THE GREAT WORLD OF NANOTECHNOLOGY

Marcos Augusto de Lima Nobre

(Organizador)

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APRESENTAÇÃO

O mundo em escala dos nanômetros tem-se mostrado cada vez mais presente no cotidiano. Em qualquer área encaixamos o nano, e muitas palavras têm sido criadas com o prefixo nano. Algo que exiba uma de suas dimensões na escala de um bilionésimo de metro pertence a este universo, que de forma gradual tem alcançado a ciência e a tecnologia. A nanociência e nanotecnologia têm modificado tintas, tecidos, metais, cerâmicas, polímeros a compreensão dos minérios e minerais, por fim criando a necessidade de cursos para otimizar a compreensão de seus conceitos aplicados a engenharia, a medicina e áreas correlatas. O mundo dos "nano" tem alcançado as ligas metálicas, os argilominerais, o ensino aplicado, a mecânicas dos fluidos e pós cerâmicos funcionais com partículas com tão baixa densidade que podem ser consideradas apenas casca. Cada um destes tópicos está sendo desenvolvido neste exato momento para ganharmos durabilidade, novos materiais mais fortes, mas com menos peso, novas técnicas de ensino para conceitos novos e inovadores, transporte mais eficiente de combustíveis e biocombustíveis em linhas e dutos cada vez menores e pós nanométricos funcionais capazes de acelerar reações químicas. Este livro traz um conjunto de textos abordando diversos aspectos dos conceitos materiais em escala dos nanômetros.

Desejo a todos uma excelente leitura!!

Marcos Augusto de Lima Nobre

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SUMÁRIO

CAPÍTULO 2

MICROSTRUCTURAL AND RHEOLOGICAL CHARACTERIZATIONS OF A CLAY MINERAL FROM THE SOUTHWEST REGION OF THE BRAZILIAN STATE OF SÃO PAULO FOR APPLICATION IN NANOCOMPOSITES

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ABSTRACT: Clay minerals are low-cost materials, widely distributed in the earth's crust and they have several technological applications such as drilling fluids, biomaterials, cosmetics, environmental remediation, polymer – nanocomposites, and others. This research presents some previous results obtained with a clay from the southwest region of the state of São Paulo, Brazil. These clays, only by visual inspection have relevant physical characteristics, for example, fine texture and softness, tactile absorption and plasticity and easy formation of films on the glassy surface. Thermal analysis and SEM images seem to evidence that the majority clay minerals present in this clay belongs to the smectite group, possibly, montmorillonite – nontronite species. The rheological characterization showed that a suspensions (60 wt%) presents thixotropic characteristics. The rheological characterization showed that this suspension has a real plastic behavior. These rheological results also contribute that 2: 1 clay minerals are present in this clay. Therefore, this clay may be a good candidate for polymer-nanocomposites and other technological applications. The authors did a brief review on structural characteristics of clay minerals, as well.

KEYWORDS: Thermal analysis. Thixotropic behavior. SEM images. Montmorillonite –nontronite species.

1 . INTRODUCTION

Clay is a type of soil constituent whose usage is intertwined to humanity's technological progress because learning to transform clay into pottery can be seen as an important development step of the prehistoric man (WAGNER et al., 1998). In this sense, clay is considered as the first truly material made by man (ANNABI-BERGAYA, 2008). Considering life, clay minerals might have had a key role in chemical evolution and in the origin of life due their ability to take up, protect against ultraviolet radiation, concentrate, and catalyze the polymerization of organic molecules (HASHIZUME, 2012).

Geologically, clays are sedimentary rocks formed by the alteration of aluminum silicates which are the main components of the rocks and its origin can be magmatic, metamorphic or sedimentary (BESOAIN, 1985). In addition, clays are fine-grained from earthy rock, generally when moistened with water acquire a certain plasticity that after drying become rigid and when fired at an elevated temperature, they can acquire high hardness. Clays, essentially contain hydrated silicates of aluminum, iron and magnesium, these constituents are clay minerals. They still contain the non-clay minerals as quartz, feldspar, carbonates and sulfates, as well as, organic matter and other impurities (SOUZA, 1989).

Therefore, clays contain primarily clay minerals. Clay minerals are part of the larger class of silicate minerals classified as phyllosilicates, or layer silicates. Clays are a mixture of clay minerals with several reasons of a specific mineral clay that contain also the associated minerals and impurities. This aspect influencing on properties and consequently, in their applications (BERGAYA; LAGALY, 2006). Figure 1 shows common definitions for clays reported in the literature.

Figure 1 - Common definition for clays own authorship.

- ☐ Natural, fine-grained rock;
- ☐ Formed by hydrated silicates of aluminum, iron and magnesium
- ☐ When moistened with water it acquires a certain plasticity;
- ☐ Drying – becomes rigid and when fired at a high temperature, they acquire high hardness;
- ☐ Non-clay minerals present calcite, dolomite, quartz, organic matter and other impurities;
- ☐ They are able to expand or swell.

