

Evaluation of the Behavior of Brazilian Bentonite Clays with Different Quantity of Quaternary Ammonium Salt

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Abstract. Paraíba is the main natural bentonite producing state of Brazil. Besides the advantage of abundance of bentonite clays, its transformation in organoclay is a simple method and there is only little study about the commercialization of Brazilian organoclays. In this work, Brazilian bentonite clay was organophilized with different quantity of a quaternary ammonium salt, such as 100, 125 and 150 wt.% in relation to Cationic Exchange Capacity (CEC) of the clay. The clays were characterized by X-ray Fluorescence (XRF), X-ray Diffraction (XRD), Thermogravimetry (TG) and Nuclear Magnetic Resonance (NMR). It was observed that with increasing amount of salt the degree of dispersion of the clay increased, leading in some cases to the delamination of the clay layers and its loss of thermal stability.

Introduction

In 2007, the Paraíba state was the main producer of raw bentonite with 88.5% of national production, followed by São Paulo (7.3%), Bahia (3.9%) and Paraná (0.2%). The domestic benefits of bentonite (dry and active powders) grew 1.39% compared to 2006. In the processing segment beyond the simple treatments of disintegration, homogenization and drying the activation is performed by the addition of sodium carbonate, leading to bentonite, being naturally polycationic in sodium. The remaining production is to produce dry clay powder [1]. Besides the advantage of this abundance of smectite clays in Brazil, the transformation in organophilic clays by surface treatments with quaternary ammonium salts is a procedure without complication, since the treated clays from Paraíba are still not commercialized for the development of nanocomposites. The main factors that control the properties of clays are the mineralogical composition of clay minerals and non-clay minerals and the particle size distributions, the content of exchangeable cations and soluble salts, the nature and content of organic components and textural characteristics of the clay [2].

The bentonite clay was organophilized with three levels of quaternary ammonium salt (100%, 125% and 150% based on the CEC of the clay). To assess the influence of the percentage of ammonium salt in the modification of the clay, they were characterized by X-ray fluorescence (XRF), X-ray diffraction (XRD), thermogravimetry (TG) and nuclear magnetic resonance (NMR).

Experimental

The 1346 clay used was activated sodium by Union Bentonit Northeast Company (BUN), located in the city of Campina Grande - PB. The used quaternary ammonium salt was Praepagen WB ® (stearil dimethyl ammonium chloride), named as PRA, supplied in the form of gel with approximately 75% active material.

The Na-MMT clay was treated organically with quaternary ammonium salt Praepagen WB (PRA) according to the procedure described elsewhere by Araújo et al. [3, 4]. The untreated clay was identified as 1346. The clay modified with percentages of 100%, 125% and 150% of the quaternary ammonium salt based in cation exchange capacity of the clay and the molecular weight of the salt was names as 1346-100, 1346-125 and 1346-150, respectively [5].

The cation exchange capacity (CEC) of the clay without modification was determined by the method of methylene blue adsorption [6]. Chemical analyses of the unmodified clay and the clay modified with ammonium salt were performed by X-ray fluorescence (XRF) a semiquantitative method in powder form, under helium atmosphere. Thermogravimetry (TG) was performed in a 50mL/min flow of air and N₂, from ambient temperature to 900 ° C, using a heating rate of 12.5 ° C / min in a platinum sample holder. The XRD analysis were conducted using copper K α radiation, voltage of 40KV, current of 30mA, 2 θ scanning from 1.5 ° to 12 ° and scanning speed of 2 ° / min. The determination of spin-lattice relaxation time (T₁) was performed on a Maran Ultra spectrometer 23, operating at 23 MHz for ¹H, using the technique of inversion-recovery (180 °-t-90 °) and the 90 ° pulse was 4.6 μ s.

