Preparation of Clay Nanocomposites Matrix

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***Abstract*- A series of sodium bentonites as raw material were purified. The purification bentonite was used to prepare clay nanocomposite with the requirement of high montmorillonite content. The methylene blue absorbed and swelling volume were selected as two indexes. And the optimal purification conditions were measured: bentonite slurry concentration of 7%, stirring time of 20min, centrifugal time of 30min, none dispersant agent requested. Then the montmorillonite content reached as high as 98.66%. The grain size, structural characterization and morphology of the purification bentonites were observed by means of X-ray diffraction, scanning electron microscopy. A better dispersibility and higher content matrix of montmorillonite were obtained by the purification process of bentonite.**

Keywords- Bentonite; Montmorillonite; Purification Process; XRD; SEM

I. INTRODUCTION

The nanocomposite material is composed of two or more solid phases. And the powder size has reached the nanometer scale in one dimension [1]. The nanocomposite material has the characters of high heat resistance, high strength, high modulus, high gas barrier property, low expansion coefficient, low density on the superiority [2-4]. So it can be widely used as a new high performance material in aviation, automobile, shipbuilding, electronics, construction, petroleum chemical industry. Bentonite is a kind of natural nano-clay. A new industrialization trend of the nanocomposites material prepared by benonite and polymer is formed. At present, the nylon 6/layer silicate nanocomposites, the polyimide/montmorillonite nanocomposites, the epoxy resin/bentonite nanocomposites, the polyaniline/bentonite nanocomposites have been developed. But the general requirement of nanocomposites is more than 95% of montmorillonite content [5-8]. So the natural bentonite should be purified. The purification methods of bentonite are generally classified into physical purification methods and chemical purification methods. In this research, the sodium bentonite was the raw materials, the applicable purification methods and the optimal purification conditions were discussed. Then the high purity of montmorillonite was prepared. And the matrix of polymer/bentonite nanocomposites preparation was ready [9].

II. EXPERIMENTAL

A. Raw Materials

The sodium bentonite in experiments was prepared from HeiShan, Liaoning Province.

B. Batch Method

The sodium bentonite was dried in the air, crushed into 200 meshes. Taking a certain amount of bentonite in distilled water of 250mL, and mechanical agitation was followed [10]. The bentonite particles was scattered in the water under the joint action of a polar water molecules force and mechanical force. And the insoluble impurities were precipitated in solution. Then the first-slurry was sucked out by siphonage, the large-diameter residue was discarded. A certain amount of dispersant was added in the first-slurry. The second-slurry was sucked out after standing for 24 hours and the common-diameter residue was discarded. The high content of montmorillonite was obtained from the centrifuge and dried. The parameters of methylene blue absorbed and swelling volume were indexes. The best preparation conditions were selected. And the high content of montmorillonite was used as matrix to synthesize the clay nanocomposites.

C. Analysis Method

1) Methylene Blue Absorbed:

The dispersing bentonite has absorbed ability of methylene blue trihydrate in aqueous solution, the adsorption quantity was called methylene blue absorbed, with 100g bentonite of adsorption methylene blue trihydrate quality (g) said [11]. The more volume of methylene blue solution requested, the higher content of montmorillonite. Therefore, methylene blue absorbed could be a major index to estimate the relative content of montmorillonite.

$$B=0.3199*N*V/G \qquad (1)$$

Where,

B—methylene blue absorbed（g/100g）

N—equivalent concentration of methylene blue per milliliter (g/mL)

V—volume of methylene blue standard solution required for the titration (mL)

G—grams of dry bentonite (g)

0.3199—provisions coefficient

2) Swelling volume:

Bentonite has the obvious property of water expansion, also the hydrochloric acid solution expansion. The gelation volume formed when bentonite was mixed with hydrochloric acid solution, which was called swelling volume [12]. It has closed relationship with the adsorption property of bentonite and content of montmorillonite, so it was also selected as an index to measure the purification conditions.

$$V_s=V/m \tag{2}$$

Where,

V_s—swelling volume (mL/g)

V—gelation volume (mL)

m— grams of dry bentonite (g)

3) Calculation of montmorillonite content:

$$M=B/0.442 \tag{3}$$

Where,

M—montmorillonite content（%）

B—methylene blue absorbed (g/100g)

0.442—provisions coefficient

D. Characterization Method

1) Grain Size:

The natural bentonite was many large size flocculation groups of different kinds of mineral particles. But the purification bentonite was high content montmorillonite particles. The grain sizes of two bentonites were measured by XRD. And the purification effect was compared by the results.

