Synthesis and characterization of organophilic clay from Cuban Chiqui Gomez bentonite

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Abstract. Smectites are clay minerals with a layered structure and nanometric thickness, high specific area and a huge variety of uses. Consisting on stacked layers of about 1nm thickness, including two silica tetrahedral and one octahedral sheet. Properties of natural Smectites can be enhanced by organic modification, due to the substitution of the exchangeable cations in the interlayer area. In fact, the properties of the modified smectite (organophilic clay) are related to its modified chemical composition and structural parameters. The interaction of smectite clays with surfactants has an important interest in the fields of drilling fluids, paints, cosmetic, ceramic industries and others. Recent applications are: remediation of contaminated areas and polymer/clay nanocomposites. The aim of this paper is to obtain organophilic clays using a bentonite from the Chiqui Gómez deposit in Central Cuba. The raw and organophilic clays were analyzed by DRX, SEM, swelling capacity in organic solvents and others.

Introduction

Bentonites are clays composed dominantly by the smectite group of clay minerals, mostly montmorillonite, whose physical properties are dictated by this one [1]. Usually in the powder form, have an important wide range of industrial uses [2]. The most important industrial clay-organic group is the [3] product of sodium bentonites and quaternary ammonium salts.

The structure of the minerals of the smectite clay group is composed by layers made up of two silica tetrahedral sheets with a central alumina octahedral sheet. These sheets are bound by common oxygen atoms. The layers are continuous in the “a” and “b” axis and are stacked one above the other in the “c” direction, with the degree of order depending on the kind of smectite clay mineral when could occurs moderately isomorphic substitutions of, for example, Al^{3+} for Si^{4+} on the tetrahedral positions and of Mg^{2+} for Al^{3+} on the octahedral positions. For these substitutions the layers have a negative charge with a deficiency of about 0,66 mono-valence cation per unit cell. This deficiency is neutralized by interlayer exchangeable cations.

The Cation Exchange Capacity — CEC and the Exchangeable Cations — EC- are important properties of the smectite clays and have great influence on their technological applications since they control the physical and chemical properties of the smectite clay minerals. There are two kinds of industrial bentonites: a) water swelling bentonites, with sodium as the main exchangeable cation and b) non swelling bentonites, with calcium or magnesium as the main exchangeable cation. The swelling bentonites give viscous water-clay dispersions at low clay concentrations. The non swelling bentonites do not have that property and are flocculated in water.

There is a growing use of high swelling smectite clays as raw material to obtain, with the addition of quaternary ammonium salts, clays with a high swelling capacity in organic solvents. These kinds of modified clay are named organophilic clays.

Organophilic clays with a high degree of swelling capacity in specific organic solvents have a diversity of industrial uses. Some of those uses are: thixotropic compounds for oil well drilling fluids, binder for special foundry molding sands, additives for high temperature lubricants, components of paints and components for a diversity of articles used in cosmetics and toiletries. Laba [4] lists de various uses of organophilic clays in cosmetics and toiletries and shows how those clays swell in the organic solvents. Lately, other use is coming more and more important for the technological advances is the application of the organophilic clay as filler in substitution of the pollutant carbon black as enhancer of the final properties of elastomeric products. Researchers [5] from the Laboratory of Particulate Raw Materials and Non Metallic Solids – Metallurgical & Materials Eng. Dept. – Polytechnic School – University of São Paulo, since 1991 has prepared and tested various organophilic clays, using a diversity of sodium modified smectite clays and different kinds of quaternary ammonium salts. This paper show results of the characterization of a natural [6] and modified Cuban smectite clay named “Chiqui Gómez” from the Central part of the Island.

Bentonite “Chiqui Gómez” is a Central – Cuba smectite clay deposit. Samples were submitted to characterization at laboratories of the Polytechnic School - University of São Paulo at the Mining & Petroleum Eng. Dept. (XRD X-ray powder diffraction, SEM Scanner Electronic Microscope, classification grain size determinations and XRF chemical analyses) and the Metallurgical & Materials Eng. Dept. (viscosity, chemical modifications and swelling in water and in organically solvents). Exchangeable cation essay was performed at the Laboratory Chemistry Institute of Sta. Catarina Federal University. These studies were done, to recommend dressing ores procedures, to improve quality on the end product [6].

Geology & characterization of Bentonite from the Chiqui Gómez Deposit

Located in Central Cuba at the Villa Clara Province, the deposit is in the Camacho geologic formation and rests over calcareous rocks from the Remedios formation. Present the following rocks sequence [6]:

1.- Cover composed by bentonite clay and vegetal organic remaining portions colored from dark gray to black.