Results e Discussion

Cationic Exchange Capacity (CEC)

The CEC result of the clay is a very important factor in choosing bentonite clay to be treated with the quaternary ammonium salts. The bentonite clay has the value of the corresponding CEC 90meq/100g clay. According to the literature [7] the higher the CEC, the higher is the exchange of sodium, present in the bentonite layers by alkyl ammonium ions. This type of ion exchange is very important since the exchangeable ions strongly influence its physical and chemical properties and its technological applications [8]. These exchangeable ions can be organic or inorganic [2].

X-ray Fluorescence (XRF)

Table 1 presents the clay chemical analyses by X-ray Fluorescence, from the 1346 clay without organophilization and after organophilization with three different percentages of the quaternary ammonium salt, PRA. It was verified that with the increase in the percentage of ammonium salt solution the chloride content increased gradually, which was expected proving an efficient exchange of sodium cations of the clay by the quaternary ammonium cations. The amount of chloride in the 1346-150 clay (1,86%) was approximately four times the amount in the 1346-100 clay (0,44%).

Table 1: Chemical composition of 1346 clay without modification and after organophilization with three different percentages of ammonium salts obtained by the technique of X-ray Fluorescence

| Determinations [%] | 1346 | 1346-100 | 1346-125 | 1346-150 |
|--------------------------------|-------------|-------------|-------------|-------------|
| SiO ₂ | 60,75 | 61,03 | 61,02 | 61,23 |
| Al ₂ O ₃ | 17,77 | 19,16 | 18,69 | 18,92 |
| Fe ₂ O ₃ | 12,79 | 12,79 | 12,49 | 12,56 |
| CaO | 2,60 | 2,12 | 2,04 | 1,93 |
| MgO | 2,10 | 1,91 | 1,99 | 1,71 |
| TiO ₂ | 1,31 | 1,42 | 1,32 | 0,70 |
| Na ₂ O | 1,14 | --- | | |
| K ₂ O | 0,84 | 0,72 | 0,78 | 0,77 |
| Cl | 0,22 | 0,44 | 1,26 | 1,86 |
| SO ₃ | 0,12 | 0,12 | | 0,11 |
| MnO | 0,07 | 0,07 | 0,08 | 0,07 |
| Cr ₂ O ₃ | 0,07 | 0,08 | | |
| P ₂ O ₅ | 0,06 | | 0,19 | |
| CuO | 0,05 | 0,07 | 0,05 | 0,06 |

| | | | | |
|------------------|------|------|------|------|
| ZnO | 0,04 | 0,04 | 0,03 | 0,03 |
| SrO | 0,04 | 0,03 | 0,03 | 0,03 |
| ZrO ₂ | 0,03 | 0,02 | 0,03 | 0,03 |
| NiO | 0,02 | | | |

X-ray Diffraction (XDR)

Figure 1 shows the XRD curves of the clay without organophilization and after organophilization using PRA in percentage of 100%, 125% and 150%. There was a maximum spacing for the 1346-100, 1346-125 and 1346-150 of 36.78 Å, 37.40 Å and 40.49 Å, respectively. These spacings correspond to the basal distance d_{001} . The presence of two basal spacing corresponds to the intercalation of the salt independent of its content. When the amount of salt increased there was a gradual increase in the degree of dispersion of clay, leading in some cases (1346-150) to the delamination of the clay mineral. Basal spacing larger than 40 Å indicates that the clay when treated with PRA to 150% CEC was above the limit of delamination of the clay mineral. The layers expanding over 40 Å are less stable than those with a smaller spacing than 40 Å, which also showed a regular structure of stacking [9]. Thus, if cations in large quantities (higher than the CEC) are used to the organophilization treatment the possibility of delamination of the clay is higher which will facilitate the production of organophilic clay-polymer nanocomposites.