2) Structural Characterization:

Each phase has its own fingerprint pattern. And the diffraction pattern of mixture was the diffraction superposition of each single-phase. The characteristic peak of inherent phases was compared to the stand characteristic peak of single-phase in database [13]. The FOM value was the reciprocal of the match rate, the smaller the value, the higher it matches. And the interplanar distances was calculated by the diffraction pattern. The changes of interplanar distance were measured.

3) Scanning Electron Microscope:

The particle shape of bentonites was enlarged a certain multiples. And the three-dimensional surface conformation of sodium bentonite was observed on the JSM-6360LV scanning electron microscope.

III. RESULTS AND DISCUSSION

A. The Indexes Measurement of Sodium Bentonite Basic Properties

Methylene blue absorbed, swelling volume were measured. The results were shown as follows, 21-23 g/100 g of methylene blue absorbed, 25-40 mL/g of swelling volume, 150 mL/g of colloid index, 155.20 mmol/100g of cationic exchange capcity, 8.5-9.5 of pH.

B. Optimal Conditions of the Modified Bentonite Preparation

1) Effect of Concentration of Bentonite Slurry

The concentration of bentonite slurry was an important factor to the effect of dispersion and purification. The experimental results were shown in Fig. 1.

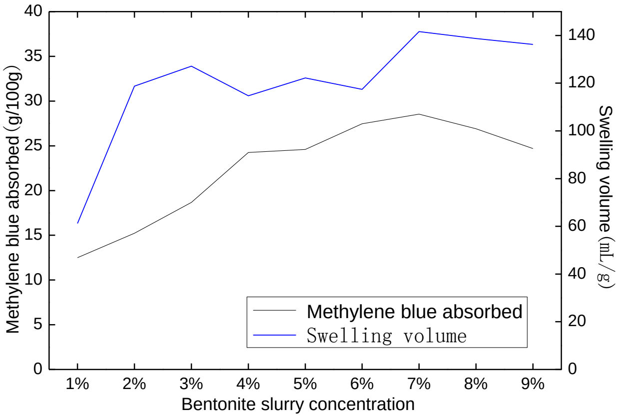

Fig. 1 Effect of concentration of bentonite slurry

It was known from Fig. 1, methylene blue absorbed and swelling volume increased with an increase concentration of bentonite slurry in the initial stage. The maximum of two indexes were 28.54g/100g and 141.61 mL/g at 7% of slurry concentration. Then, the methylene blue absorbed and swelling volume was decreased gradually.

This was because there was not enough bentonite in slurry when the concentration was too low. So the content of montmorillonite was low per milliliter. And the low concentration would also increase the follow dewatering load. But the flowability of the slurry became worse when slurry concentration was too high, which was not conducive to stirring. And the mechanical force provided from stirring was weak, the purification efficiency decreased. Considered, the slurry concentration of 7% was selected, the montmorillonite content of 64.57% was calculated.

2) Effect of Dispersant Types

The dispersing agent was added in the slurry to improve the flowability. So the detrital minerals subsided down rapidly. According to experimental method, the sodium carbonate (SC), sodium chloride (SCl), sodium pyrophosphate (SP), sodium dodecyl carbonate (SDC), and sodium silicate (SS) were selected as dispersing agents. The results were shown in Fig. 2.

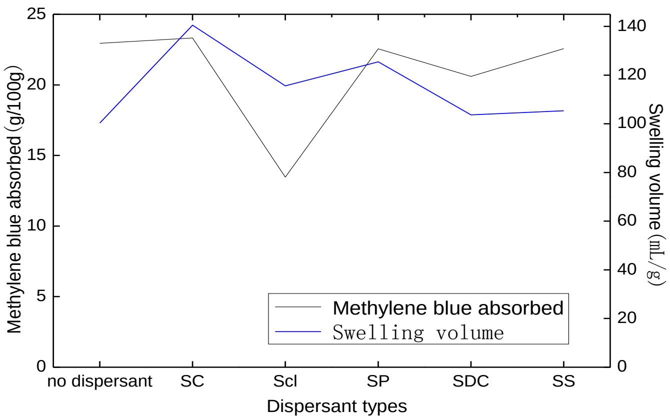

Fig. 2 Effect of dispersant types

Fig. 2 showed that, methylene blue absorbed reached 22.95 g/100 g and swelling volume reached 100.35 mL/g at none dispersing agent in slurry. The sodium carbonate was the best type in five dispersant agents. But methylene blue absorbed reaches 23.32 g/100g and swelling volume reached 110.56 mL/g when sodium carbonate added. This result was similar to the result without dispersing agent. These results can be explained as a higher capability of water-dispersible on sodium bentonite. The Na^+ charge density of sodium bentonite was smaller. So the cohesive energy of Na^+ and montmorillonite crystal was smaller, about 1000cal/mol. The particles of montmorillonite were not easy to form floc under the attraction of the positive charge and negative charge. By reductio ad absurdum, assume that the effect of sodium carbonate as dispersing agent was better, the explanation has been given in next batch experiments.

