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Purification of commercial grade bentonite from LamDong, Vietnam for nano-size montmorillonite

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ABSTRACT

The article will report the purification of Dilinh bentonite sample deposits of Lamdong province in Vietnam. The combination of sonication, sedimentation and dispersant $(NaPO_3)_6$ were applied to increase the montmorillonite (MMT) content. To evaluate the effect of $(NaPO_3)_6$ concentration, X-ray diffraction, Infra-red spectra, X-ray fluorescence spectra, dynamic light scatteringand scanning electron microscopy analyses were carried out. The results showed that, when $(NaPO_3)_6$content increased, the fraction of MMT increased and that of quartz decreased. The optimum $(NaPO_3)_6$ content was 5 wt%,to eliminate maximum of quartz and other non clay minerals, the recovery yield was 71.2%.This was a high quality MMT selection process; the purified MMT is suitable for application as nanofiller in high performance polymer nanocomposites.

Introduction

Bentonite is clayregularlygenerated from the alteration of volcanic ash, mainlyconsisting of smectite minerals, usually montmorillonite with 2:1 structure. Bentonite shows strong colloidal properties,when contacting with water its volume expands several times, creating a gelatinous and viscous fluid. The notable properties of bentonite (swelling, water absorption, hydration, viscosity, and thixotropy) drive it a valuable material for a broad spectrum applications.[1-3,12,13]Vietnam has many rich sources of bentonite deposits named Di Linh - Lam Dong, CoDinh – Thanh Hoa, Tuy Phong – Binh Thuan, etc. Vietnam bentonite is exploited and mostlyused as ceramic materials, construction materials, and environmental treatment. The reason is that the MMT content in bentonite is not high, so it cannot be used directly in some high-tech industries, but need to be enriched and modified. Through analysing commercial bentonite samples available in Vietnam, the sample from Di Linh showed high content of MMT, low impurities and small particle size [4,5]. With the aim of increasing the purity of commercial bentonite, so giving high MMT content, improve physical and chemical properties, making a wider range of application and rasing its value, this report will present the purification process of Di Linh bentonite and achived results.

Experimental

Chemicals

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In the study, commercial bentonite from DiLinh, LamDong (provided by HiepPhu Company) were selected. The average size particles of the bentonite were smaller than 6 µm.

$(NaPO_3)_6$ and distilled water were used for purifying the bentonite. All chemicals were analytical grade.

Purification of bentonite with $(NaPO_3)_6$ and sonification

In this research, bentonite was treated in water with $(NaPO_3)_6$ as a dispersing agent. 20 g of commercial bentonite was dispered in deionised water with weigh bentonite/water ratio: 1/30. $(NaPO_3)_6$ was added with 1, 5, 7 weight percent of bentonite (noted as A solution). The A solution was stirred at 500rpm for 1 hour then sonicating for 12 hours, sedimentation time was 12 hours. The upper part of A solution was collected (350 ml, noted as A1 solution). Add 350 ml deionized water to the lower part and same sedimentation process was repeated at least two times to collect A2 and A3. Mix A1, A2 and A3 together. After centrifugation for 15 min at 500, the solid fraction was dried at 80 °C for 4 hours and weighted to determine the yield of the separation method. Untreated bentonite sample was denoted as B0, bentonite samples treated with $(NaPO_3)_6$ 1, 5, 7 wt% were denoted respectively B1, B5, B7.

Characterization techniques

Bentonite samples (untreated and treated) were characterized by X-ray powder diffraction (XRD, λCuKα1=154.06 pm) using D5005 (Hanoi University of Science). XRD patterns were collected from 2θ = 2° to 80° by step of 0.03°/s. Furier transform infra-red measurements (FTIR) were carried out on FTIR Affinity - Shimadzu from 400 to 4000 cm^{-1} using an average of 64 scans and a resolution of 2 cm^{-1}. A Zeta Nano ZS Zetananosizer (Malvern Instruments) was used for the determination of particles size distribution (size range: 2 nm–10 µm). Before measurements, particles were dispersed in water and sonicated. The morphology of the samples was observed by scanning electron microscopy (SEM), using aS- 4800 microscope (Hitachi). The chemical composition of both bentonites was supplied by the producer and treated samples also determined by X-ray fluorescence measurements (XRF)

