Research paper

# A comparative study of different routes for the modification of montmorillonite with ammonium and phosphonium salts

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ABSTRACT

The objective of this work was to use a statistical tool to study and evaluate the main parameters in the preparation of organo-montmorillonite (O-Mt) by using different compounds and reactional routes (aqueous, semi-solid and supercritical $CO_2$ medium) aiming a better relationship between efficiency and environmental impact. For this, ammonium-modified montmorillonite (AmMt) and phosphonium-modified montmorillonite (PhMt) were prepared according to design of experiments. The samples were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), Fourier transform infrared (FTIR) and contact angle. XRD and TGA analysis showed that the compounds were incorporated in the montmorillonite providing an efficient modification by all the reactional routes employed. The clay interlayer spacing was expanded and AmMt showed the largest $d_{001}$ while PhMt showed better thermal stability. Statistical analysis indicated that the process parameters had low or no significance in the organo-montmorillonite characteristics. XRD, TGA and FTIR showed that the $d_{001}$, yield and chemical environment of the O-Mt changed with the amount of organic compound and washing process. The contact angle test showed that the surface tension of montmorillonite was reduced with organophilization. It was concluded that semi-solid method could be a good, efficient and environmentally friendly alternative to prepare O-Mt.

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## 1. Introduction

Nowadays, there is a large field of study focusing clays as nanofillers for polymeric materials, especially bentonite which the main clay mineral is montmorillonite (Breakwell et al., 1995; Lee and Lee, 2004; Bergaya et al., 2006; Paiva et al., 2008; Khalaf and Hegazy, 2012; Liu et al., 2014). Montmorillonite is a 2:1 layered aluminosilicate of smectite group, electrically charged with negative charges that are compensated by inorganic cations, such as $Na^+$ and $Ca^{2+}$. The great interest in the study and use of these materials are due to their excellent properties, such as low particle size, high specific surface area, aspect ratio, cation exchange capacity (CEC) and absorption and adsorption capacity, as well as high abundance and low cost (Utracki, 2004; Bergaya et al., 2006). However, there are limitations to the use of these minerals in their raw form due to the large amount of impurities and surface incompatibility with the polymer, once it has hydrophilic characteristics. Therefore, it is necessary a prior purification of these materials and its modification to make them organophilic/hydrophobic (Utracki, 2004;

Bergaya et al., 2006; Paiva et al., 2008; Zanini, 2008; Alves, 2012; Alves et al., 2016). Organo-montmorillonite (O-Mt) has been extensively used in various applications, and more recently as reinforcement in clay polymer nanocomposites (CPN).

The need to obtain superficially modified clays aiming at thermal stability and compatibility with polymers has resulted in intensification in the search and studies of new substances in the recent years. Cationic surfactants based on quaternary ammonium salts have been the organic compounds mostly used to organoclays production (Breakwell et al., 1995; Paiva et al., 2008; Thompson et al., 2008; Sarkar et al., 2011; Khalaf and Hegazy, 2012; Takahashi et al., 2013;). However, these kind of compounds are known to have poor thermal stability and in some cases toxicity (Paiva et al., 2008; Sarkar et al., 2012). Others organic compounds with higher thermal stability and lower toxicity have been used to clay minerals functionalization, mostly in laboratory scale, such as ionic liquids based on phosphonium salts (Ha and Xanthos, 2009; Livi et al., 2010, 2011a, 2011b) and imidazolium salts (Ha and Xanthos, 2009; Livi et al., 2010, 2011a, 2011b; Takahashi et al., 2013), nonionic surfactants (Guégan, 2010, 2013; Li et al., 2012; Guégan et al., 2014; Silva et al., 2014) and anionic surfactants (Du et al., 2010).

The production of organoclays can be made by various routes, being the cation exchange the most used. This consists in replacing inorganic

cations present in the interlayer spaces of clay minerals by organic cations of long chains. The exchange reaction is preferably made with sodium-clay minerals than calcium-clay minerals due to monovalent cations of sodium allow greater water interleaving in the interlayer spaces (higher hydration), further increasing the space between the layers, which facilitates the entry of organic cations (Bergaya et al., 2006; Utracki, 2004; Paiva et al., 2008). The preparation of this material by traditional routes involves environmental impacts due to the use of large amounts of water. Then, the need to seek and study new cationic intercalation compounds and new processes that minimize the environmental aspects in the area of cationic modification of clay minerals, aiming its efficiency dispersion in polymer matrices, comes every day to be more intensified.

Recent studies have also been considering the development of new routes of cation exchange, targeting the reaction yield with attention to environmental impacts and costs associated with these processes. The methods of clay minerals intercalation with organic compounds are fast, efficient and practical, as the organophilization in aqueous dispersion. The methodology is quite simple. The major disadvantage of this method is the use of large amounts of solvents, manly water (to reaction and wash steps) generating high operating costs and environmental impact (Utracki, 2004; Bergaya et al., 2006; Paiva et al., 2008; Paiva and Morales, 2012). The use of alternative systems such as supercritical $CO_2$ (Naveau et al., 2009; Livi et al., 2011a), solid/solid (Ogawa et al., 1989; Zhuang et al., 2015), and "semi-solid" state (Paiva and Morales, 2012), promise to be less impactful to the environment, since they do not consume or generate waste solvents.

There is still no clear-cut processing condition such as reaction time, temperature, agitation, pressure, amount of reagent and solvent to conduct an effective and reaction using these methods as we can see in the literature different conditions been applied (Breakwell et al., 1995; Lee and Lee, 2004; Paiva et al., 2008; Avalos et al., 2009; Ha and Xanthos, 2009; Naveau et al., 2009; Dweck et al., 2011; Livi et al., 2011a; Paiva and Morales, 2012; Zhuang et al., 2015). There are also aspects of solubility of organic substances in relation to the dispersion media, and studies in this area are still scarce.

Currently, purified and organophilic clays do not have large-scale production in Brazil and the world market for this product has a limited number of manufacturers and high costs. In this work the modification of bentonite extracted from a mine located in Vitória da Conquista, Bahia-Brazil with different surfactants was studied. Thus, this work yet proposes a comparative study of different routes of modification of clay minerals in aqueous, semi-solid or supercritical $CO_2$ medium, aiming efficiency and low environmental impact. For this, design of experiments and statistical studies were made with the objective to evaluate some key parameters and their influence in the process and in the final modified clay characteristics.

## 2. Materials and methods

### 2.1. Bentonite

The bentonite used in this study was extracted from Vitória da Conquista, a city in the south of Bahia state in Brazil. This clay is mainly composed of montmorillonite (Mt) and fractions of nontronite, kaolinite and quartz. The raw bentonite was selected, purified by elutriation and characterized according to previous work (Alves, 2012; Alves et al., 2016). The montmorillonite was characterized as a polycationic montmorillonite named as pure polycationic montmorillonite (PP-Mt). A CEC of 89,28 meq/100 g was determined by an ammonium acetate method, using a Kjeldahl distillation system (Chapman, 1965 apud Shah et al., 2013). The surface and pore properties were determined by BET method using $N_2$ adsorption–desorption isotherms gained at T = 77 K in a Micromeritics ASAP 2010 equipment, as following: BET surface area = 42,82 $m^2$/g; micropore volume = 0,0045 $cm^3$/g; micropore area = 10,28 $m^2$/g.