Clay minerals present important characteristics, such as:

I. Mineral particles of microscopic sizes, generally equal to or less than 2 μm ($<$ 0.002 mm), high surface area; expandable or not;

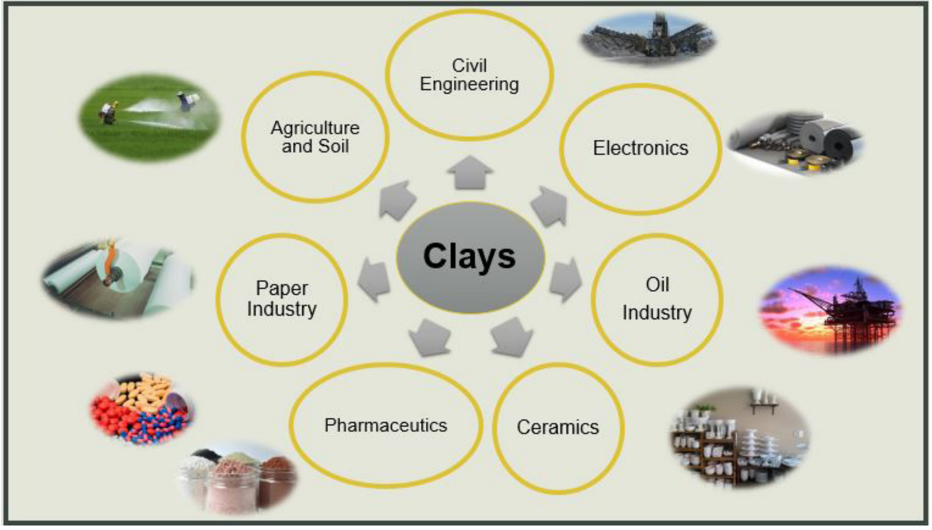
II. Most are crystalline materials, and they have in common platy morphology and perfect (001) cleavage as consequence of their layered atomic structures and its atoms have a regular, organized arrangement with angles between their faces, which have defined sides. Chemical composition: Si, Al, O, (Mg, K) and H (hydrogen);

III. High aspect ratio, high porosity, some clay minerals non swelling;

IV. Cation exchange capacity (CEC). CEC represents the amount of exchangeable cations required to balance the charge deficiency, expressed as milliequivalents per 100 grams of dry clay.

Clay minerals are used in several industrial applications: as active principles or excipients in pharmaceutical formulations, oil refining and absorbents, animal feeds, fillers in paint and plastic, coating paper, etc. (CARRETERO, 2002; ZHOU; KEELING, 2013). Another relevant area of technological application concerns with nanocomposites to produce new materials with catalytic, photochemical, electrical and magnetic properties (ANNABI-BERGAYA, 2008; ZHOU; KEELING, 2013). Figure 2 presents the broad spectrum of applications for clay minerals.

Figure 2 - Applications for clay minerals from own authorship.



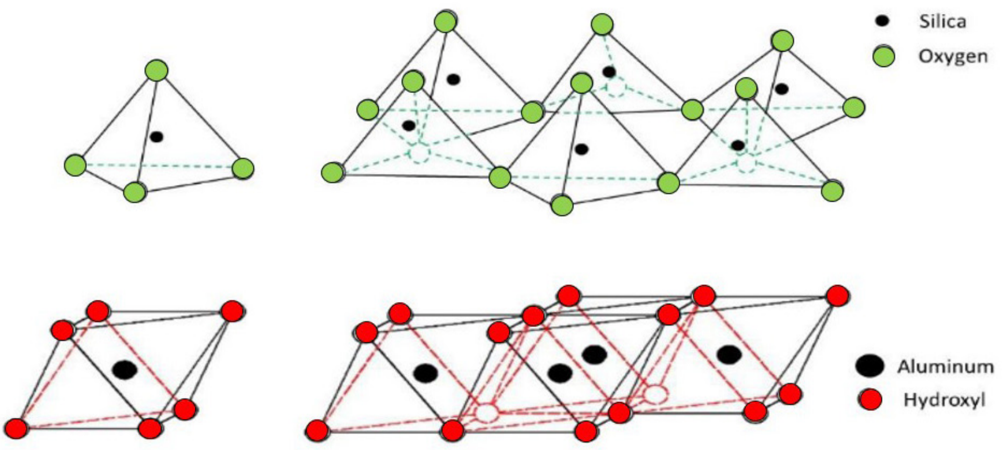
In order to evaluate potential applications of a clay it is extremely important and necessary to know which types of clay minerals are present in a soil sample. This research has the following main objectives: (i) characterize a clay from the southwest region of the state of São Paulo, Brazil and (ii) develop technological applications and knowledge in an area of strategic relevance, that is, to acquire knowledge of our mineral wealth.

This chapter presents a brief review on structural characteristics of clay minerals and preliminary results of the characterization of this clay: thermal analysis, rheological, microestrutural. Other studies have already been carried out and others are still in progress (MESQUITA, 2019; NASCIMENTO ABREU, 2018; FERREIRA LOPES, 2016).

2 . CHEMISTRY STRUCTURE AND CLASSIFICATION OF CLAY MINERALS

Clay minerals are hydrous aluminum silicates and classified as phyllosilicates (as leaf) or layer silicates. All phyllosilicates are made of two distinct structural units: (i) silica tetrahedron with a silicon ion tetrahedrally coordinated with four oxygen and (ii) an aluminum or magnesium octahedron with an aluminum or magnesium ions octahedrally coordinated with six oxygen or hydroxyls (Figure 3). Several of these structures are linked to form, respectively, a tetrahedral sheet (T) and an octahedral sheet (O). These basic units, tetrahedral (T) and octahedral (O) are linked together to form a distinct layer, that is, different combinations of these sheets make up the layers known as T-O and T-O-T. Thus, there are two types of layers, depending on the rations of the component sheets: 1: 1 layer has one tetrahedral sheet and one octahedral sheet – only T-O repetitions and 2:1 layer has an octahedral sheet between two opposing tetrahedral sheets – T-O-T repetitions.

Figure 3- Illustration of basic unit and tetrahedral sheet (upper unit) and basic unit-octahedral Sheet (below unit) (adpted from GENEDY et al., 2014).