2.- Bentonite clay gray – light green with organic remaining portions up to 2,0%, the lesser fraction of 63 μm varies from 89,40 to 98.10%. This layer extends for all the deposit, is main part of the mineralogical useful substance and the thickness goes from 0,15 up to 0,70 m.

3.- Bentonite clay gray – light green, with rest of Mn and Fe. Grain size fraction < 63 μm from 89,01 up to 98,30%; $CaCO_3$ goes from 0,80 up to 6,38%. This layer is the basic part of the raw material and is found by all the deposit with exception of a sterile area to the north of the same. The thickness varies from 0,20 up to 1,90 m in the probable reserves.

4.- Bentonite clay gray to green clear until yellowish with visible presence of $CaCO_3$ of dirty white color. Grain size fraction < 63µm varies of 68,20 up to 91,00% and the grade of CaCO3 from 4,0 to 19,52%, presents sterile areas in all the deposit. Thickness 0,10 - 0,80 m.

5.- Clay with some sand until much sand, of gray to medium brown color with bigger grains of calcareous and volcanic rocks. Thickness 0,20 - 0,30 m. Sterile.

6.- Sands somewhat argillaceous color ash - medium brown. Thickness 1,10 m. Sterile.

7.- Sand of thick until medium grains of quartz, feldspars and fragments of volcanic rocks. Maximum thickness cut 3,50 m.

Tables 1 show the ores characteristics, the industrial studied parameters of the Chiqui Gómez bentonites and table 2 the reserves and potential resources.

Table 1 Chemical & Technologic characteristic of natural bentonite Chiqui Gómez [7]

Oxide	Mean %	EC (meq/100g)	Mineralogical Composition
SiO_2	58,63	Mg = 24,18	Montmorillonite = 13,0 - 17,9%
Al_2O_3	14,20	Ca = 22,47	Nontronite = 37,2 - 48,2%
Fe_2O_3	9,5	Na = 3,28	$CaCO_3$ = 2,10%,
TiO_2	0,95	K = 0,32	Variation coefficient: 38,51.
CaO	1,18	Plasticity: 34,0 - 54,3	Specific gravity: 2,60 g/cm^3
MgO	2,11		
Na_2O	1,45	Volumetric weight: 1,35 – 1,64 g/cm^3	Swelling: 4 cm^3
K_2O	0,24		
SO_3	< 0,10	Plastic water: 53,4 - 90,0	Viscosity: 1,8 cp.
P_2O_5	0,03		
MnO	0,33	Grain size classification:	
PPI	10,65	>0,2mm=0,64 – 3,0%; -0,2+0,1mm=1,02 – 7,79%;	
CEC (meq/100g)	50,50	< 0,063 mm = 80,5 - 99,12% mean: 94,5%.	
pH	7,00	variability coefficient: 38,51	

The raw material is formed by bentonite with organic remaining portions, clean bentonite and by times bentonite with $CaCO_3$, constituting one technological type. The clay is composed by the mineral mixture of smectites (nontronite 37,2 - 48.2%; montmorillonite 13,0 - 17.9%) and goethite next to organic substance. [7].

The bentonite is a layer of small thickness (0,70 – 1,90 m), occupying a large area, extending outside of the current limits of the studied deposit. According API standards viscosity of this bentonite (table 2) is LOW; Permeability = LOW; Resistance in Green (kg/cm^2) is mean, agglutination in green (kg/cm^2) 0,92 and in dry 5,07.

The technological type of bentonite is characterized by: 94% of grain size < 0,063 mm; high CEC 50,15 meq/100g; and grade of $CaCO_3$ <2,14%. It was studied for foundry uses and it is recommended for soils corrector.

Table 2. Reserves & Resources (1000t) [6]

Proven	55.714
Probable	280.408
Possible + Hypothetical	4883,084

Nanocomposites bentonite / rubber

Production of different types of polymers involving nanoparticles substances of different nature it's being object of improved studies by different world-wide high level research centers. Nanoparticles are particles of less than 100nm sized that exhibit new or enhanced size-dependent properties compared with larger particles of the same material. Clays mineral are the fine-grained natural materials [3], less than 1 µm in diameter and hundred times more fine in thickness; an important reason to do a technological study of this organophilic clay [8].