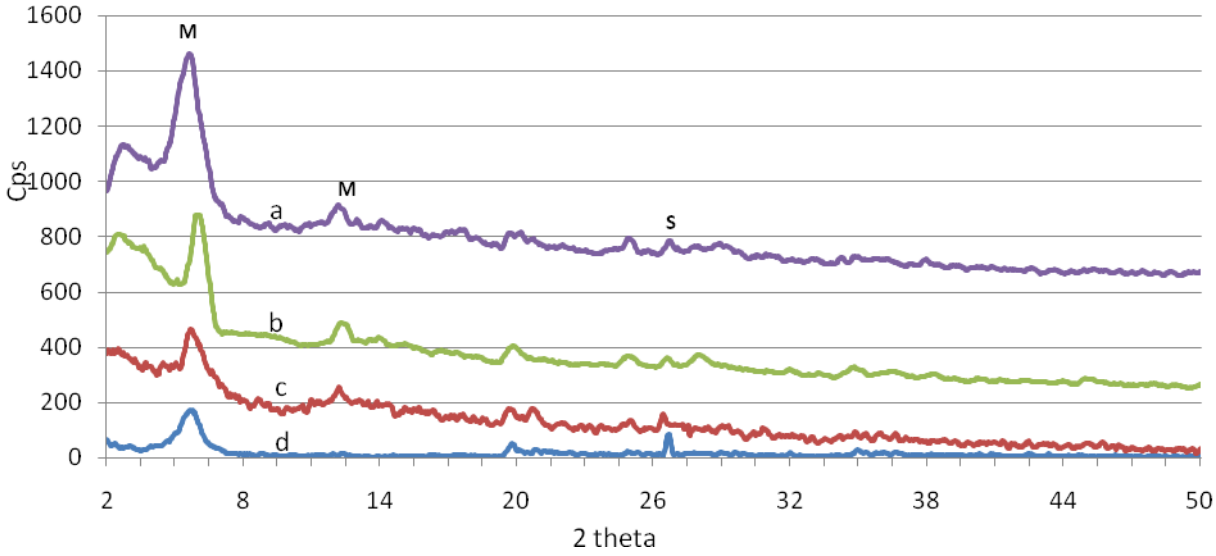

Figure 1: XRD diffactogram ofuntreated sample B0 (d) and treated samples with different $(NaPO_3)_6$ content from 1 to 7 wt% B1 (c), B5 (b), B7 (a)

Results and discussion

XRD analyses

XRD analysis of B0 sample (Fig. 1d showed characteristic peaks of MMT structure at 2θ = 5.8° and 12.1° (denoted as M). Peak denoted as S at 2θ26.5° were specified for α_SiO_2 phase. The XRD pattern of B0 sample prove that commercial bentonite from Dilinh – Lamdong have many impurities[6].The results were in good agreement with the chemical composition of both bentonites was supplied by theproducer that the bentonite was~65% MMT, ~30% quartz, kaolinite and other impurities. When the dispersing agentwas added, the amount of quartz in the refined samples decreased as the content of the dispersion increased. In XRD spectrum of sample B1 $(NaPO_3)_6$1 wt %) (Fig. 1c) the characteristic peak intensity of MMT was higher, the peaks characteristic for

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quartz were weaker and the noise peaks of non-clay mineral almost disappeared. XRD diagram of B7 (Fig. 1a) sample showed that most of MMT characteristic peaks are stronger, much higher than that of B5 sample. In the sample, there is a small amount of free quartz with typical peak at 26.6°; the intensity is weaker than that of B5.

FT-IR analyses

The full infra-red spectra (not shown), registered from400 to 4000 $cm^{-1}$of treated and untreated bentonites revealed the characteristic bands of MMT. Spectra of the raw bentonites presented two bands at 780 and 802 cm^{-1} (Fig. 2a) which were characteristic of quartz[7-11]. After purification, the intensities of these bands were very low, confirming the strong decrease in the quartz content of LamDong samples. These results completely agree with the XRD analysis results.

Size distribution analysis results

Figure 3 showed very broad particle size distributions of the untreated materials (maximum centered at about µm for Di Linh with an asymmetric tail in the range of micron/submicron sizes. The laser granulometry analyses showed that treating process strongly increased the number of submicron-sized particles attributed to MMT and decreased the number of larger particles. Especially, the dispersing agent allowed a significantimprovement of the separated amount of submicron-sized particlesand revealed the presence of very small traces of coarser impurities.

