

## **TG CHARACTERIZATION OF ORGANICALLY MODIFIED MONTMORILLONITE**

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### **Abstract**

Montmorillonite was modified with octadecyltrimethylammonium chloride, under different reaction conditions, as evidenced by TG and XRD. TG curves presented two degradation peaks (295 and 395°C). At low salt concentrations, only the 395°C-degradation appeared, which increased with reaction time to the limit of 9 g of salt/100 g of clay. The second peak presented a limit at 17/100 *m/m* of salt/clay ratio. XRD analysis confirmed clay organic modification as the basal distance increased, showing greater reaction time effect than the salt mass effect, and with only one *d*-spacing. This suggested that an intercalation complex was formed but also that octadecyltrimethylammonium was adsorbed on the external surfaces of clay particles.

**Keywords:** ammonium salt, montmorillonite, thermogravimetric analysis

### **Introduction**

Clay minerals, which present a layered structure, have been employed as host materials for alkylamines and ammonium salts and, as such, have been incorporated into polymeric matrices in order to produce composites with special properties [1]. The alkylamines with long hydrocarbon chains are introduced in the basal interplanar layers of the clay minerals as neutral molecules and the ammonium salts are incorporated by ion exchange. The interaction between this organic compounds and the clay can be followed by thermogravimetric analysis (TG) as long as the interaction leads to changes on the decomposition temperatures of the organic material. In this work, it was studied, through TG and XRD, the modification of a montmorillonite by quaternary ammonium salts with view to its utilization in the production of polymeric nanocomposites.

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## Experimental

### *Materials*

Octadecyltrimethylammonium chloride was kindly supplied by Herga Indústrias Químicas Ltda. The clay mineral employed was original from the State of Paraíba - Brazil, and its mineralogical analysis indicated a content of 70% of smectite and 30% of quartz. The structural formulae, derived from its chemical analysis, allowed the estimation of the cation exchange capacity (CEC) as 144 meq/100 g of original clay. This material was sieved and the fraction with particle size smaller than 400 mesh was employed (MMT).

### *Preparation of the organically modified clay*

The alkylammonium exchanged clay was prepared by the reaction of octadecyltrimethylammonium chloride, previously dissolved in ethanol:water 1:1, with MMT at different concentrations, in order to produce water suspensions with 11:100, 22:100 and 50:100 of salt to clay mass/mass ratios. The suspensions were shaken for different periods of time, at 70°C. After that, the suspensions were centrifuged at 4000 rpm. The solid residues were transferred to a Buchner funnel and washed several times with 1:1 ethanol:water solution, until no chloride was detected through reaction with a 0.1 M AgNO<sub>3</sub> solution, and then air dried. The dried clays were ground with a mortar and pestle, and sieved to collect the 50–60 µm fractions. These preparations were conducted in duplicates, standard deviation determined in the calculations from TG data was 0.5 mass%. In order to compare results two control materials were prepared: (1) the clay alone (MMT) was submitted to the treatment described above, including preparation and washing procedures; (2) MMT treated in the same way, was mixed with dried alkylammonium salt at room temperature. Both materials were immediately analysed by thermogravimetry.

### *XRD*

X-ray powder diffraction patterns were obtained by using a Rigaku X-ray diffractometer equipped with CuK<sub>α</sub> radiation.

### *TG*

Thermogravimetric curves were obtained in a Shimadzu thermal analyser model TG51, conducted up to 800°C, at 10°C min<sup>-1</sup> in N<sub>2</sub> atmosphere. Experiments were conducted at least in duplicates.

## Results and discussion

The thermogravimetric analysis of montmorillonite (MMT) after being submitted to treatment, indicated a mass loss in the range from room temperature to 150°C, due to

dehydration, and a mass loss from 200 up to 800°C of 4.5%, which can be attributed to dehydroxylation (Fig. 1). The TG curve for the octadecyltrimethylammonium chloride showed 98.5% of mass loss at 255°C (Fig. 2). Similarly, the TG curve for the control-mixture of MMT and ammonium salt, showed only one sharp peak at 255°C, thus indicating the presence of only free octadecyltrimethylammonium chloride. The TG curves for MMT treated for different periods of time, with solutions with different concentrations of the alkylammonium salt (Figs 3 and 4), have shown significant differences. MMT modified with 100:11 (MMT:salt) ratio presented a TG curve with only one broad peak of mass loss centered at 395°C (area A from 300 to 500°C). Increasing the ratio of salt to clay resulted in the formation of a second degradation broad peak centred at 295°C (area B from 200 to 300°C).