The organophilic clays comes gaining importance in world-wide level due to its uses in the clay / polymeric nanocomposites elaboration, materials with high economic and industrial potential of use. The LMPSOL –PMT-EPUSP since the beginning of the decade of 2000, among other applications with it, is studying to obtaining several types of clay - polymeric nanocomposites which are constituted in a new kind of nanomaterials. In specific way, lately it comes researching the obtaining of organophilic clay / rubber nanocomposites (NAOB) [9], where a small amount of organophilic clay substitutes the pollutant carbon black, maintaining or improving the final properties of the obtained material and its possible applications into the industrial production. Between the methods to characterize organophilic clays and to determine its adequacy for the elaboration of the nanocomposite with natural rubber there are: swelling in organic solvents, XRD – X ray diffraction, SEM – scanning electronic microscopy and others. This paper show and discuss results obtained from analysis of organophilic clays produced in laboratory with the Cuban "Chiqui Gómez bentonites. Tests were made to the clays as received and after became organophilic clay by a process with ammonium quaternary.

Characterization of an Organophilic bentonite Chiqui Gómez.

Table 3 Swelling in organic solvents (mL)

Organic solvents	Kerosene	Toluene	Soy oil	Acetone	Ethanol absolute	Methanol	Technician isopropyl alcohol
Without shake	6	7	6	5	3,5	3,5	4
Hand shake	6	9	8	4	3	3	5

The Chiqui Gómez bentonite clay presents a swell average in non polar organic solvent and a bad swell in polar organic solvent.

The curve of XRD of the natural mineral (Fig. 1) show the characteristic peak of the smectites, d=1,5 nm. Meanwhile, the XRD curve of the modified clay (Fig. 2) show an expansion of d to 3,4 nm showing the influence of the ammonium quaternary on the clay.

XRD – X ray diffraction

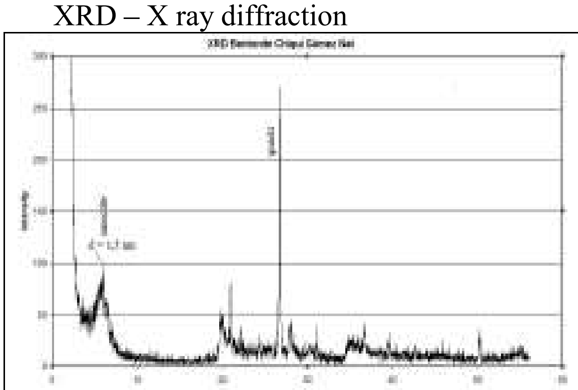

Figure 1 Natural bentonite

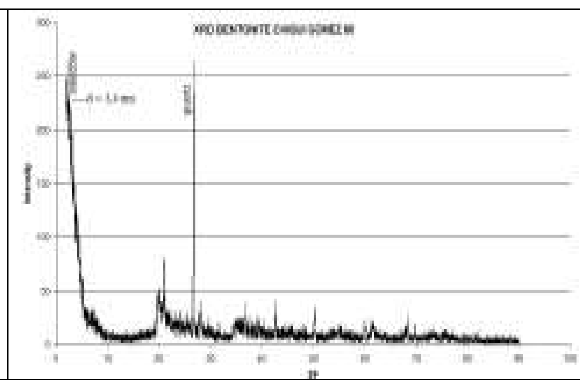

Figure 2 Organophilic clay

SEM

Photos at figures 3 and 4 are from the same crystal of organoclay. At right photo it is possible to see crystal layer lesser than 500 nm in diameter.

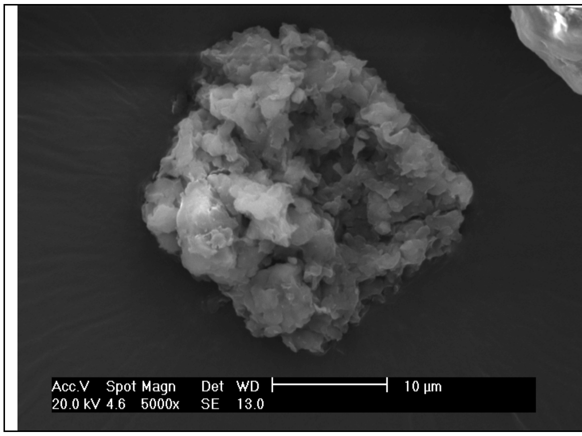

Figure 3 A crystalline stacked grain of bentonite.