### 2.2. Surfactants

Two surfactants were used in this study. A quaternary ammonium salt: Arquad® 2HT-75 di(hydrogenated tallow) dimethyl ammonium chloride (DHTDMA), with about 88% of active material supplied by Sigma-Aldrich; and an ionic liquid trihexyl tetradecyl phosphonium chloride (THTDP), with 95% purity supplied by Sigma-Aldrich. The structural formulas of surfactants are shown in Fig. 1.

### 2.3. Organophilization methods

Three organophilization media were considered: aqueous dispersion, semi-solid and supercritical $CO_2$. The experiments were carried out according to distinct designs of experiments (DOE) that were dependent on the intercalation process. The DOEs were analyzed using the Statsoft Statistica 7.0 software. The statistical analysis was used to verify the significance of the effects, both main and interaction effects of the input variable considered in the process responses. p-Value and 90% level of significance were used to analyze the results, thus a p-value lower than the level of significance ($\alpha = 0.10$) indicates significant contribution of the factor with a 90% of confidence.

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In the case of aqueous dispersion and in semi-solid method, only one DOE was made including both processes, since one of the parameters evaluated was the amount of solvent (water). Therefore, the lower level ($-1$) of this variable was a large amount of solvent (aqueous dispersion method) and the upper level was a small fraction of solvent (semi-solid method). The others variables of this design were: type and amount of organic salt according to the CEC, and pre-treatment of the clay mineral with sodium carbonate to transform it in a sodium-Mt. In the method with supercritical carbon dioxide the following factors were studied: the type and amount of the organic reagent, amount of ethanol that was used as co-solvent for the washing process.

#### 2.4.1. Aqueous dispersion (AD)

Purified polycationic montmorillonite (PP-Mt) was pre-treated with sodium carbonate. For this 20 g of clay were dispersed in 200 g of deionized water under magnetic stirring at 50°C for 20 min. Sodium carbonate (1,5 CEC) was added to the dispersion and maintained at the same temperature and stirred for 1 h. After the dispersion was filtered and washed two times with about 500 ml of deionized water each. The sample was dried at 60°C for 24 h and deagglomerated and sifted through a 200 mesh sieve (74 μm aperture).

The preparation of organo-montmorillonite (O-Mt) by aqueous dispersion was similar to the procedure described above for sodification.
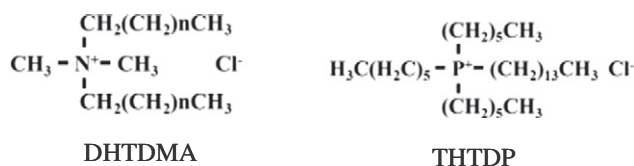


**Fig. 1.** Structural formulas of surfactants (n = 12–16).

Sieved and dried clay (1 g) was dispersed in 5 and 45 wt% of clay/water dispersion under magnetic stirring at 80°C for 20 min. The amount of surfactants according to the experimental design were solubilized in ethanol and then added to the dispersion and maintained at the same conditions for 1 h. The samples were filtered and washed two times with about 200 ml of deionized water each. O-Mt based in the phosphonium salt were washed the first time with 200 ml of deionized water and the second time with 200 ml of a solution (1:1 volume) of ethanol/water. After the samples ware dried at 60°C for 24 h and deagglomerated and sifted through a 200 mesh sieve (74 μm aperture).

### 2.4.2. Semi-solid (SS)

The synthesis of organoclay by cations exchange by reactions in the solid-solid state can be made, but is rarely used. The main advantage of this method is precisely the non-use of solvents in the process, making it more economical and more environmental friendly than the aqueous dispersion (Breakwell et al., 1995; Bergaya et al., 2006; Zhuang et al., 2015). An alternative route would be the reaction in semi-solid medium, which is the result of an adaptation in the solid-solid method, where a small amount of water is added in the system to improve the intercalation of the cations (Paiva and Morales, 2012).

The organophilization process was as follows: sieved and dried clay (1 g) and the amount of surfactant according to DOE were mixed directly in a mortar and pestle of agate to the homogenization of the mixture. After, deionized water equivalent to 85 wt% (clay/water) at 80°C was added and mixed again with mortar and pestle in order to obtain a homogeneous mixture. The resulting slurry was allowed to stand for 1 h. It was not possible to dry the O-Mt samples prepared with the ionic liquid (phosphonium salt). This samples showed a sticky appearance due to excess of ionic liquid adsorbed on the external surfaces of the clay mineral, thus it was not possible to remove it by drying. Therefore, all of the samples were washed, dried and sifted as previous case.

### 2.4.3. Supercritical $CO_2$ (SCO)

Recently, supercritical fluids such as supercritical $CO_2$ have been using to intercalation of organic compounds in clay minerals. These fluids have been applied as solvents in many applications because of their low viscosity, high diffusivity, low surface tension, good solubility for many organic compounds and are considered environmental friendly (Giles and Howdle, 2001; Li et al., 2006; Hossain et al., 2009; Naveau et al., 2009; Livi et al., 2011a;).

A 20 ml high-pressure reactor (SPM20, ThatTech) was used, with a magnetic stirrer for mixing the reaction medium and sapphire windows for viewing of internal system. 1 g of dried clay was mixed with the desired surfactant amount in a mortar and pestle in order to obtain a homogeneous mixture. The mixture was placed into the reactor with the test amount of ethanol. Then 5 g of $CO_2$ at room temperature was loaded into the reactor, to an initial pressure of about 50 bar. The system temperature was adjusted to 60°C and the pressure increased to 200 bar at a rate of 10 bar/min. The reaction was conducted for 1 h and then the system was depressurized at a constant rate of 5 bar/min. Then the samples were washed, dried and sifted.

The sample were named as AmMt or PhMt$_x$/y, where AmMt means ammonium-modified montmorillonite and PhMt phosphonium-modified montmorillonite; "x" is related with surfactant amount based in the CEC; and "y" is related with the reaction medium – aqueous dispersion (AD), semi-solid (SS) and supercritical $CO_2$ (SCO). Furthermore, a study was performed in parallel to evaluate the effects of the washing process in the properties and characteristics of the modified clays. Thus, some samples were characterized before and after washing (as in the procedure), and after an additional washing with 200 ml of ethanol/water (1:1 volume) in order to evaluate the effect of an additional solvent in the removal of unreacted surfactant. These samples were named with the following acronyms: BW - before washing; AW after the usual washing; and AW2 after the extra washing with ethanol/water.

### 2.5. Characterization

X-ray diffraction (XRD) were used to evaluate the basal spacing $d_{001}$ of the clay mineral and its variation caused by intercalation of each compound. The analysis was carried out with a Shimadzu XRD-7000 equipment operating at Cu Kα radiation (λ = 1.54 Å), voltage 40 kV, current of 30 mA, and scanned range of 1.5–10° (2θ) at 1.5°/min.

Thermogravimetric analysis (TGA) were used to determine the thermal stability and the amount of organic species intercalated between the layers and adsorbed on the surface of the O-Mt samples. Analyses were performed on a TA Instruments SDT 2960 equipment under nitrogen gas atmosphere with flow of 100 ml/min, heating rate of 10°C/min from 40 to 700°C (the samples were stabilized at 40°C for 15 min), with approximately 10 mg of sample in alumina crucibles. TA Universal Analysis software was used to determine the temperatures and mass loss involved in the thermal events. The amount of intercalated organic species was estimated by the method published by Dweck et al. (2011).