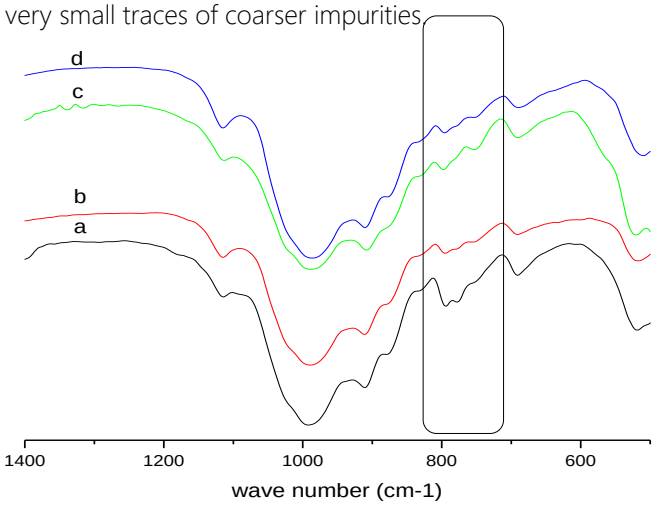

Figure 2: Infra-red spectra of B0 (a), B1 (b), B5 (c) and B7 (d)

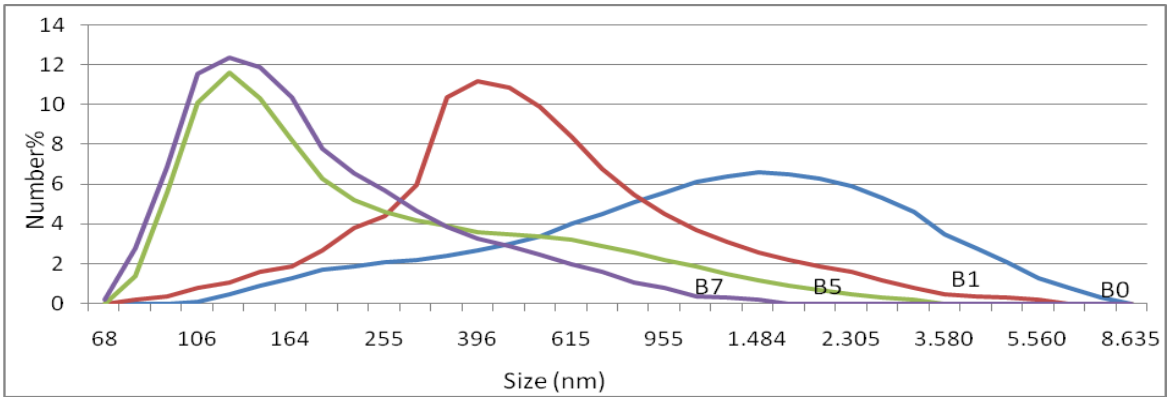

Figure 3: Size distribution of bentonite samples B0, B1, B5, B7

SEM image of bentonite samples

Initially commercial Di Linh bentonite morphology (Fig 4.a) showed that the nanoclays were lined with each other. The bentonite particles stacked in thin layers and on top of which there are some small particles of several hundred nanoscale or more, we think this could be SiO_2 particles.SEM image in Fig. 4b of B1 shows that mainly MMT plates are enlarged and layered together. In addition, images of smaller particles are not film-like but of impurity appear. The image (Fig. 4c and 4d) of B5 and B7 showed that the bentonite plates with nano thickness expanded into thin layers, and no other pictures of the impurities appeared.

Chemical composition of treated and untreated bentonit samples

The weight components of oxides and carbonates of all samples are presented in Table 1. We have found that commercial bentonite from Di Linh has quite a diverse composition. The contents of Al_2O_3 and SiO_2 are both

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high, making up the main component of montmorillonite MgO content is nearly 2.06 wt %, and CaCO3 is 0.68 wt %, showing that B0 is bentonite alkaline earth. Other oxides are as low as 0.035 to 1.11% by mass, only K_2O is 1.411%. Especially, Fe_2O_3 content is quite high at 11.063 wt %, this creates yellow brown on B0, Fe can participate in the montmorillonite structural network or in the form of iron oxide mixed in the sample. The results of component analysis by XRF method showed that the post-treatment bentonite component has a quite large SiO_2 content of 61.46 wt %, Fe_2O_3 being 10.41 wt %, and $CaCO_3$ of 0.27 wt %.