3) Effect of Dispersant Amount

The sodium carbonate was selected as a dispersant to measure the optimal condition of dispersant amount.

Fig. 3 shows that, the methylene blue absorbed decreased with an increasing amount of dispersant agent. For the swelling volume, the tendency was downward too. So the assumption above did not hold. And the purification effect was better without dispersing agent in slurry. The methylene blue absorbed was 26.03g/100g, swelling volume was 110.56 mL/g, and the content of montmorillonite calculated was 58.89%.

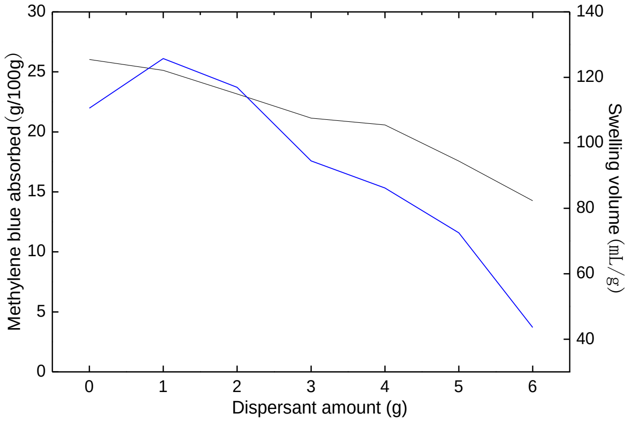

Fig. 3 Effect of dispersant amount

4) Effect of Stirring Time

The adequate stirring time played an important role to the dispersing effect of bentonite. The results were shown in Fig. 4.

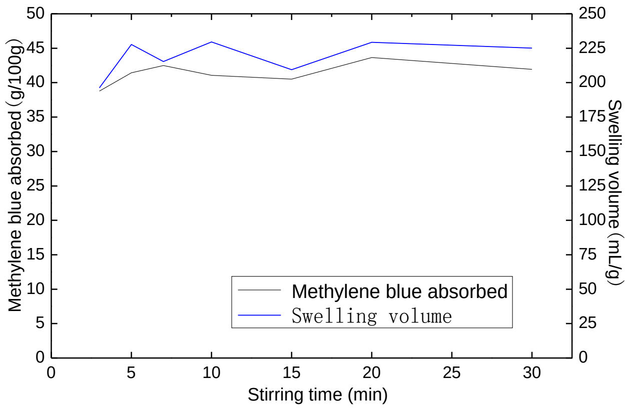

Fig. 4 Effect of stirring time

The methylene blue absorbed reached maximum of 43.66 g/100 g, the swelling volume reached 229.52 mL/g from 10 min to 20 min. The content of montmorillonite was 98.77%. The 20 min of stirring time was selected. Bentonite suspend readily with the form of crystalline aggregates in water, the hydrophobic film was formed as the action of the particles of bentonite surface and the electrolyte, the further dispersing effect of inside particles has been prevented. So the applied shear force was needed to release the inside particles. The appropriate stirring time provided the appropriate shear force strength.

5) Effect of Centrifugal Time

A certain degree of centrifugal force was used to improve the purification effect significantly. The results were shown in Fig. 5.

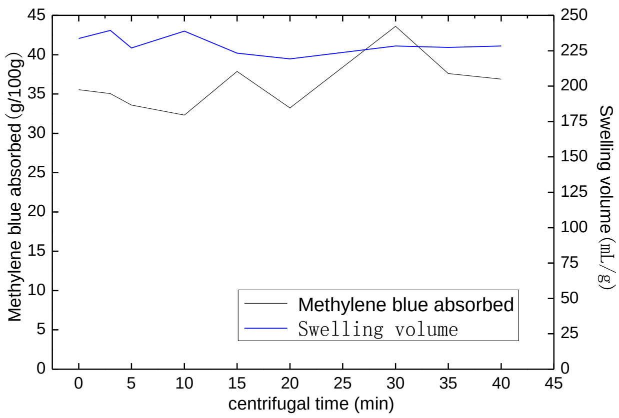

Fig. 5 Effect of centrifugal time

The methylene blue absorption was 43.61 g/100g at centrifugal time of 30min, the content of montmorillonite was 98.66%. And the tendency of swelling volume changed slightly with the increase of centrifugal time. So the 30min was selected as the optimal parameter. The slurry that was purified by natural subsidence process was further refined. A centrifugal force was provided by high-speed rotation, some of fine-grained detrital mineral had been separated by that. Then the slurry with the particle size of less than 5μm was obtained.