Fourier transform infrared (FTIR) spectra were performed at room temperature by ATR method using an Agilent Technologies Cary 630 equipment. The scanning range of 4000 to 400 cm$^{-1}$ were obtained by the co-addition of 64 scans with a resolution of 4 cm$^{-1}$.

Surface tension values of modified clays were determined by sessile drop method contact angle at room temperature on a Kruss DSA 100 drop shape analyzer. The measurements were obtained using 3 μl of water as test liquids on modified clays conformed as pressed discs. The surface tension values were calculated using state equation theory.

## 3. Results and discussion

The design matrixes with decoded controllable input variables are presented in Tables 1 and 2, where are also shown the results for the functionalization in an aqueous medium and supercritical $CO_2$, considering the $d_{001}$ obtained by XRD and the yield by TGA. In Table 2, one of the factors studied was the washing of the sample after reaction in order to evaluated its effect on the process responses. However, the same factor has not been studied with THTDP compounds since the excess of ionic liquid unreacted on the sample surface did not allow the XRD analysis in powder form, so only the washed samples could be analyzed.

Some representative diffractograms are shown in Fig. 2. The XRD reflection of PP-Mt. related to a $d_{001}$ of 1.55 nm (2θ = 5.69°) shifted to lower 2θ values after functionalization with both surfactants and for the two methods, indicating that the organic cations intercalated the PP-Mt. interlayer. The XRD patterns of DHTDMA-modified montmorillonite functionalized in both system, SS and SCO, were similar, where the XRD reflection emerged at 2θ around 2.3°, which corresponds to a $d_{001}$ around 3.8 nm. The typical XRD reflection of THTDP-modified montmorillonite is presented in the both samples PhMt$_{100}$/AD (BW and AW) at 2θ around 3.3° ($d_{001}$ around 2.7 nm) (Naveau et al., 2009), but for the sample PhMt$_{100}$/SCO$_{2.0}$-AW the XRD reflection appeared at 4.55° ($d_{001}$ = 1.94 nm). The results suggest that almost all O-Mt samples presented paraffin-type structures which corresponds to d-value >2.2 nm, excepting the PhMt$_{100}$/SCO$_{2.0}$-AW, in which the d-value indicates a bilayer structures (Lagaly et al., 1976). The XRD pattern of PhMt$_{100}$/SCO-AW indicated that THTDP compound did not intercalate effectively into the PP-Mt. layers using supercritical $CO_2$ medium. According with the equation proposed by Gherhardi (1998) (apud Mandalia and Bergaya, 2006) to calculate the theoretical chain length (lc) of surfactants based on the number of carbon atoms present in the main chain, the DHTDMA (18C) has a lc of 2.37 nm and the THTDP (14C) of 1.86 nm. Considering the Mt. layer thickness of 0.96 nm and length of the polar head of 0.45 nm, it was possible to calculate the theoretical d-value of the AmMt of 3.77 nm and PhMt of 3.27 nm (Mandalia and Bergaya, 2006). Comparing the theoretical values with the actual values, the results suggest that DHTDMA species were arranged in an ordered all-trans conformation in the interlayer space with the chains

**Table 1**
Design matrix for functionalization in an aqueous medium.

| Experiment | Sample | Amount (CEC%) | Dispersion (wt% clay/water) | Sodification | DHTDMA | | THTDP | |
|---|---|---|---|---|---|---|---|---|
| | | | | | $d_{001}$ (nm) | Yield (%) | $d_{001}$ (nm) | Yield (%) |
| 1 | Am/PhMt$_{100}$/AD | 100 | 5 | No | 3.1 | 85 | 2.6 | 61 |
| 2 | Am/PhMt$_{150}$/AD | 150 | 5 | No | 3.8 | 90 | 2.6 | 61 |
| 3 | Am/PhMt$_{100}$/SS | 100 | 85 | No | 3.5 | 84 | 2.5 | 62 |
| 4 | Am/PhMt$_{150}$/SS | 150 | 85 | No | 3.8 | 91 | 2.4 | 63 |
| 5 | Am/PhSMt$_{100}$/AD | 100 | 5 | Yes | 3.9 | 92 | 2.6 | 56 |
| 6 | Am/PhSMt$_{150}$/AD | 150 | 5 | Yes | 3.8 | 93 | 2.6 | 56 |
| 7 | Am/PhSMt$_{100}$/SS | 100 | 85 | Yes | 3.7 | 86 | 2.6 | 55 |
| 8 | Am/PhSMt$_{150}$/SS | 150 | 85 | Yes | 3.9 | 96 | 2.6 | 57 |
| 9 | Am/PhMt$_{125}$/AD | 125 | 45 | No | 3.7 | 87 | 2.5 | 60 |
| 10 | A/PSMt$_{125}$/AD | 125 | 45 | Yes | 3.7 | 92 | 2.5 | 59 |
| 11 | Am/PhMt$_{125}$/AD | 125 | 45 | No | 3.6 | 90 | 2.4 | 67 |
| 12 | A/PSMt$_{125}$/AD | 125 | 45 | Yes | 3.6 | 86 | 2.5 | 62 |
| 13 | Am/PhMt$_{125}$/AD | 125 | 45 | No | 3.6 | 92 | 2.5 | 62 |
| 14 | Am/PSMt$_{125}$/AD | 125 | 45 | Yes | 3.1 | 85 | 2.6 | 57 |

almost or totally perpendicular to the Mt. layers, while the THTDP species were arranged in a paraffinic-type with a conformation less ordered where the chains were not perpendicular to the layers. It makes sense, since when the packing density or the chain length decreases, the intercalated chains tends to assume a disordered structure resulting from an increase in the gauche/trans conformer ratio (Lagaly et al., 1976).

Thermogravimetric analysis is useful to identify intercalated and adsorbed organic species in O-Mt by investigation of degradation mechanisms. The evolution of the mass loss as a function of temperature (TGA) and the derivative of TGA curves (DTG) performed at AmMt$_{150}$/SS and PhMt$_{150}$/SS samples as well as the washing effect are shown in the Fig.3, and its relative mass loss values in the Table 3. Three characteristic peaks of montmorillonite are presented in PP-Mt. curve at 77, 134 and 469°C, corresponding to loss of free adsorbed water, interlayer water and dehydroxylation of the aluminosilicate lattice, respectively (Utracki, 2004; Bergaya et al., 2006). The DTG curve of DHTDMA compound (Fig. 3(a)) revealed three decomposition peaks at 206, 231 and 356°C, which probably corresponds to decomposition of species with chains of 14, 16 and 18 carbons, as the organic compound is a mixture of these three components (Sarkar et al., 2011). The DTG curve of THTDP (Fig. 3(b)) only showed one decomposition peak at 380°C. The modified montmorillonite samples, both AmMt and PhMt, had less adsorbed water amount (approximately 1–2 wt%) then PP-Mt., which is a typical characteristic of organic (hydrophobic) clay minerals. The water was removed below 50°C because it is weakly physically adsorbed in the hydrophobic-Mt. (Xie et al., 2001).