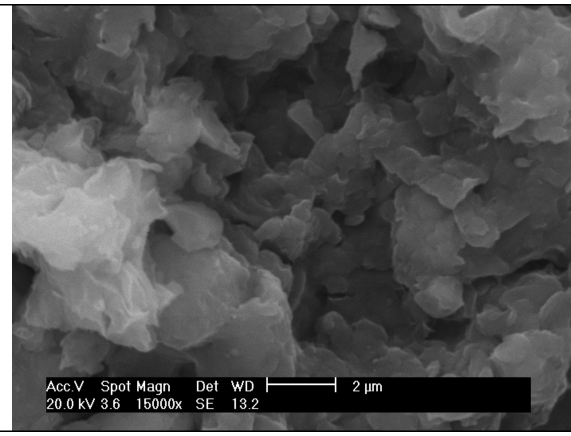

Figure 4 Detail in the proper grain showing the size of the component of the grain.

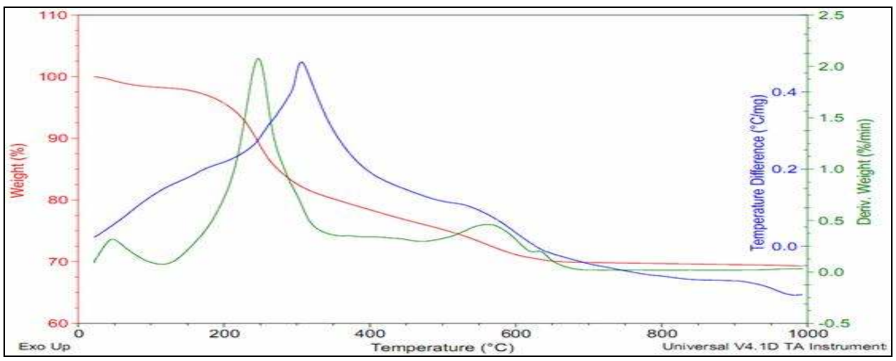

Figure 5 Thermal analysis of organophilic bentonite Chiqui Gómez

By the TG curve we can see that the loss of organic material was around 25%, which is roughly the experimental expected value. Up to 100 ^{o}C (DTG) we see a peak for the water lost by humidity, between 450-600 ^{o}C water lost by dehydroxylation and between 600 ^{o}C and 650 ^{o}C for residual carbon material loss. The DTA peak includes almost all the cited peaks.

Nanocomposite organophilic clay / rubber

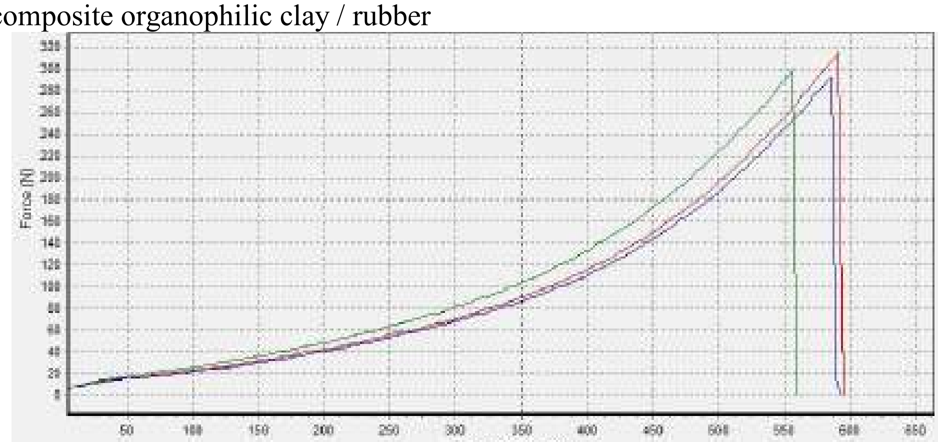

Figure 5 Stress-strain curves of a rubber nanocomposite with 10 pcr of organophilic clay.

The same composition with 40 pcr of carbon-black show tensile strength lesser than 11 MPa. The results on three samples were 22,4 ; 19,5 and 17,5 MPa respectively. This mechanical characterization proves the better service of the organoclay as a filler of the rubber than the traditional and pollutant carbon black.

Conclusion

The Bentonite Chiqui Gómez mineral is a well characterized natural product of a mixture of clays from the smectite group. This paper has demonstrated that this clay can be modified to produce organophilic clay. Besides the uses for metallurgy and soil corrector, Bentonite Chiqui Gómez after became organophilic can be used as filler with rubber substituting with advantages carbon black to produces nanocomposites material for several industrial uses, for example: in the automotive industry, sole of shoes, play-ground tiles and many others.

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