Assuming these areas are related to the amount of organic salt adsorbed by the clay, an isothermal adsorption curve at 70°C was constructed, considering each area separately (Fig. 5). A maximum value for the mass loss was found for each of these two temperature ranges. For the temperature range A, this maximum loss was of 9 per 100 g of clay, independently of the fact that more salt had been added, while for

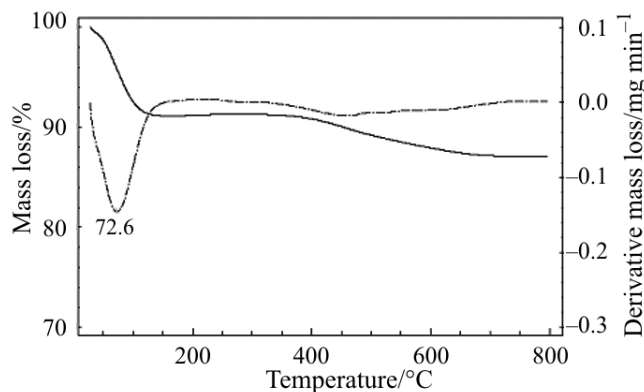


Fig. 1 TG curve of washed and dried montmorillonite

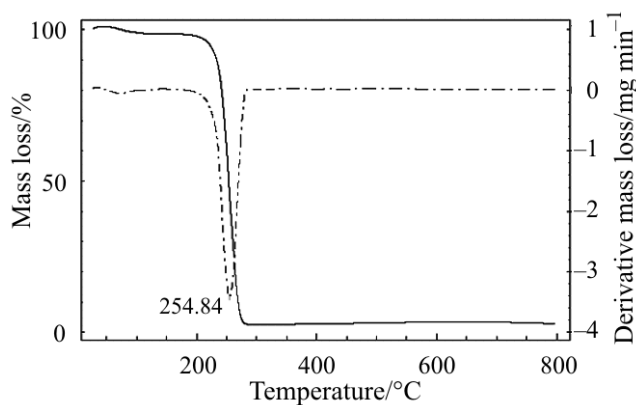


Fig. 2 TG curve of octadecyltrimethylammonium chloride

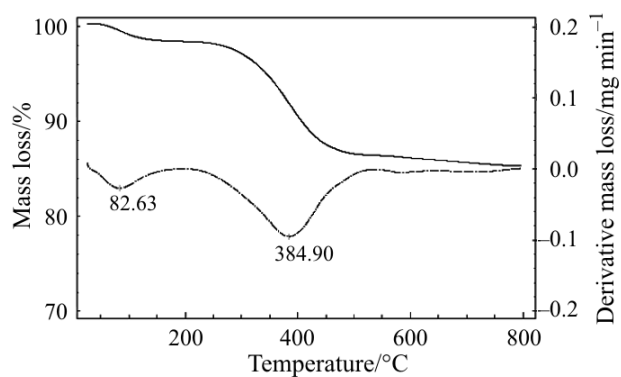


Fig. 3 TG curve of 100:11 MMT:salt (2 h) showing one main broad peak

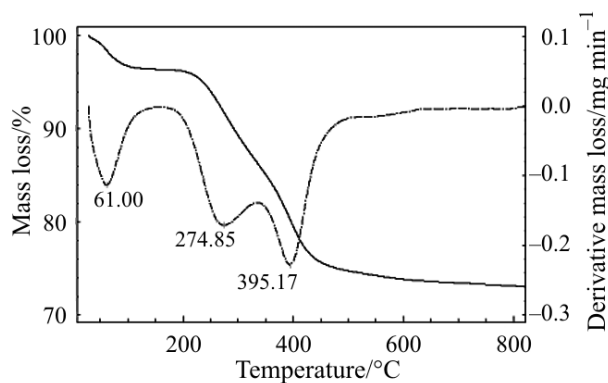


Fig. 4 TG curve of 100:22 MMT:salt (3 h) showing two main peaks at 295 and 395°C

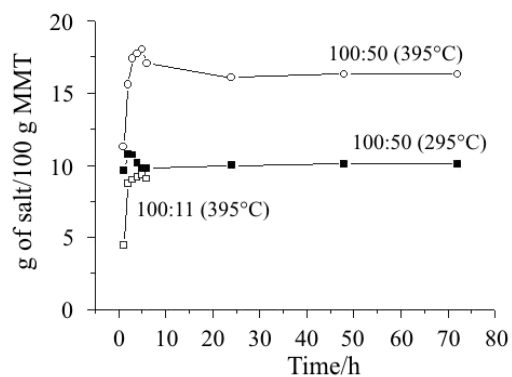


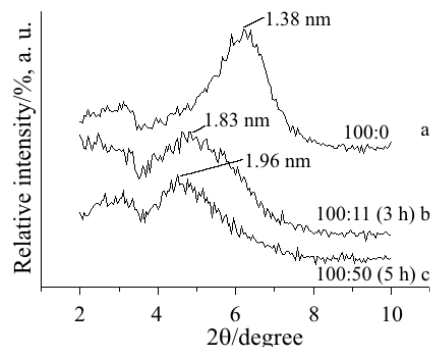
Fig. 5 Isothermal adsorption at 70°C, comparing different MMT:salt ratios at the two degradation temperatures

the lowest temperature range (B), this value increased up to 17 g per 100 g of clay, as higher salt concentrations were employed. These maxima were achieved within 3–5 h of reaction. In order to correct for eventual mass loss due to dehydroxylation that could be occurring in parallel to the organic salt degradation, the mass loss of 4.5% found for MMT has been deducted from all calculations.

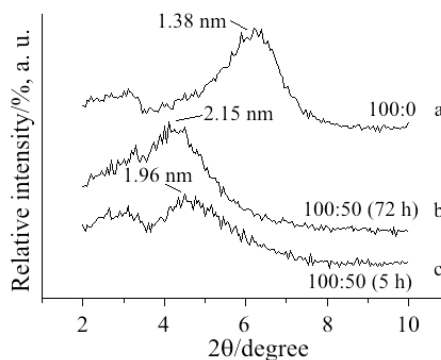
From these results it is evident that there is a mass limitation for salt incorporation by the clay, of about 26/100 mass/mass, which corresponds to mass losses from regions A and B. This value corresponds to a *CEC* of 119 meq/100 g of MMT.

The mass losses at these two temperature ranges were interpreted as an indication that two different types of association took place between the clay and the alkylammonium salt. One possibility could be that each degradation temperature corresponds to a different arrangement of the alkylammonium ions between clay layers. It was suggested [2, 3] that alkylammonium ions can arrange in one, two or more layers, horizontally or tilted, in the gallery or interlayers. In this case, the one-layer arrangement would be first formed and would degrade at higher temperatures. The analysis of XRD diffraction patterns should help interpreting these results.