The AmMt$_{150}$/SS-(BW and AW) samples in Fig. 3(a) presented three overlapping DTG peaks between 200 and 450°C due to different mechanisms of decomposition of organic species (Xie et al., 2001). The multiple mass loss events are associated with the interlayer "nano-effect"

on the reaction kinetics, product transfer, and volatilization (Xie et al., 2002). Usually organic modified montmorillonite has two kinds of organic species linked to its structure: the physically adsorbed on the clay mineral surface by *van der Waals interactions* due to unreacted compounds; and the intercalated species between the interlayer spaces by *ionic bonds* due to cation exchange reaction. Therefore, the first mass loss with DTG peak at 253°C was probably due to the physically adsorbed species on the edges and/or on the external surface of Mt. layers since the peak reduced in the first washing with water and it disappeared after the second washing with ethanol/water. The PhMt$_{150}$/SS-BW, in Fig. 3(b), also presented three overlapping DTG peaks between 300 and 550°C. The first mass loss stage with DTG peak at 372°C match with THTDP DTG peak indicating that it probably corresponds only to unreacted adsorption species on surface of Mt. platelets. However, after the first washing (PhMt$_{150}$/SS-AW) this stage between 300 and 450°C was divided into two overlapping peaks at 357 and 396°C, and after the second washing (PhMt$_{150}$/SS-AW2) the peak at 357°C disappeared, remaining only the second peak. Therefore, the DTG peak at 357°C can be correlated with the mass loss due to adsorbed compound, and in PhMt$_{150}$/SS-BW sample, the first peak due to the large amount of unreacted compound probably overlapped the second peak.

Others studies considered that the first mass loss stage is not only associated to surfactant excess (Xie et al., 2002) and it could be also associated to a part of the surfactant intercalated in the peripheral position or to species that are physically adsorbed by $\pi$-SiOH interactions at the edges of the Mt. layers (Livi et al., 2011a). According to these studies, these species are not easily removed by simple washing because it is linked by strong bonds but it could be degraded at same temperature of physically adsorbed species because it is not thermally stabilized by Mt. platelets since it is not in a confinement position. Therefore, the

**Table 2**
Design matrix for functionalization in supercritical $CO_2$.

| Experiment | Sample | Amount (CEC%) | Ethanol (ml) | Wash | DHTDMA | | THTDP | |
|---|---|---|---|---|---|---|---|---|
| | | | | | $d_{001}$ (nm) | Yield (%) | $d_{001}$ (nm) | Yield (%) |
| 1 | Am/PhMt$_{100}$/SCO$_{0.5}$-BW | 100 | 0.5 | No | 3.8 | 83 | – | – |
| 2 | Am/PhMt$_{150}$/SCO$_{0.5}$-BW | 150 | 0.5 | No | 3.8 | 94 | – | – |
| 3 | Am/PhMt$_{100}$/SCO$_{2.0}$-BW | 100 | 2 | No | 3.8 | 83 | – | – |
| 4 | Am/PhMt$_{150}$/SCO$_{2.0}$-BW | 150 | 2 | No | 3.9 | 90 | – | – |
| 5 | Am/PhMt$_{100}$/SCO$_{0.5}$-AW | 100 | 0.5 | Yes | 3.5 | 87 | 1.8 | 37 |
| 6 | Am/PhMt$_{150}$/SCO$_{0.5}$-AW | 150 | 0.5 | Yes | 3.9 | 98 | 1.6 | 29 |
| 7 | Am/PhMt$_{100}$/SCO$_{2.0}$-AW | 100 | 2 | Yes | 3.5 | 89 | 1.9 | 47 |
| 8 | Am/PhMt$_{150}$/SCO$_{2.0}$-AW | 150 | 2 | Yes | 3.8 | 93 | 1.9 | 39 |
| 9 | Am/PhMt$_{125}$/SCO$_{1.25}$-BW | 125 | 1.25 | No | 4.0 | 84 | – | – |
| 10 | Am/PhMt$_{125}$/SCO$_{1.25}$-AW | 125 | 1.25 | Yes | 3.6 | 88 | 1.7 | 33 |
| 11 | Am/PhMt$_{125}$/SCO$_{1.25}$-BW | 125 | 1.25 | No | 3.8 | 83 | – | – |
| 12 | Am/PhMt$_{125}$/SCO$_{1.25}$-AW | 125 | 1.25 | Yes | 3.5 | 87 | 2.0 | 47 |
| 13 | Am/PhMt$_{125}$/SCO$_{1.25}$-BW | 125 | 1.25 | No | 3.9 | 84 | – | – |
| 14 | Am/PhMt$_{125}$/SCO$_{1.25}$-AW | 125 | 1.25 | Yes | 3.2 | 90 | 1.9 | 39 |
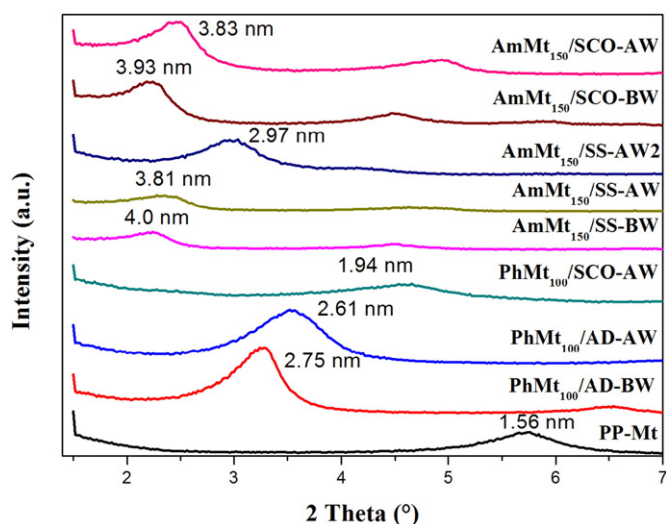
**Fig. 2.** XRD patterns of AmMt and PhMt samples. Before washed (BW), after washed (AW) and after a second washing (AW2).

**Table 3**
Relative mass loss of adsorbed and intercalated species.

| Sample | Adsorbed species (%) | Intercalated species (%) | Yield (%) |
| --- | --- | --- | --- |
| AmMt$_{150}$/SS-BW | 12 | 29 | 87 |
| AmMt$_{150}$/SS-AW | 7 | 30 | 91 |
| AmMt$_{150}$/SS-AW2 | 0 | 31 | 92 |
| PhMt$_{150}$/SS-BW | 24 | 16 | 52 |
| PhMt$_{150}$/SS-AW | 6 | 19 | 61 |
| PhMt$_{150}$/SS-AW2 | 0 | 19 | 63 |

disappearance of the first peak after second washing is an indication that it is associated with unreacted surfactant removal.