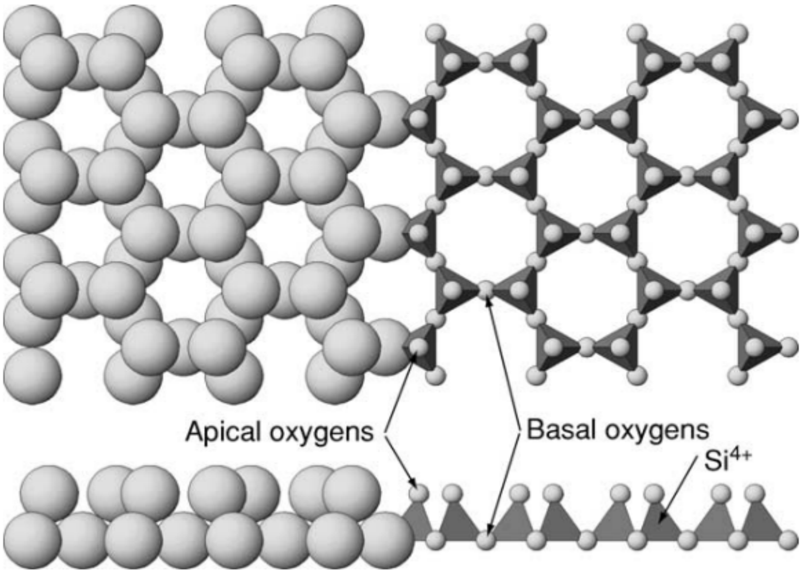
2.1 THE 1:1:LAYER TYPE

Clay minerals are presented as tetrahedral sheets and overlapping octahedral sheets. The tetrahedral sheet consists of SiO_4 tetrahedra arranged such that three of the four O^{2-} ions of each tetrahedron are shared with three nearest-neighbor tetrahedral (BRIGATTI; GALAN; THENG, 2006). These shared O^{2-} ions are all in the same plane and they are referred to as basal oxygens.

The fourth O^{2-} ion of each tetrahedron is not shared with another SiO_4 tetrahedron and is free to bond to other polyhedral elements. These unshared O^{2-} ions are referred as apical oxygens. Since each basal oxygen contributes a charge^{-1} to each Si^{4+} ion, the addition of H^+ ions to the apical oxygens to form hydroxyls should result in an electrically neutral tetrahedral sheet(SCHULZE, 2005). Figure 4 has a schematic representation of the tetrahedral sheet.

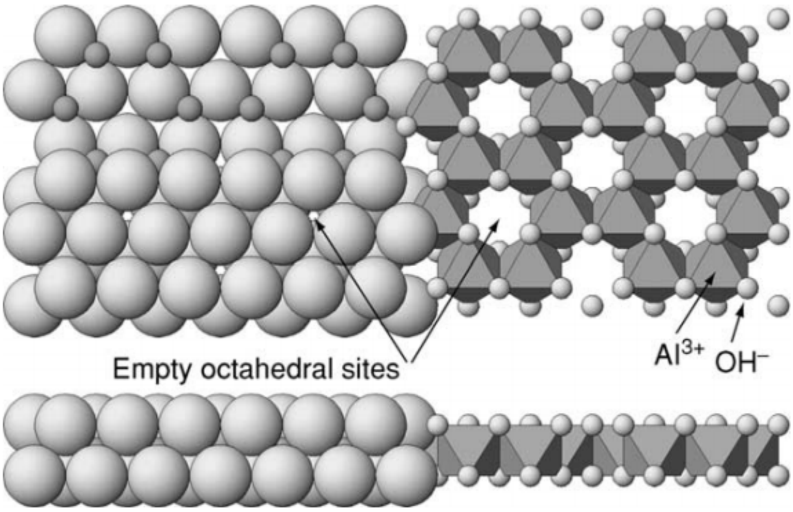
The 1:1 layer or TO layer usually has the tetrahedral sites occupied by Si^{4+} and the octahedral sites by Al^{3+} or Mg^{2+}, in this type of layer there is no charge or a very small charge. Examples of clay minerals of 1:1 layer: serpentine minerals, Kaolinite, dickite, nacrite and halloysite.

Figure 4- (left side) Tetrahedral sheet as a sphere packing model and a polyhedral model (right side) (SCHULZE, 2005).



In the octahedral sheets, the union between an octahedron O and an adjacent one occurs through shared edges. Some common tetrahedral cations are: Si^{4+}, Al^{3+} and Fe^{3+}, while more common octahedral cations are Li^+, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, V^{3+}, Cr^{3+} and Ti^{4+} (BRIGATTI; GALAN; THENG, 2006). Figure 5 has a schematic representation of the octahedral sheet.

Figure 5- (left side) Octahedral sheet as a sphere packing model and a polyhedral model (right side) (SCHULZE, 2005).



2.2 THE 2:1:LAYER TYPE

The clay mineral of this 2:1 layer have some characteristics in their structures: without charge, variable charges and in the interlayer space can have cations and water molecule. This 2:1 layer type represents a broader class of clay minerals.

The 2:1 layer structure consists of two tetrahedral sheets with one bound to each side of an octahedral sheet (Figure 6). There are four planes of anions. The outer two consist of the basal oxygens of the two tetrahedral sheets, while the two inner planes consist of oxygens common to the octahedral sheet and the two tetrahedral sheets, plus the hydroxyls belonging to the octahedral sheet (BARTON,2002). As in the tetrahedral sheet, the connection with the adjacent sheets takes place through oxygen atoms (BRIGATTI; GALAN; THENG, 2006). Some examples of clay minerals of 1:1 layer: pyrophyllite, micas, vermiculites, chlorites and smectites.

In general, clay minerals are classified in according to the number and arrangement of tetrahedral and octahedral sheets in their structural arrangements (SCHULZE, 2005). The structure of these two groups, which are subdivided into other groups according to charge of these structure (Figure 6).

Figure 6 - Structures of the two main groups of layers clay minerals 1: 1 and 2: 1 (SCHULZE, 2005).