C. Analysis of the Structure of Raw and Modified Bentonite

1) Grain Size:

The two bentonites were characterized of grain size. The results were showed in Fig. 6 and Fig. 7.

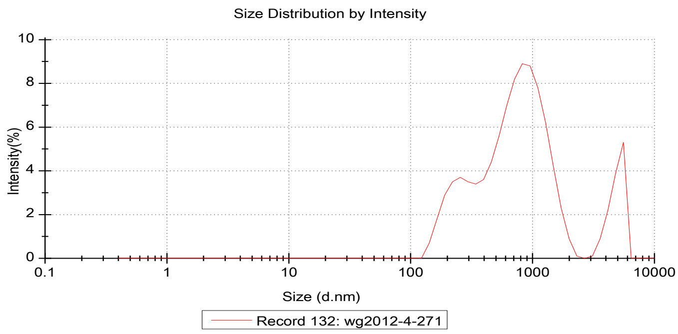

Fig. 6 The grain size of sodium bentonite

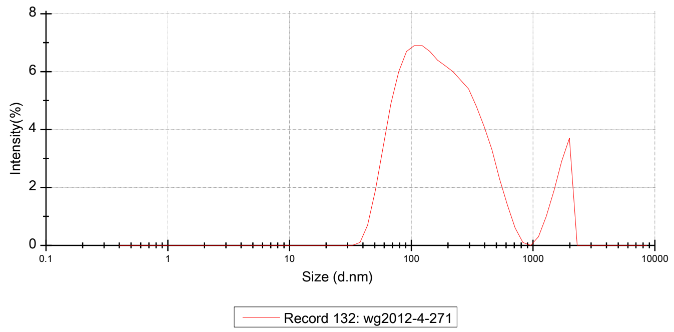

Fig. 7 The grain size of purification bentonite

The grain size density of sodium bentonite reached maximum at 800.0-825.0 nm, which was 8.9%. And the max grain size density of purification bentonite was 6.9% at 91.28-105.7 nm. So the grain size of two bentonites had a change after purified process. The grain size of purification bentonite almost reached the nanoscale, and could been used as a matrix of nanocomposites.

2) XRD

The purification bentonite was identified by phase search. The basis for identification was the polycrystalline diffraction PDF card in database, edited by JCPDS. The results were shown in Fig. 8.

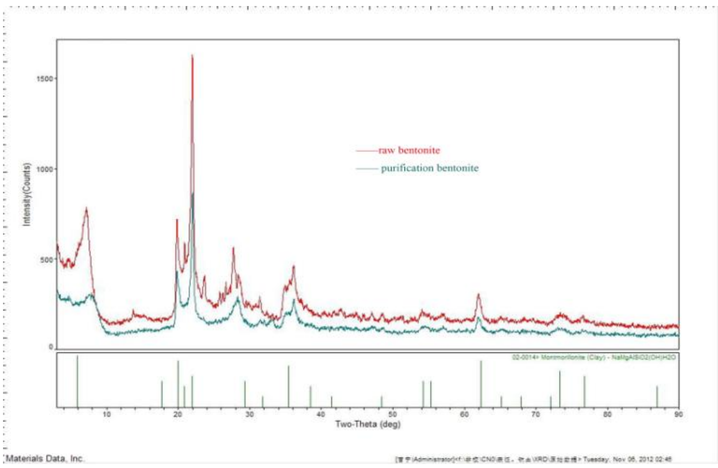

Fig. 8 Phase ID report of the purification bentonite

The characteristic peak of purification bentonite was matched to the montmorillonite card of No.02-0014, FOM value of 3.4. So the purification bentonite was proved as montmorillonite. The basic crystal structure was not changed by the shear force of the purification process, still had all characters of montmorillonite. So the purification bentonite could be used as a matrix.

Bentonite was a material of layered structure, the small-angle of XRD diffraction peaks could be used to study the mesoporous structure. The results were shown in Fig.9.