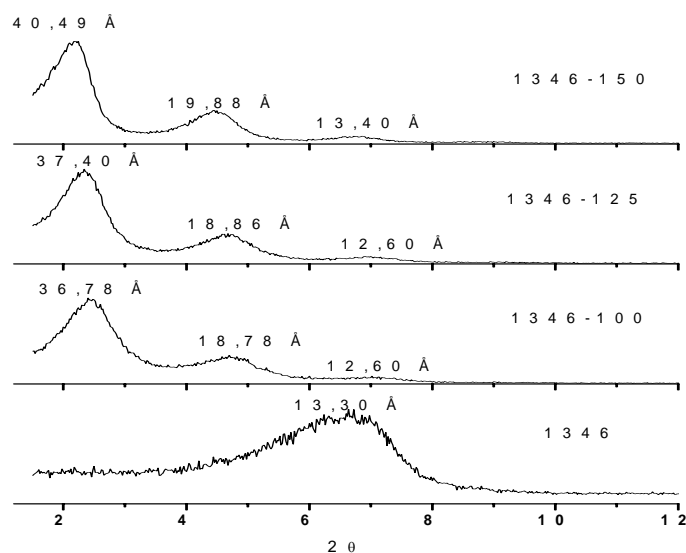


Figure 1: X-ray diffraction patterns of 1346 clay without modification and after organophilization with percentage of PRA salt in the proportions of 100%, 125% and 150% of CEC of the clay

Thermogravimetry (TG)

Figure 2 shows the thermogravimetric curves of the 1346 clay without modification and after the organophilization with 100%, 125% and 150% of PRA salt in the air and N₂ atmospheres. In air atmosphere, it may be observed that for the unmodified clay there are two decomposition steps: one between 20°C and 105°C related to the loss of adsorbed water and the other between 360°C and 580°C, corresponding to the clay mineral desidroxilation. For the clays modified with different amount of salt, four decomposition steps related to the ammonium salt decomposition are observed: between 200°C and 280°C, corresponding to the initial decomposition of the salt and between 290°C and 280°C, corresponding to the final decomposition, probably of part of carbon C₁₆ present on the PRA salt structure, since it is less stable than part of carbon C₁₈ that occurs between 420°C and 605°C and between 620°C and 755°C. In N₂ atmosphere, for the unmodified clay, two decomposition steps were observed: one between 21°C and 101°C corresponding to the loss of adsorbed water and the other between 376°C and 600°C corresponding to the clay mineral

desidroxilation. For the clays modified with different amounts of salt, three decomposition steps are observed: one decomposition starting in 200°C to 369°C, probably due to the decomposition of part of carbon C₁₆ present in the PRA salt structure, another between 375°C and 500°C and the other between 520°C and 890°C, related to part of carbon C₁₈.