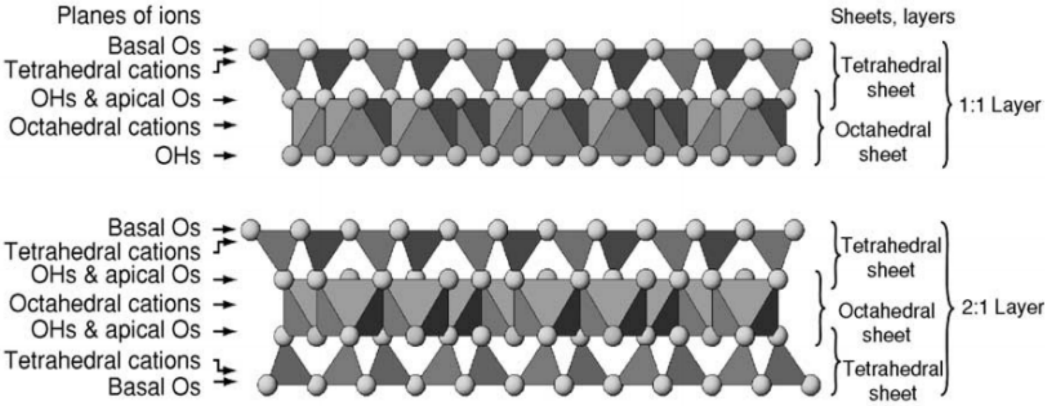


Table 1 shows the division according to the types of layers and within each division, the layer charge as another criterion for classification. Within these subdivisions, we have subgroups based on whether clay minerals are trioctahedral (Tr) or dioctahedral (Di).

Table 1 - Classification of phyllosilicates according to the structural arrangement Tr= trioctahedral and Di = dioctahedral; x = charge per unitary formulae (MOORE; REYNOLDS, 1989).

Layer Type	Group	Subgroup	Species
1:1	Serpentine – Kaolin (x~0)	Serpentines (Tr)	Chrysotile, antigorite, lizardite, berthierine
		Kolins(Di)	Kaolinite, dickite, nacrite, halloysite
2:1	Talc – pyrophyllite (X~0)	Talc (Tr) Pyrophyllite(Di)	
	Smectite (x~0.2 – 0.6)	Smectite (Tr) Smectite (Di)	Saponite, hectorite Montmorillonite, beidellite, nontronite
	Vermiculite (x~0.6 – 0.9)	Vermiculites (Tr) Vermiculites (Di)	
	Illite (x< 0.9 > 0.6	Illite (Tr) ? Illite (Di)	
	Mica (x~1.0)	Micas (Tr)	Biotite, phologopite, Lepidolite
		Micas (Di)	Muscovite, paragonite
	Brittle mica (x~2.0)	Brite micas (Di)	Margarite
	Chlorite (x variable)	Chlorites(Tr , Tr)	Common, name based on Fe2+, Mg2+, Mn2+, Ni2+
		Chlorites (Di , Di)	Donbassite
		Chlorites (Di , Tr)	Sudoite, cookeite (Li)
		Chlorites (Tr , Di)	
2:1	Sepiolite – palygorskite	Inverted ribbons (with x variable)	

2.3 DIOCTAHEDRAL AND TRIOCTAHEDRAL

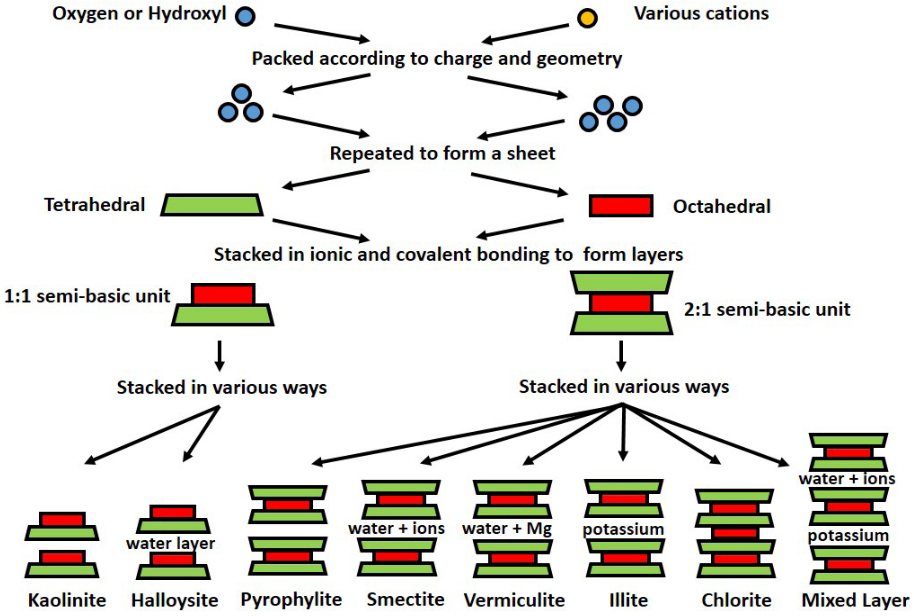
In layer silicates, whether the brucite or gibisite structure occurs depend on the valence of the cation that occupies octahedral sheets. The structure of these sheets can be: (i) dioctahedral or (ii) trioctahedral. Trioctahedral structure results when divalent cations (Mg^{2+}, Fe^{2+}) occupy the octahedral site, thus, the layer exhibits a geometry similar to brucite [$Mg(OH)_2$], such that electrical neutrality is maintained. In this structure, the ratio of divalent cations to oxygens is 1:2 and all three possible sites in the octahedron are occupied. Dioctahedral structure results when the cations are trivalent (Al^{3+}, Fe^{3+}), the charge balance is maintained by leaving one of every three octahedral cation sites empty. In this arrangement, the ratio of trivalent cations to oxygens is 1:3 and the layer exhibits the gibbsite [($Al(OH)_3$]. The tetrahedral and the octahedral sheets are linked into a single layer by sharing the apical oxygens of tetrahedra and corners of MeO_6 octahedra. These arrangements form a variety of layered silicates, for example, the structural difference between kaolinite and antigorite is that the layers are formed by trioctahedral arrangement to kaolinite and dioctahedral arrangement to antigorite. However, these clay minerals have specific properties (MOORE; REYNOLDS, 1989; BARTON,2002).