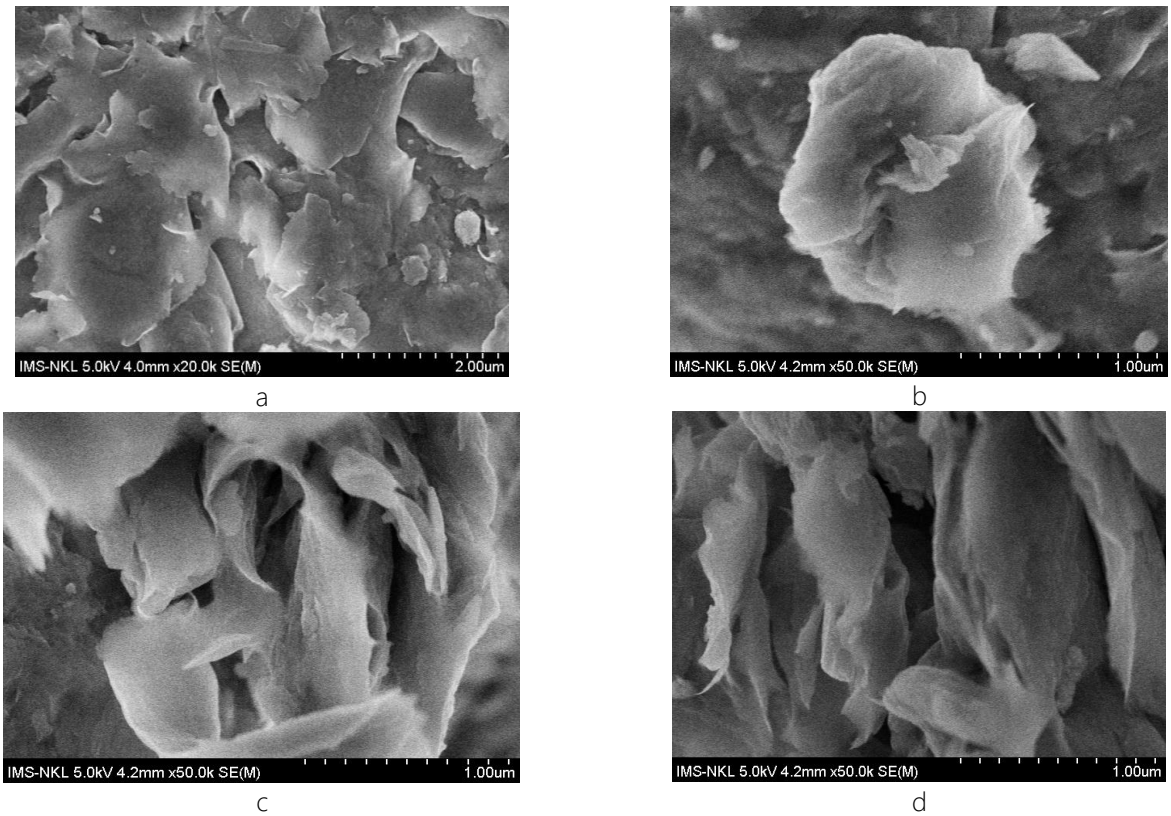

Figure 4: SEM images of B0 (a), B1 (b), B5 (c), B7 (d) samples

The weight of the selected sample were 14.65 g so the recovery efficiency of B1 sample was 73.25%. The results of component analysis showed that component B5 had total SiO_2 content decreased to 59.508 wt %, Fe_2O_3 was 10.011 wt %, $CaCO_3$ was 0.624 wt % in volume. This result is completely consistent with XRD and FTIR analysis. The results of the weight of the recruited sample was 14.35g, the recovery efficiency of B5 was 71.75% with the input.The results of component analysis showed that the post-recruiting bent component has a total SiO_2 content of 55.315 wt %, Fe_2O_3 of 12.81 wt % and $CaCO_3$ of 1.813 wt % of volume. The results of the weight of the selected sample were 14.24g, the recovery efficiency by the input of B7 was 71.2%. In this mode, after centrifugation and washing process with deionized water, we found that there were still a residual phosphorus amount, so the use of 7% $(NaPO_3)_6$ solution is unreasonable, causing wastefulness in chemicals, water and time of experiment.

Table 1: The weight components of oxides and carbonates of bentonite samples

Samples	Composition (weight percent)					
	MgO	Al_2O_3	SiO_2	K_2O	$CaCO_3$	Fe_2O_3
B0	2.065	19.279	64.049	1.411	0.677	11.063
B1	2.271	22.576	61.459	1.508	0.270	10.412
B5	1.505	19.318	59.508	1.645	0.624	10.011
B7	2.649	18.963	55.315	1.248	1.813	12.807

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Conclusion

From the above results, we believe that the use of $(NaPO_3)_6$ as a dispersant is very necessary for the extraction process of clean MMT from quartz SiO_2 and non-clay in the commercial, content $(NaPO_3)_6$ in the optimal solution is 5%. Using sodiumhexamethylphotphate as Di Linh bentonite dispersion aid in water leads to strong distribution of bentonite particlesin the entire water volume, the particles settle slowly, thus improving the montmorillonite recovery efficiency, better removal quartz SiO_2 and non-clay

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