On the AmMt DTG curves, the second and third peak at about 320°C and 420°C, and on the PhMt DTG curves, the peaks at about 396°C and 495°C corresponds to the ammonium and phosphonium cations intercalated in the montmorillonite interlayer space (Xie et al., 2001; Livi et al., 2011a). The confinement effect is quite pronounced in thermal degradation of these species as can be seen in both DTG graphs since that the thermal degradation is significantly retarded in >100°C when compared with the pure surfactants. Analyzing the TGA and DTG curves of both organo-modified montmorillonite, the initial temperature of thermal degradation ($T_{onset}$) and the maximum temperature of release associated with the second event gradually increased as the sample was washed. The $T_{onset}$ (determined by the tangent method on TGA curves) of AmMt$_{150}$ was about 220°C, 225°C and 280°C to the samples

interpretation of the first thermal event and the quantification of unreacted species is complex and can be an error source to calculate the reaction yield. However, as in the two graphs in Fig. 3, the
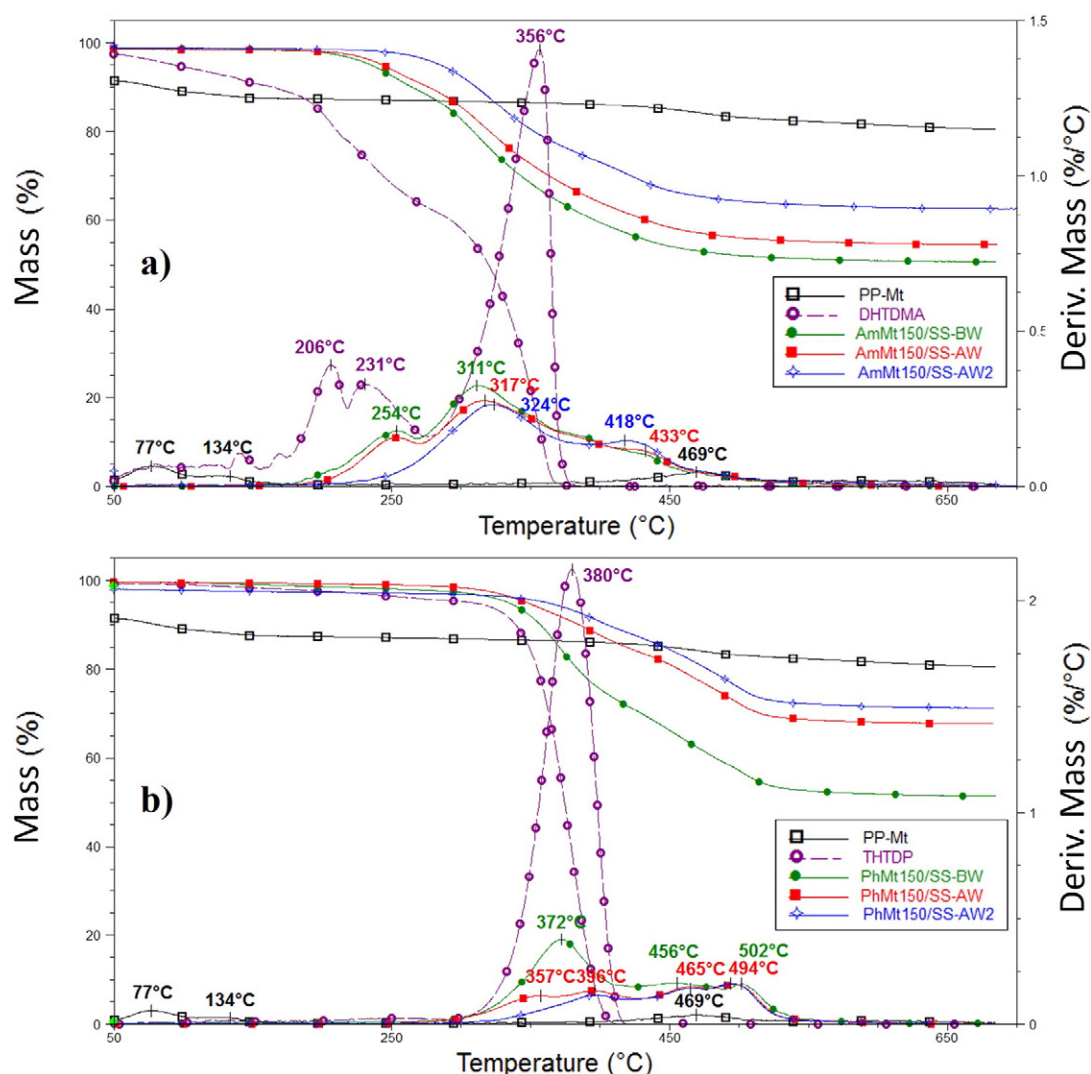


**Fig. 3.** TGA and DTG curves. (a) AmMt and (b) PhMt. Before washing (BW), after washing (AW) and after a second washing (AW2).

BW, AW and AW2; to the $PhMt_{150}$ was about 340°C, 346°C and 356°C to samples BW, AW and AW2. Therefore, it is an indication that the reduction of residual surfactant on the Mt. surface increases the thermal stability of the material since these species start to degrade at lower temperatures than the intercalated species. In general, the thermal stability of PhMt samples was about 100°C higher than AmMt samples.

Pareto's charts of each selected response for both DHTDMA and THTDP are shown in Fig. 4. The Pareto chart indicates the statistical significance of the factor and interaction effects in descending order, where the dashed line represents the significance threshold to 90% confidence. The effects in the left side of that line are considered statistically insignificant and in the right side are considered statistically significant.

According to the Fig. 4(a), none of the studied factors showed significant effect in the $d_{001}$ response using the DHTDMA compound. It was expected that the d-value would increase with the amount of surfactant, however, in this case, the results suggest that for all samples the surfactant amount was high enough to make the Mt. layers intercalated. For the THTDP compound (Fig. 4(c)), sodification factor had a significant effect with a positive value, which means that $d_{001}$-value increased when the Mt. was functionalized with this compound in the sodium state (level + 1).

Analyzing the Fig. 4(b), the DHTDMA organic compound amount factor had significant effect on the yield response with positive value. Therefore, it means that when we increase the amount of this reagent in reaction, the yield increases as well. Meanwhile for the process with THTDP, the sodification factor was a significant effect on yield response (Fig. 4(d)) with a negative value. This result was not expected because this means that when sodium clay was used (level + 1) the yield tends to decrease.

According with Fig. 5(a), regarding the organophilization with DHTMA in SCO, only the wash factor showed a significant effect with a negative sign on the $d_{001}$ response, thus the washing process reduced the d-value. Regarding the reaction yield (Fig. 5(b)), all of the main effects and the interaction between the amount factor and ethanol were significant. As was in the process in aqueous medium with DHTDMA, the yield increases when the surfactant amount increases. The ethanol factor and 1by2 interaction had negative sign, so the yield decreases when the ethanol amount increases. The wash factor had a significant effect on reducing d-value, while it had a significant effect on increasing the yield. Probably this step modifies the conformation and the

intercalation of cations within the interlayer space, since the dispersion of the samples in the wash solvent may be considered as a new reaction medium, thereby promoting the cation exchange with the adsorbed species near the clay mineral edge and modifying the characteristics of material. The use of ethanol as co-solvent has not proved very efficient, showing to be negligible and with negative signal.

With regard to functionalization with THTDP compound, Fig. 5(c) and 5(d), although none of factors had shown significant effect, the best results were obtained with increasing of ethanol co-solvent, and reducing the amount of organic compound. Therefore, the use of ethanol in the reaction medium improves the intercalation of the cations of the ionic liquid, but the use of excess reagent complicates the intercalation.