2.4 MIXED LAYERED CLAY MINERALS

All of these terms are synonymous: mixed layering, interlayering, and interstratification. These terms are used for clay minerals formed of two or more kind of layers. According to this reference, the mixture of more than two components is rare, or maybe, we need to learn to identify them, as well. Illite/smectite mixed layered clay minerals are the most common; this kind of clay minerals may be more common than either discrete illite or discrete smectite. (MOORE; REYNOLDS, 1989).

The layered materials and phyllosilicates present the phenomenon of polytypism that is a special case of polymorphism. Most of clay minerals have polytypic forms (MOORE; REYNOLDS, 1989). In the Figure 7 has a schematic representation of the formation for clay minerals.

Figure 7 - Schematic representation of the formation for clay minerals (adapted from MITCHELL and SOGA, 2005).



The purpose of this review is to highlight the structural feature in the formation of clay minerals – their ability in forming peculiar layered atomic structures, each species within a group has specific properties. Consequently, clay minerals present a broad spectrum of applications in different areas: oil industry, paper industry, ceramic, agriculture, electronics, biomaterials pharmaceutics, cosmetics, environmental remediation, catalysts, polymer nanocomposites and other areas (CYGAN et al., 2009; HEINZ, 2012; JOSHI et al., 2009; KURIAN; KAVITHA, 2016; MAITI; BHATTACHARYYA, 2013; UNAL et al., 2017; ZHOU et al., 2016).

3 . METHODOLOGY

3.1 CLAYS

The natural clays investigated were obtained from the southwest region of the state of São Paulo. First, we removed some grasses and vegetable residues manually (using a sieve like those used in domestic activities). After this, it was carried out the wet sieving (80, 150, 200, 270 and 400 mesh). Almost all material passed through the sieving column, except for the larger debris, which it were retained in the first sieve. After this step, the powder (400 mesh) was dried naturally; this powder was used to the thermal analysis and rheological characterization. The microscopy (SEM) analysis was carried out a suspension from the powder (400 mesh). Two distinct materials were obtained: (i) fast sedimentation, it was dried at 100 ºC and (ii) suspended part it was naturally dried. Extraction process from clays from the soil: cleaning the surrounding area at a depth about 1.5 m.

3.2 THERMAL ANALYSIS

The TGA analysis was carried out using 18.869 mg of in natural clay, platinum crucible, from room temperature to 950 °C, 10 °C min^{-1} under a dynamic atmosphere of nitrogen with 40 mL min^{-1} in a Shimadzu TGA-51H instrument. The DSC analyses was conducted using 6.600 mg of powder of clay and an empty crucible was used as reference in aluminum closed crucibles, from room temperature to 500 °C, 10 °C min^{-1} under a dynamic atmosphere of nitrogen with 40 mL min^{-1} , DSC – 60 Shimadzu instrument. The powders that passed through 400 mesh sieve.

3.3 RHEOLOGICAL ANALYSIS

The suspensions were prepared from dry mass with the powder 400 mesh. Suspensions with 60 wt% were prepared with distilled water. The suspensions were prepared before of the rheological measurements with manual agitation. The rheological measurements were performed with a R/S + Rheometer using a vane geometry from Brookfield within of 600 mL container, at room temperature. We used two modes of acquisition of measures: control rate mode (CR) and in control stress mode (CS).

3.4 MICROSTRUCTURAL CHARACTERIZATION

The scanning electron microscopy images were obtained at Electron Microscopy and Microanalysis Laboratory (LMEM), State University of Londrina (UEL) using a microscope FEI Quanta 200. Secondary electrons were used to acquire the images. The samples were put on the supports (*stub*) and a layer of gold was deposited on their surfaces (Sputter Coater - BAL-TEC SCD 050).

4 . RESULTS AND DISCUSSION

4.1 PHYSICAL CHARACTERISTICS OF CLAYS

The natural clay samples as received presented some relevant physical characteristics, for example, fine texture, smoothness and absorption by tactile perception, plasticity, white color with gray undertones and easy spreadability on the glass surfaces. Only by visual inspection, this clay presents desirable physical characteristics. Therefore, from this observed initial characteristics that originated the following research & development project: "Structural, Microstructural and Rheological properties of Clay from São Paulo State for the production of Polymer-Clay minerals Composites".

Figure 8 shows some photographs of this clay. Figure 8 (a) shows a photograph from the original place of this natural clay, in which its color can be seen as well as their ability to form a plastic solid. Figure 8 (b) presents a photograph of a suspension, in which can be observed a phase separation; one phase settles very fast while the other remains in suspension. Figure 8 (c) shows the powder after dried naturally.

Figure 8: Clays features: (a) their original place, (b) in suspension and (c) the powder after drying naturally.