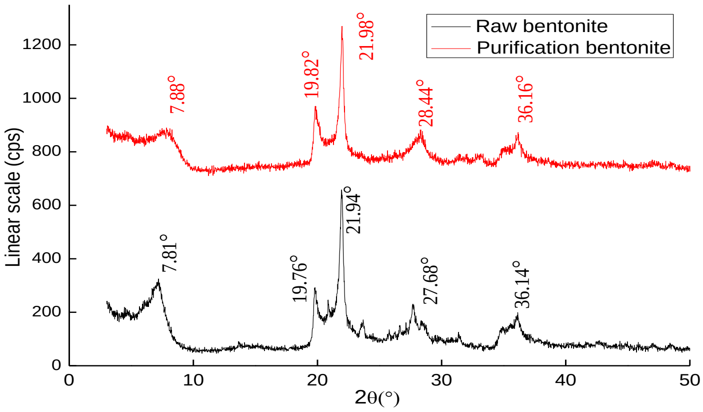

Fig. 9 X-ray diffractograms of two bentonites

The diffraction angle 2θ of raw bentonite was 7.199°. The diffraction angle 2θ of purification bentonite was 7.881°. The interplanar distance d was calculated according to 2θ and Bragg equation: $2d\sin\theta = \lambda$. The interplanar distance of raw clay was 1.4718nm, which was larger than purification clay (1.2001nm) obviously. The bentonite was filled with some impurities and other kinds of minor. So the interplanar distance of raw bentonite was larger, the bentonite was congregated into a big flocculation clumps. The purification benonite was a large number of montmorillonite particles without little impurities. So the interplanar distance of pure phase was smaller.

3) Scanning Electron Microscopy:

The sample was enlarged a certain multiple to observe the surface of three-dimensional conformation, shown in Fig. 10 and Fig. 11.

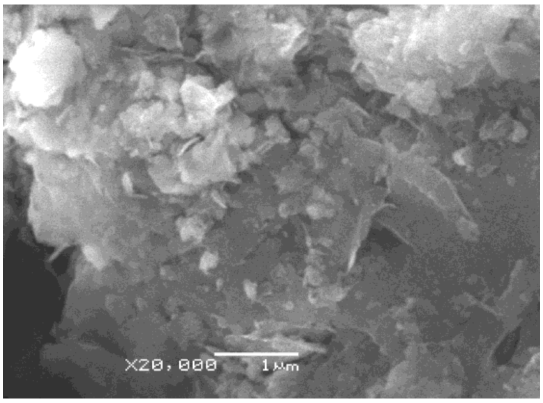

Fig. 10 SEM image of sodium bentonite

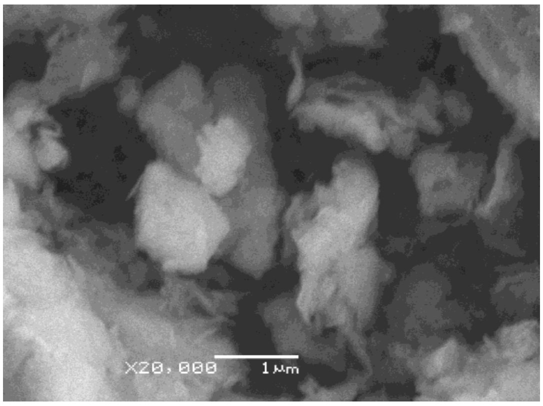

Fig. 11 SEM image of purification bentonite

The particles of raw bentonite were close together and formed an aggregate clump. But the particles of purified bentonite were dispersed and formed into some disperse clumps. So the purified bentonite has characters of flater surface area, better continuity, clear outline, and obvious hole. The organic matter could enter the interlayer easily and prepared the bentonite composite. So the purified bentonite as a matrix to prepare the nanocomposites has obvious advantages.

IV. CONCLUSIONS

For the sodium bentonite, a maximum content montmorillonite of 98.66% was found for 7% slurry concentration at a stirring time of 20min and a centrifugal time of 30min. None dispersant agent requested.

Purification process was summarized by the various steps in experimental. The step of natural sedimentation, secondary graded deposition, centrifugal was the physical method. Exploration of the factor of dispersant type and amount was informed that the purification effect without dispersant agent was better. So the chemical method was not used in this purification process. And it was a low-cost and green technology.

Analysis results of XRD showed that the interplanar distance of raw clay was 1.4718nm. The interplanar distance of purification clay was 1.2001nm, which was decreased in varying degrees. And the PDF card number was 02-0014.

Analysis results of scanning electron microscopy showed that the purified bentonite has the characters of flater surface area, better continuity, clear outline, obvious hole. The purified bentonite as a matrix to prepare the nanocomposites has obvious advantages.

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