The variation in d-value and reaction yields as a function of the washing in both modified-Mt. are presented in Fig.6. According to Fig. 6(a) and 6(b), the yield gradually increased while the d-value gradually decreased as the samples were washed. The washing process caused the shifting of the XRD reflection to higher 2θ values, comparing to non-washed samples, reducing the d-value. It was more pronounced in the $AmMt_{150}$/SS-AW2, which is the sample with a second washing with ethanol/water solution as was made for the PhMt samples. Gradual washing process resulted in a corresponding decreasing in the basal spacing in both AmMt (Fig. 6(a)) and PhMt (Fig. 6(b)) samples.

A hypothesis for the yield increase is that, the washing process could be acting as a reaction medium and in this way moving and intercalating part of the excess surfactant species to interlayer spaces, increasing the yield. The washing may also modifies the conformation and the intercalation of cations within the interlayer space, since in the wash solvent may act as a new reaction medium. Other hypothesis for d-value reduction is based on the work of Zhuang et al. (2015). They reported that the intercalation of organic species into clay minerals is a complex process and the mechanism depends of various factors, and they proposed a mechanism of intercalation called as "stacking of organo-motmorillonite". Two distinct d-value can be obtained by this mechanism: i) a smaller d-value by the species intercalated into interlayer space; ii) a larger d-value by molecular beams intercalated (adsorbed) between neighbor organo-montmorillonite particles. Therefore, it is possible that in this study, surfactant molecules adsorbed on the external surface of one Mt.-platelets had linked with others surfactants molecules adsorbed on others Mt.-platelets creating intercalated
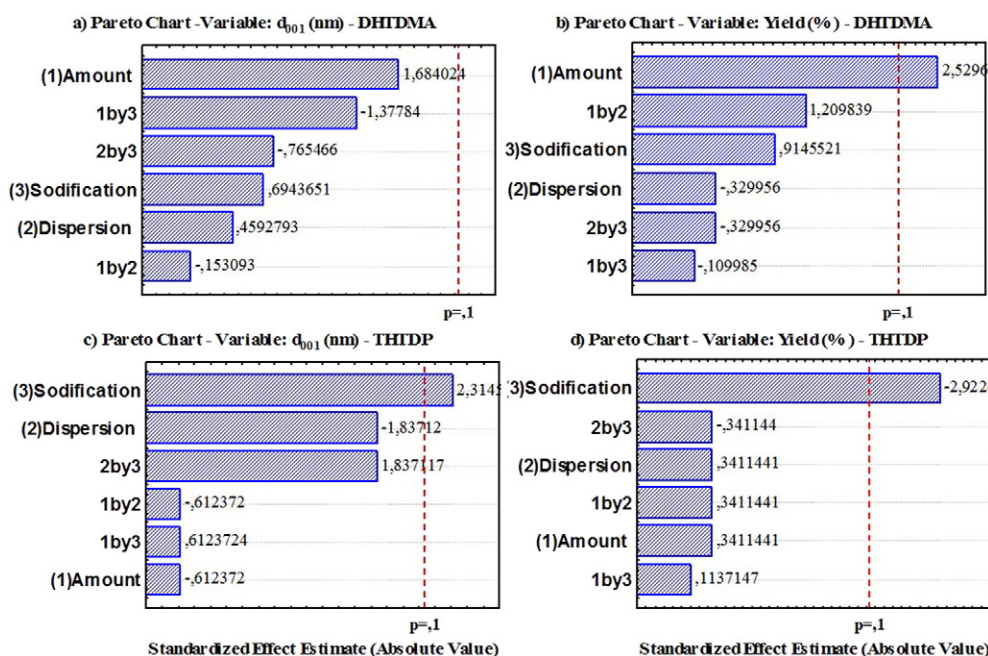


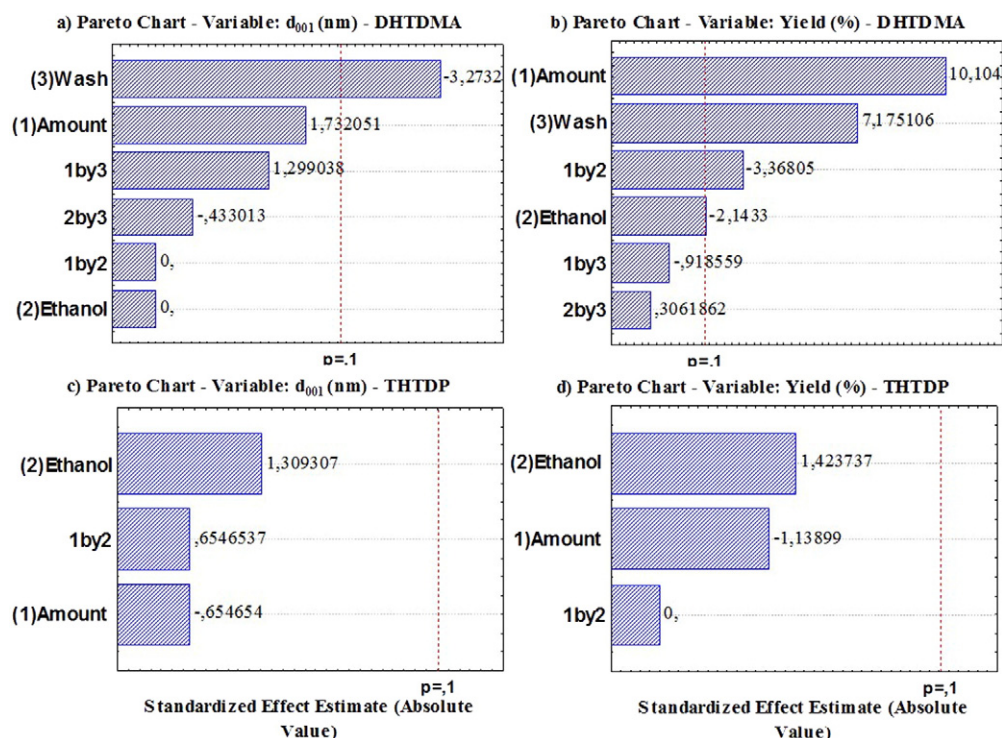Fig. 4. Pareto's charts for process responses in an aqueous medium.

Fig. 5. Pareto's charts for process responses in supercritical $CO_2$.

"molecular beams" with d-value larger than the obtained by the cation exchange species. The washing could destroy this structure. Assuming that, two or more XRD reflection would be expected for samples before washing. It is possible that there was an overlap of XRD reflection generated by these two basal distances, prevailing in XRD patterns the reflection due to the higher d-value, but the most probable effect was the change of the organic salt conformation from the perpendicular paraffin-type to a non-perpendicular structure into the clay mineral layers.

The organophilization with THTDP compound was not as efficient as with DHTDMA using all of the methods proposed. However, the modification in aqueous medium showed better efficiency than supercritical $CO_2$ since the maximum yield obtained was of 67% and d-value of 2.6 nm for the reaction in aqueous medium, and 47% and 2.0 nm for supercritical $CO_2$ (Tables 1 and 2). Experimentally it was observed that it was very difficult to work with the ionic liquid, mainly due to its low water solubility and high viscosity. Therefore, this poor solubility possibly may have hampered the intercalation and transport of cations between the clay mineral layers in addition to the structural conformation of the cations that have a long chain of 14C and three

medium chain of 6C, which can result in steric hindrance. For the modification with DHTDMA, the two cases were efficient, in which the results showed high similarity with yield about 90% and d-value about 3.5 nm.