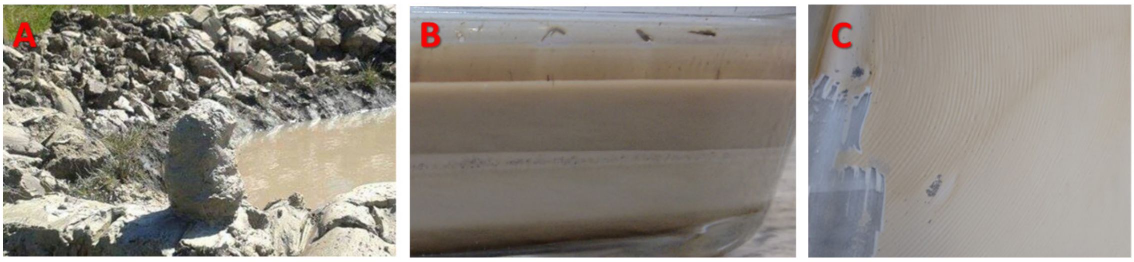


Figure 9 presents some photographs of the powder after the sieving process, the results showed that the sieving process is not effective in classifying this clay. These powders have a cohesive strength and their natural tendency is to form soft agglomerates. Thus, in subsequent studies, three fractions of powder were separated using only the decanting and drying process; more details information to see these references (MESQUITA, 2019; NASCIMENTO ABREU, 2018).

Figure 9: Powders after the sieving process: (a) Tyler 200, (b), Tyler 270 and (c) Tyler 400.

4.2 THERMAL ANALYSIS CHARACTERIZATION

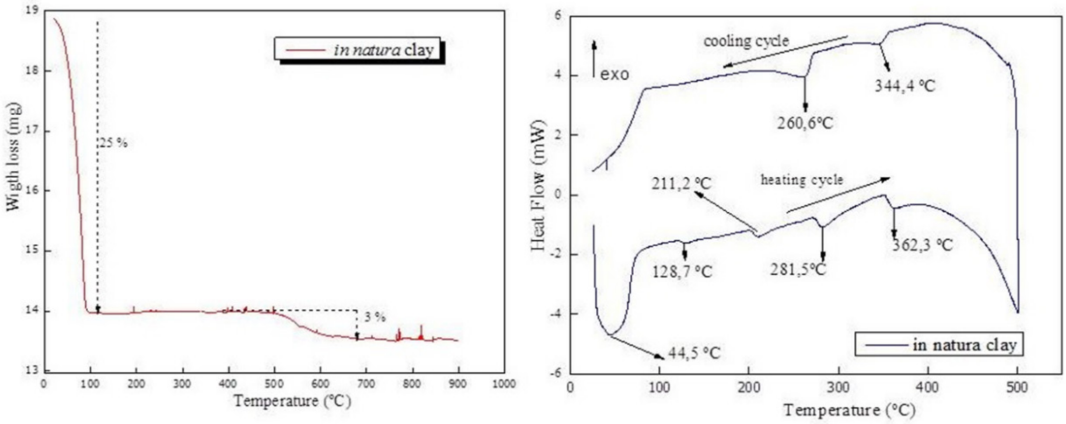
Figure 10 (a) shows the results of TGA and the DSC results are presented in the Figure 10 (b). From TGA curve, the sample presented two weight loss regions, losing approximately 28 wt% of the original mass.

The first event between 25 to 200 °C exhibits a decomposition of 25 wt% of the original mass. This thermic event is associated with loss of free water adsorbed on the clay surface and water coordinated to the exchangeable cations (MORAIS et al., 2020). Possibly, some thermal event in this interval can be associated with organic matter. Organic matter was not removed to avoid the destruction of the chemical structures of clay minerals.

The second thermic event between 500 and 700 °C with a 3 wt% weight loss was attributed to the dehydroxylation process (DE ALMEIDA NETO; VIEIRA; DA SILVA, 2014). Considering the shape of the curve and the mass losses, the mineral group that corresponds to these features is the smectite group (nontronite and/or montmorillonite) (FOLDVARI, 2011). Other hypothesis would be kaolinite group (fireclay), but its first mass loss is less than the smectite group.

Figure 10 (b) shows the DSC curve in which an endothermic peak occurs between 45 °C to 80 °C due to dehydration and decomposition of the volatile organic compounds present in the clay. Signs of second-order reactions are noticeable in the DSC curve between 120 and 362 °C. It seems to be due structural transitions and some reversible phenomenon were observed in the cooling curve.

Figure 10. (a) TGA analysis and. (b) DSC analysis.



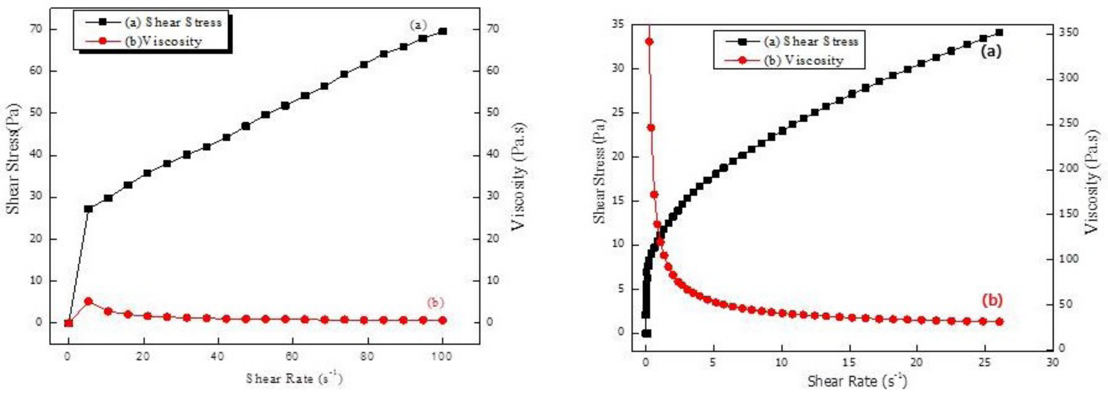
(a) (b)

4.3 . RHEOLOGICAL CHARACTERIZATION

The main rheological parameters of suspensions are viscosity, shear rate, yielding stress, plasticity, thixotropy and rheopexy. The CR mode measures, the shear stress (τ) imposed to a suspension when the velocity gradient or shear rate ($\dot{\gamma}$) changes. The response of shear stress shows a linear relationship after shear rate about 10 s^{-1} and in the viscosity curve there is an increase in the shear stress as a function of shear rate being almost constant after this rate. Figure 11 (a) shows the flow curve of suspensions 60 wt% in the CR mode, the rheological behavior of Bingham plastic fluid can be attributed because there is critical level of stress that must be attained to initiate the flow.