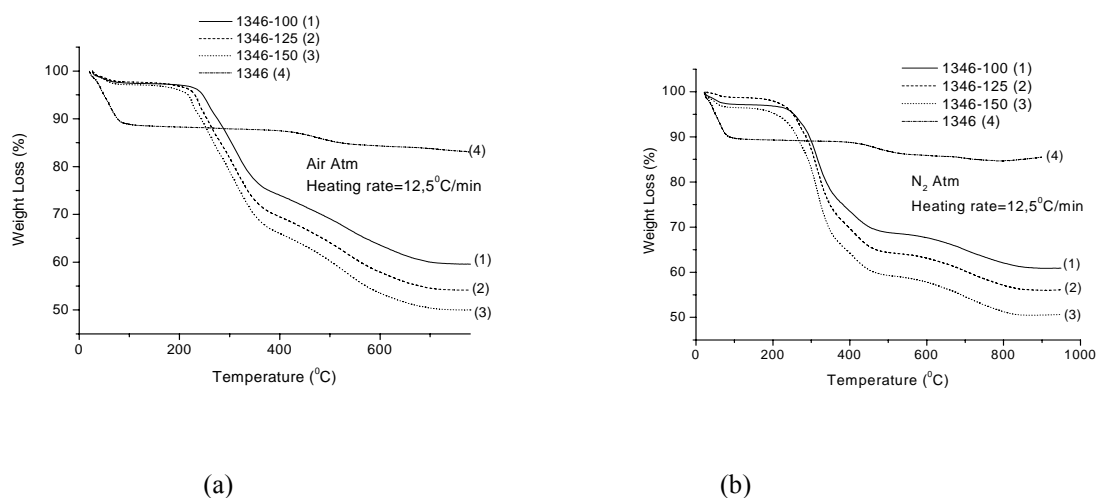


Figure 2: TG curves of 1346 clay without modification and after organophilization with three different percentages of PRA salt in atmospheres of air (a) and nitrogen (b).

Nuclear Magnetic Resonance (NMR)

Table 2 shows the time relaxation values T_{1H} , intensity and domains numbers for the clay without modification and after the organophilization with 100%, 125% and 150% of PRA salt. The smallest values of T_{1H} represent regions of high mobility, as it is the water case. The median values represent the amorphous regions with higher freedom and the highest values represent regions with limited freedom, which may be characteristic of rigid amorphous regions (due to formation of agglomerates) or crystalline regions.

The results shown in Table 2 reveal that there were alterations on the clay mobility with the addition of the ammonium salt, due to different obtained values. The highest values of the intensity, which are found in bold, show that the respective relaxation time are part of the domains that control the relaxation process. The values found for the 1346 sample are different for the samples after the organophilization with the salt. The time that controls the organophilized clays relaxation is intermediary, while for the unmodified clay ($T_{1H}=0,3ms$) is the most mobile. It may be also observed that for the organophilized samples, the value of dominant T_{1H} increased when the amount of quaternary ammonium salt was increased. Increasing the amount of salt from 100 (1346-100) to 125% (1346-125) the dominant time almost doubled, passing from 1,3ms to 2,5ms, and tripled (3,9ms) when the amount of salt was increased to 150% (1346-150). Hence, the domain mobility which controls the relaxation also changed. The 1346-125 clay has higher molecular mobility in function of smaller values of relaxation time, besides having less domains, showing a better dispersion of the salt in the clay when compared to the other organophilized clays. In general, the organophilized clays showed smaller T_{1H} values than the unmodified clay. This indicates an increase of the molecular mobility between the clay layers when different amount of PRA salt were added. These modifications were caused by the interactions created between the clay lamellae and the quaternary ammonium salt.

Table 2: T₁H values obtained by low-field NMR of 1346 clay without modification and after organophilization with percentage of PRA salt in the proportions of 100%, 125% and 150% of CEC of the clay

| Sample | T ₁ H[m] | Intensity [%] |
|----------|---------------------|---------------|
| 1346 | 0,3 | 89 |
| | 5,5 | 10 |
| | 250 | 01 |
| 1346-100 | 0,2 | 28 |
| | 1,3 | 53 |
| | 4,4 | 18 |
| 1346-125 | 47,2 | 01 |
| | 0,2 | 30 |
| | 2,5 | 64 |
| 1346-150 | 13 | 06 |
| | 0,1 | 15 |
| | 3,9 | 53 |
| | 20,0 | 05 |

Conclusions

Brazilian bentonite clay was organophilized with different quantity of a quaternary ammonium salt, such as 100, 125 and 150 wt.% in relation to Cationic Exchange Capacity (CEC) of the clay. It was observed by XRF that with the increase in the percentage of ammonium salt solution the chloride content increased gradually, and by XRD, that there was a gradual increase in the degree of dispersion of clay, leading in some cases (1346-150) to the delamination of the clay mineral. By Thermogravimetry, it was observed the decomposition of part of carbon C₁₆ and C₁₈ present in the PRA salt structure. By NMR, the results revealed that there were alterations on the clay mobility with the addition of the ammonium salt, due to different obtained values. The 1346-125 clay presented higher molecular mobility in function of smaller values of relaxation time, besides having less domains, showing a better dispersion of the salt in the clay when compared to the other organophilized clays.

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