The FTIR spectra of PP-Mt. and some samples of AmMt and PhMt functionalized by all the reactional medium studied and the respective pure organic compounds are shown in Fig. 7.

All FTIR spectra of AmMt (Fig. 7(a)) and PhMt (Fig. 7(b)) showed characteristic bands of aliphatic chains between 2849 $cm^{-1}$ and 2928 $cm^{-1}$ due to $CH_2$ symmetric and asymmetric stretching vibration and a band between 1460 $cm^{-1}$ and 1471 $cm^{-1}$ due to $CH_2$ bending vibration as well as in the respective organic compound (Xiang et al., 2010; Sarkar et al., 2011; Chang et al., 2014; Guégan et al., 2014; Zhuang et al., 2015). However, it did not appear in PP-Mt. As PP-Mt., all modified samples showed characteristic infrared bands of montmorillonite. Absorption bands from 3694 $cm^{-1}$ to 3619 $cm^{-1}$ are attributed to OH stretching vibration from inner-layer OH (Al—OH and Si—OH) from 990 to 1005 $cm^{-1}$ is assigned to the stretching vibration band of Si—O—Si, and at 912 $cm^{-1}$ and 510 $cm^{-1}$ represent Al—Al—OH
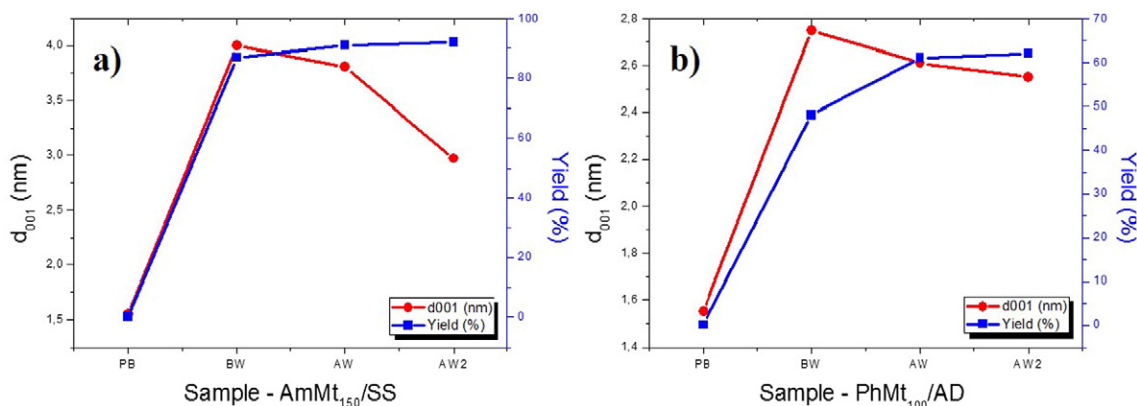


Fig. 6. Evaluation of d-value and reaction yield as a function of washing step of (a) AmMt and (b) PhMt samples.
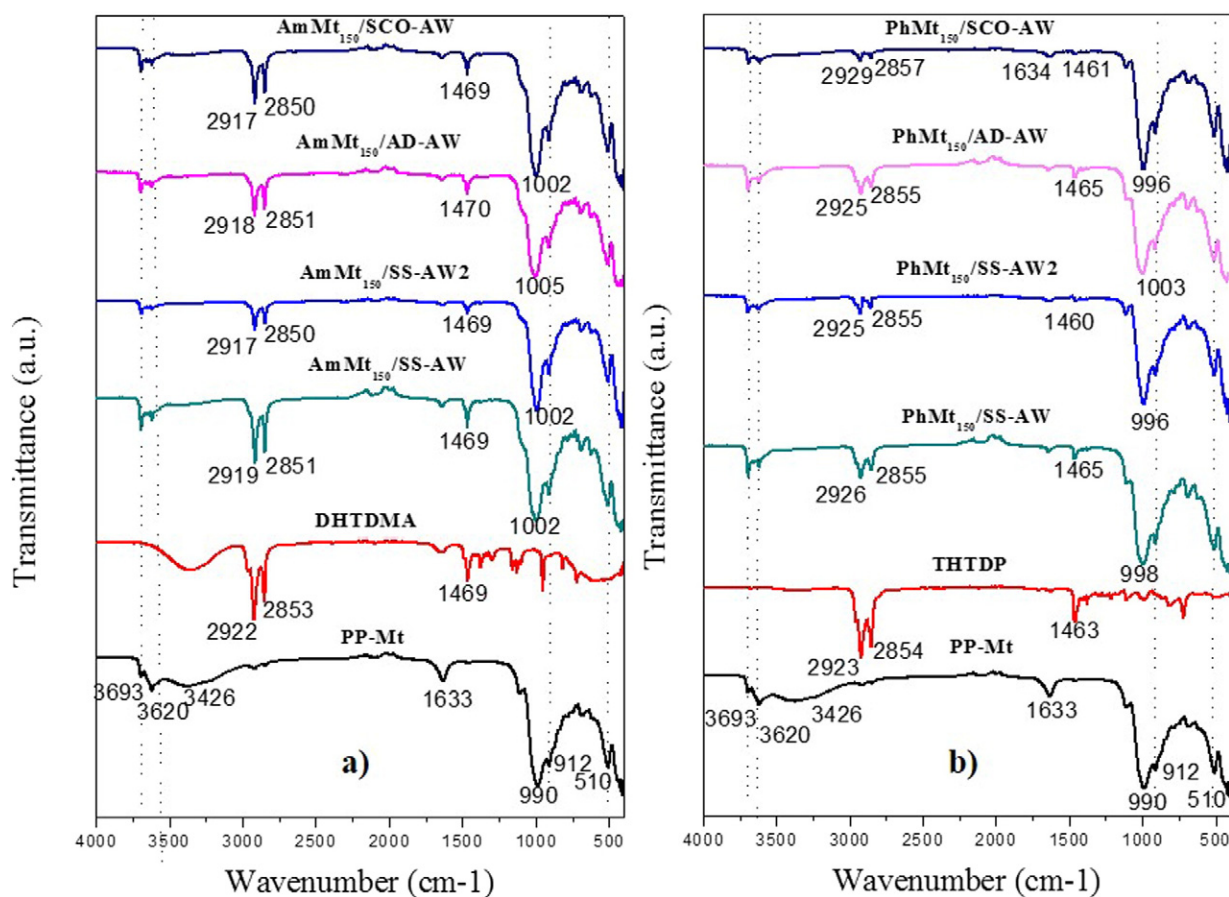
**Fig. 7.** FTIR spectra of PP-Mt., (a) DHTDMA and AmMt samples, and (b) THTDP and PhMt samples.

