle of modified $Mg(OH)_2$

Sample	Specific surface area/($m^2 \cdot g^{-1}$)	Contact angle/($^\circ$)
Before modification	48.0 ± 0.5	Almost zero (entirely wetted)
After modification	47.1 ± 0.5	135.2

As shown in Table 2, the contact angle of the modified magnesium hydroxide is 135.2° , compared with unmodified magnesium hydroxide which has more change. At the same time, the specific area of modified magnesium hydroxide has little change. This means the surface of modified magnesium hydroxide changes the hydrophilicity (entirely wetted) from the hydrophobicity, and the effect of the modification is very good. It can also improve the mechanical performance of magnesium hydroxide. The main reason is that as the flame retardant of the polyethylene, a lot of magnesium hydroxide particles will extrude on the surface. Moreover, the interface of the particles and the polyethylene is very distinctive. The surface of the particles is not soaked by the resin. When the modified superfine magnesium hydroxide is added, the particle surface of magnesium hydroxide has floc formation. The interface is more blurry. Its tolerance with polymeric material is good. The effects for the mechanical performance of polymeric

products will be improved.

The SEM image of the modified magnesium hydroxide is shown in Fig.5. The modified superfine $Mg(OH)_2$ is also platelet-shaped the distribution of the particle size is in a narrow range, and it can improve the flame retardant of the magnesium hydroxide[17].

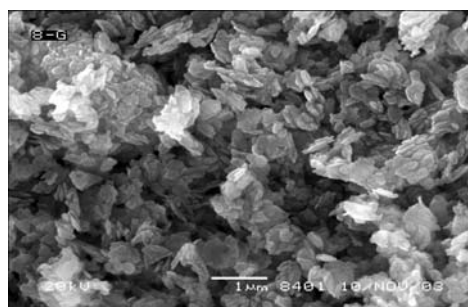


Fig.5 SEM image of modified magnesium hydroxide

3.4 Limiting oxygen index(LOI) study of superfine $Mg(OH)_2$

The flame retardant performance of magnesium hydroxide after modification was measured by the oxygen index of material. The measurement of oxygen index was conducted according to the standard of ISO 4589 – 1984 <Measurement of plastics flammability according to oxygen index>. The result of measurement is shown in Fig.6.

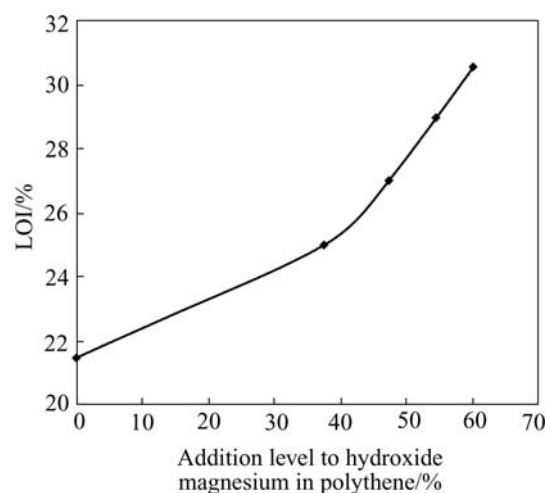


Fig.6 Variation of polyethylene's limiting oxygen index with addition level of $Mg(OH)_2$

It can be seen from Fig.6 that the limiting oxygen index increases from 21.5% to 32.5% when the addition volume of $Mg(OH)_2$ in polyethylene increases from 0% to 60%, the material's oxygen index increases with the addition of $Mg(OH)_2$. The material's limiting oxygen index reaches 32.5%, if the amount of $Mg(OH)_2$ is 60%, the increment is 17%. But a too high addition of $Mg(OH)_2$ may have an adverse impact on material's

mechanical performances, etc. So a proper addition of magnesium hydroxide in polymer is required.

4 Conclusions

1) Saline bischofite is selected as a raw material, while ammonia was selected as the precipitator. When the temperature is 55 °C, and ammonia and the bittern are instilled simultaneously, the superfine environmentally friendly Mg(OH)₂ is obtained by means of controlling other technical conditions during the reaction process.

2) The results of the laser granularity analysis and SEM analysis show that the product has a mean granularity of 200-300 nm, and it is platelet-shaped. Moreover it has a good dispersion. The superfine Mg(OH)₂ sample is an ideal flame retardant additive for macromolecule synthetic materials of plastics, synthetic rubber, synthetic fibre, etc.

3) After being modified by sodium stearate modification, the contact angle of the magnesium hydroxide has largely changed; the polyethylene material has a limiting oxygen index of 32.5% when the addition of Mg(OH)₂ increases to 60%. Therefore the modification efficiency is good and the flame retardant performance is significantly improved.

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