The diffractograms of these organically modified MMT, shown in Figs 6 and 7, registered an increase in the basal distance of the original montmorillonite, from 1.38



**Fig. 6** XRD pattern showing a – MMT, b – and c – modified MMT, with salt concentration as shown



**Fig. 7** XRD pattern for a – MMT, b – and c – modified MMT showing effect of different time

to about 2.15 nm. The maximum increase was detected for samples submitted to longer reaction times, although keeping the broad peaks. Little change was observed on this pattern at higher salt concentrations. These results confirm the modification of this montmorillonite by the organic salt.

The peak in 3.3 nm observed in all diffractograms is discussed by Chipera and Bish [4] who, quoting Moore and Hower, attribute it to the result of an ordered interstratification of dehydrated smectite and smectite with one water layer.

The XRD pattern can be interpreted as follows. The fact that only one *d*-spacing was observed for experiments with different amounts of salt suggests that the intercalation complex is characterized by the TG peak at 395°C. The shift of the XRD peak from 1.96 to 2.15 nm (Fig. 7) can be attributed to re-orientation of the long organic salt chain between MMT layers. The peak at 295°C, not being related to a second interlayer arrangement of organic chains, suggests that adsorption to the external surface of clay aggregates is taking place [5, 6]. In this case, the *CEC* should be re-calculated considering area A in TG, which results in 29 meq/100 g. This value, lower than that estimated from the structural formula, can be explained admitting that part of the cations are not exchangeable.

## Conclusions

An organically modified clay was prepared from octadecyltrimethylammonium chloride and a montmorillonite, as evidenced by TG and XRD. A maximum of 26 g of the salt was incorporated to 100 g of clay, resulting in an average basal distance of 2.15 nm. Further improvements in the procedure for preparing the materials are needed to produce a more uniformly modified clay.

## References

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