Disperse systems, which at rest can build up an intermolecular/inter-particle network due polar forces, van der Waals forces etc. These forces restrict the motion and give to the substance a solid character with a viscosity very high. External forces, if smaller than those forming the network, deform the solid material elastically. Only when the external forces are strong enough to overcome the internal forces, this shear stress to start the flow, then this is called yielding point. After this, the solid flowing as liquid (SCHRAMM, 1994). In the CR mode, this critical stress cannot identify with precision and the rheological behavior could be of Bingham plastic fluid.

Figure 11: Experimental flow curves (a) CR mode and (b) CS mode.



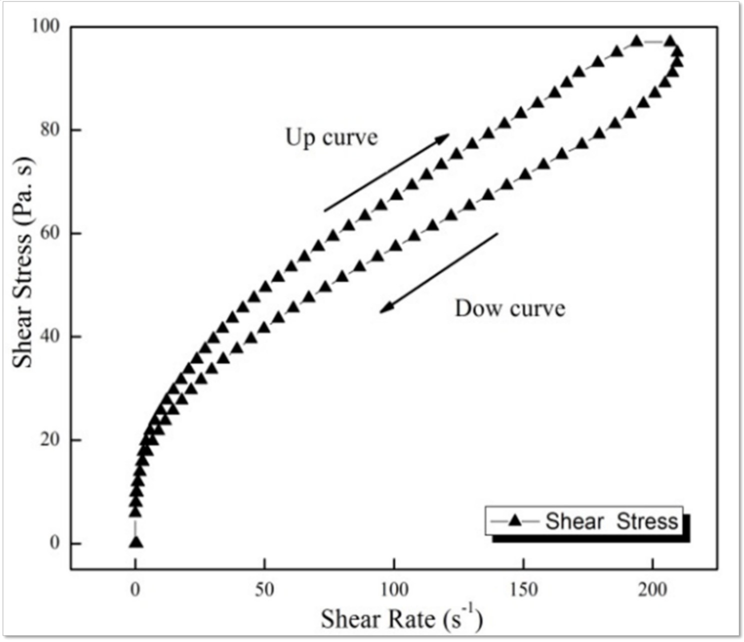
(a) (b)

The controlled shear stress rheometer (CS mode) are designed to provide higher sensitivity between similar samples at a lot low values of shear rate (SCHRAMM, 1994). Figure 11 (b) shows the results of characterization of a suspensions (60 wt%), but now the measure was carried out in the CS mode, that measures the stress rate ($\dot{\gamma}$) imposed to suspension when the velocity gradient or shear stress (τ) changes. In this mode of measurement can be determined the critical shear stress (yielding point or initial critical stress) needed to start the flow. The viscosity curve is a characteristic of a structured fluid that have a decrease of viscosity at higher shear rate and the phenomenon is characteristic of concentered suspensions.

Thixotropy is a phenomenon that describes that the viscosity decrease by the increasing shear rate, it is time-dependent and shows a reversible character. This time-related particle/molecule-interaction creates a three-dimensional network structure often called gel. In general, these bonds are hydrogen or van der Waals bonds and are relatively weak, breaking easily this network structure when the dispersion is subjected to shear stress over an extended period of time, which lead to a less viscous state, called sol (SCHRAMM, 1994).

The viscosity of thixotropic materials does not follow the same path on structure breakdown and recovery, they form hysteresis loop, which then returns to a point lower than the initial shear stress. The area within of this hysteresis loop represents the energy consumed in structure breakdown, in the Figure 12 shows the hysteresis loop of the clay suspension 60 wt%. Therefore, this clay presents thixotropic characteristics. The potential and degrees of thixotropy depend of the kind of clay minerals that are present in the clays. If there are more component from 1:1 layer structure of kaolin or 2:1 layer structure of montmorillonite. Comparing both groups, the 2:1 group has large specific surfaces, high activity, a high cation exchange capacity and electric charge on the mineral surfaces. Suspension of bentonite (main component is montmorillonite) is a typical example of thixotropic behavior, while kaolin showed almost no degree of thixotropy, illite presented a small effect about this behavior (ZHANG et al., 2017)

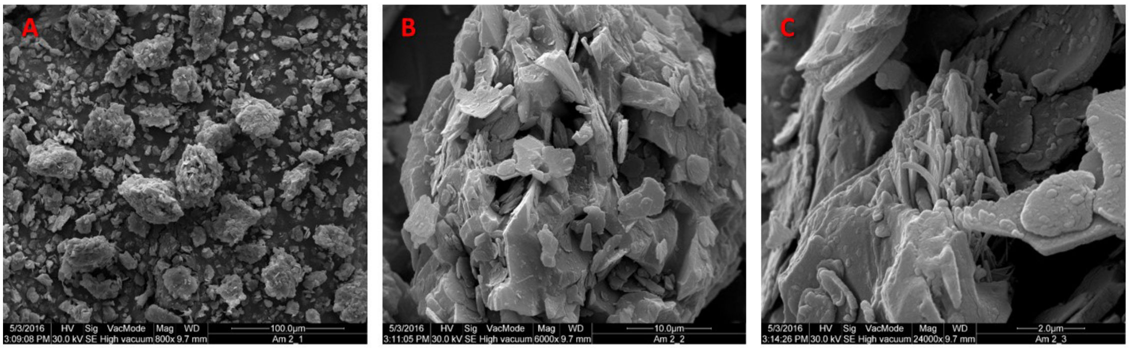
Figure 12: Experimental flow curves that shows thixotropic behavior.