deformation and Si—O—Si bending vibration (Davarcioglu, 2012). In PP-Mt., the bands at 3426 $cm^{-1}$ and 1633 $cm^{-1}$ are assigned to the OH stretching and bending modes vibration of adsorbed water, and at 1115 $cm^{-1}$ to out of plane stretching vibrations of Si-O-Si bonds (Avalos et al., 2009; Zhuang et al., 2015). Therefore, FTIR studies provided evidence that the all samples were modified with the two compounds regardless of the medium used. The bands appearing at 2917–2919 $cm^{-1}$ to AmMt samples (Fig. 7(a)) and at 2921–2926 $cm^{-1}$ to PhMt samples (Fig. 7(b)) assigned to the asymmetric stretching vibration of $CH_2$, as well the bands appearing at 2850–2851 $cm^{-1}$ to AmMt samples and at 2851–2855 $cm^{-1}$ to PhMt samples assigned to the symmetric stretching vibration of $CH_2$ can be a indicative of the conformational ordering (gauche-trans conformer ratio), packing density and interactions of the surfactant in the organo-modified montmorillonite (Sarkar et al., 2011; Guégan et al., 2014). The shift of both $CH_2$ stretching vibration (asymmetric and symmetric) bands to higher wavenumber between the spectrum of $AmMt_{150}$/SS-AW and $AmMt_{150}$/SS-AW2, and as well $PhMt_{150}$/SS-AW and $PhMt_{150}$/SS-AW2 was indicative of a disordered structure in the interlayer space of Mt. due to the washing process (Sarkar et al., 2011; Guégan et al., 2014). In Fig. 7(a), the spectrum of $AmMt_{150}$/SS-AW showed lower wavenumber value in $CH_2$ stretching vibration bands than for $AmMt_{150}$/AD-AW and $AmMt_{150}$/$SCO_{2.0}$-AW samples, which indicates higher ordered all-trans conformations of DHTDMA in the Mt. structure. Thus, it is an evidence of the efficiency of the semi-solid method. In Fig. 7(b), $PhMt_{150}$/SS-AW and $PhMt_{150}$/AD-AW showed asymmetric stretching (both at 2926 $cm^{-1}$) and symmetric stretching (both in 2855 $cm^{-1}$) at lower frequencies than $PhMt_{150}$/$SCO_{2.0}$-AW, indicating that the reaction by $CO_2$ supercritical medium resulted in PhMt with disordered conformation, as was expected. In addition, compared with the spectrum of PP-Mt., the absorption of Si-O-Si at 990 $cm^{-1}$, shifted to a higher wavenumber in all of modified

samples. The shifts indicate that the environment of SiO groups in montmorillonite structure had changed, probably due to interactions with the alkyl chains of the surfactants. In general, the spectrums of AmMt samples showed lower wavenumber ($CH_2$ stretching vibration bands) than the PhMt samples. The double tallow chain of DHTDMA resulted in more ordered solid-like surfactant conformation in the modified montmorillonite than the single chain of THTDP (Sarkar et al., 2012). Therefore, all of the FTIR results are in agreement with previous results of XRD since the conformational ordering of organic compounds (surfactant arrangement) in the interlayer spaces is correlated with d-value variation, in other words, the samples with larger d-value (paraffinic-type with almost or totally perpendicular chain) showed a better ordered surfactant conformation (Guégan et al., 2014).

The contact angles and surface tension (ST) determined by the sessile drop method on pressed powder of PP-Mt., AmMt and PhMt samples are shown in Fig. 8 and Table 3.

Both surfactants made the montmorillonite more hydrophobic than PP-Mt. as can see in Fig. 8, since the contact angle between the water drop and sample surface increased to the modified montmorillonite.
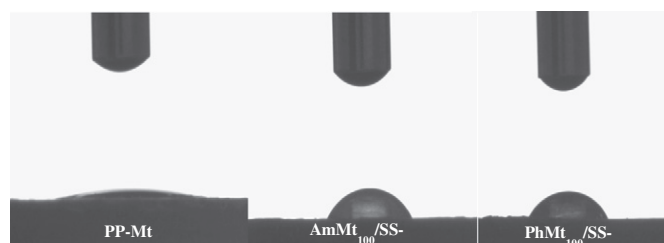


**Fig. 8.** Images from contact angle tests.

**Table 4**
Determination of the surface tension on PP-Mt. and on modified montmorillonites by contact angles with water.

| Sample | Contact angle θ (°) | Surface tension (mN/m) |
|---|---|---|
| PP-Mt | 15,2 ± 7,23 | 69,70 ± 2,13 |
| AmMt$_{100}$/SS-AW | 66,9 ± 7,37 | 43,08 ± 4,51 |
| AmMt$_{100}$/SS-AW2 | 65,4 ± 9,58 | 44,03 ± 5,85 |
| AmMt$_{150}$/SS-AW | 64,7 ± 4,49 | 44,44 ± 2,74 |
| AmMt$_{150}$/SS-AW2 | 61,5 ± 7,63 | 46,40 ± 4,60 |
| AmMt$_{150}$/AD-AW | 65,5 ± 4,76 | 43,98 ± 2,90 |
| AmMt$_{150}$/AD-AW2 | 66,2 ± 4,02 | 43,52 ± 2,45 |
| AmMt$_{150}$/SCO-AW | 74,9 ± 2,68 | 38,17 ± 1,66 |
| PhMt$_{100}$/AD-AW | 67,0 ± 2,27 | 43,02 ± 1,39 |
| PhMt$_{100}$/SS-AW | 71,2 ± 6,05 | 40,46 ± 3,73 |
| PhMt$_{150}$/SS-AW | 62,6 ± 3,85 | 45,72 ± 2,33 |
| PhMt$_{150}$/SS-AW2 | 69,9 ± 3,03 | 41,26 ± 1,86 |
| PhMt$_{150}$/SCO-AW | 37,7 ± 3,35 | 59,97 ± 1,76 |

In consequence, the surface tension decreased from around 70 mN/m in PP-Mt. to around 40 nM/m in AmMt and PhMt samples, which is in agreement with the literature (Liu et al., 2011, 2014; Livi et al., 2011a, 2011b; McLauchlin et al., 2011).

Regarding the amount of surfactant and the effect of washing process in surface tension of the samples, no significant changes were detected between the samples with 100% and 150% of CEC, and after the first and second washing. However, Table 4 showed that there was a small increase in ST value between AW and AW2 in AmMt samples while for PhMt samples there was a small decrease. AmMt$_{150}$/SCO-AW showed a smaller ST value than the samples obtained by aqueous dispersion and semi-solid, it was probably due to an effect of supercritical $CO_2$ in the environment of surfactant and montmorillonite, but Livi et al. (2011a) reported no difference between the methods. As expected, PhMt$_{150}$/SCO-AW presented higher surface tension, since that sample was not efficiently modified, resulting in a sample more hydrophilic due to largest amount of the remaining inorganic cations between the interlayer spaces.

## 4. Conclusions

The functionalization of a montmorillonite with ammonium and phosphonium salt by aqueous, semi-solid and supercritical $CO_2$ medium was confirmed by the results of XRD, FTIR, TGA-DTG and contact angles. It was concluded that the semi-solid method can be suggested as the best alternative since the DOE results to d-value and yield were similar or better than the others methods, and also due to its supposed lower environmental impact as it do not use a large amount of solvent and do not generates high amount of effluents. Furthermore, the process in supercritical $CO_2$ was not effective for modifying clay minerals with phosphonium salt.

Ammonium-modified montmorillonite showed larger d-value (about 3.8 nm) than phosphonium-modified montmorillonite (about 2.7 nm), however, the latter showed to be about 100°C more thermal stable. These two compounds present interesting properties to be combined in order to get organo hybrid-modified montmorillonite with high thermal stability and high basal spacing to be used in CPN by a simple and eco-friendly process.

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