4.4 MICROSTRUCTURAL CHARACTERIZATION

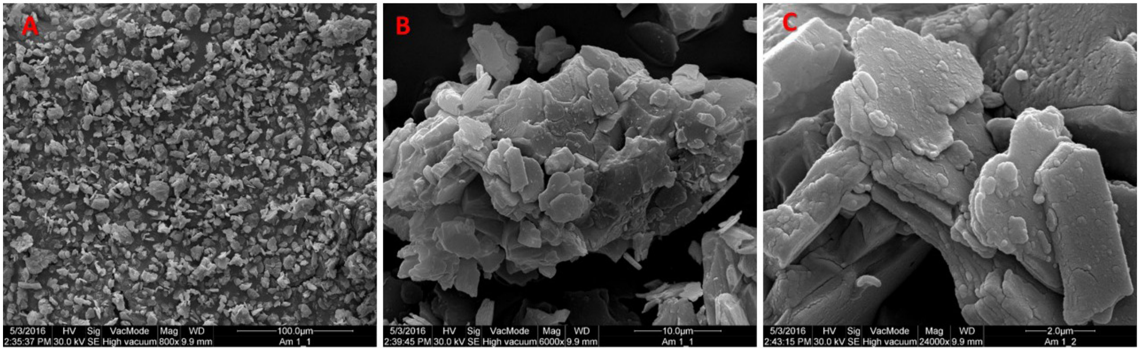
The morphology of the powders was studied by scanning electron microscope (SEM). The SEM images of clay powders that passed through 400-mesh sieve in same magnification which are presented in the Figure 13. At low magnification (Figure 13a) shows the formation of large agglomerates, in the Figure 13b shows these agglomerates at a higher magnification and a morphology as microtubes and platy morphology can be observed in these SEM images (Figure 13c).

Figure 13 - SEM micrographs of the powders that passed through 400-mesh sieve clay. (a) 800x magnification, (b) 6000x magnification e (c) 24000x magnification.



The SEM images of clay powders that they were obtained from the part that remained in suspension in same magnification are presented in the Figure 14. Figure 14a, at low magnification, shows a more uniform distribution when compared with previous powders, therefore, this sample had less agglomerates. Figure 14b shows a cluster with platy morphology as well small crystallites. In high magnification, Figure 14c shows this like platy morphology. This kind of morphology is characteristic of many clay minerals.

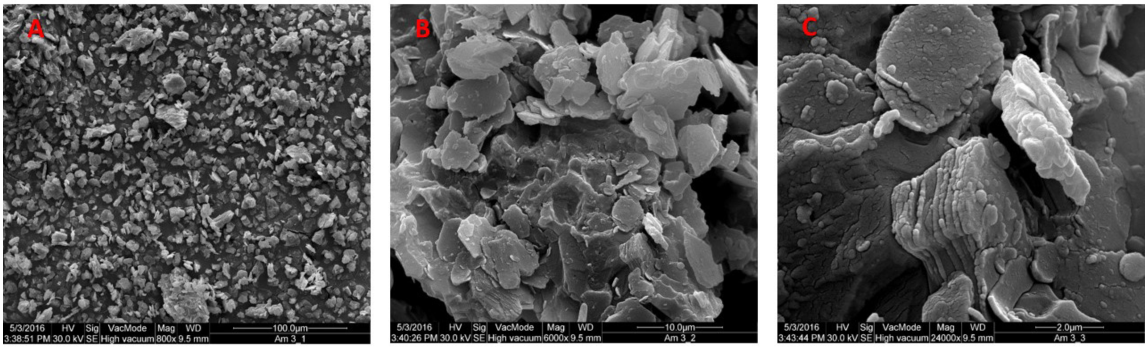
Figure 14 - SEM micrographs of the clay sample. (a) 800x magnification, (b) 6000x magnification e (c) 24000x magnification.



The SEM images of clay powders which obtained by fast settling in same magnification are presented in the Figure 15. In low magnification image, Figure 15a shows a distribution with less agglomerate than then others do. In the Figure15b shows this kind of platy morphology at a higher magnification, in the Figure 15 c shows this platy morphology, structures with different colors and small crystallites.

Halloysite presents several morphologies, such platy, spheroidal crystals, hollow tubular, among others. Tubular structure is the most common for this mineral. Other examples of these kind of structures are chrysotile and imogolite (DUARTE et al., 2012). Other authors have also argued that montmorillonite – nontronite series have a micromorphology as microtubes (ECE et al., 1999). The results of scanning electron microscopy appear to corroborate that clay minerals from the smectitie group are present in this clays.

Figure 15 - SEM micrographs of the clay sample. (a) 800x magnification, (b) 6000x magnification e (c) 24000x magnification.



5 . CONCLUSION

The powders presented homogeneity, fine texture, and cohesive strength by visual inspection and SEM micrographs.

Considering the shape of the curve and the mass losses, the mineral group that corresponds to these features is the Smectite group (nontronite and/or montmorillonite). Other hypothesis is kaolinite group (fireclay and/or ball clay), but its first mass loss is less than the Smectite group.

Rheological characterization showed plastic behavior and the phenomenon of thixotropy and the CS mode shows greater sensitivity for determination of the initial critical stress (yielding point). This study showed that the clays studied offer potential to be used as reinforcement for polymer matrices and other technological applications.

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ÍNDICE REMISSIVO