

# SUPERCRITICAL CARBON DIOXIDE : A NEW METHOD FOR THE ORGANOMODIFICATION OF NATURAL CLAYS

Elodie Naveau<sup>a</sup>, Cédric Calberg<sup>b\*</sup>, Michaël Alexandre<sup>a</sup>, Christine Jérôme<sup>a</sup>, Christophe Detrembleur<sup>a</sup>

<sup>a</sup>Center for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6a, B-4000 Liège, Belgium

<sup>b</sup>Laboratoire de Chimie Industrielle (CIOR), University of Liège, Sart Tilman, B6a, B-4000 Liège, Belgium

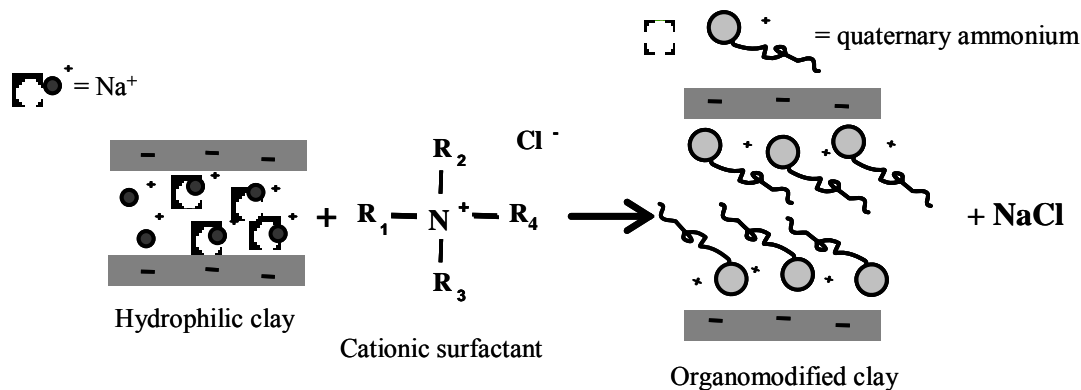
cedric.calberg@ulg.ac.be

## INTRODUCTION

Clays, and more specifically 2 :1 phyllosilicates consisting of aluminosilicate or magnesian silicate negatively charged stacked layers separated by van der Waals spacings where inorganic counteranions (sodium, calcium, ... cations) are located, can be associated with polymers to give interesting new materials called polymer/clay nanocomposites.

Polymer/clay nanocomposites have been intensively studied these two past decades because very small amounts of clay have shown to greatly improve a bunch of polymer properties, if nano-dispersion in the polymer matrix (exfoliation) is achieved<sup>1,2,3</sup>. This exfoliation, however, appears difficult to obtain due to the incompatibility between the naturally hydrophilic clay, and the most usually hydrophobic polymer matrix. Therefore, an ionic exchange between the interlayer cations of the clay and a cationic surfactant is necessary to render the interlayer spacings of the clay sufficiently organophilic to enhance the polymer/clay affinity.

**Figure 1** : Schematic representation of ionic exchange in layered silicate



Such organomodified layered silicates are industrially prepared via a water process. However, this process strongly limits the range of surfactants that can be used to water-soluble oniums, which may be a problem when looking for organoclays with a better compatibility with specialty polymers, such as polymers that require a high processing temperature or fluorinated polymers<sup>4-5</sup>.

In order to investigate non water soluble surfactants, supercritical carbon dioxide (sc CO<sub>2</sub>) appears to be a very promising medium. This environmentally benign, inexpensive and non-flammable solvent is currently attracting an increasing deal of attention.

Indeed, the high diffusivity, low viscosity and near-zero surface tension facilitates solute transfer relative to classical solvents<sup>6</sup>. Furthermore, since CO<sub>2</sub> is a gas at ambient conditions (critical parameters: 73.8 bar, 31.1 °C), the tedious drying procedure associated with water is circumvented and the recovered product is free of residual solvent upon depressurization. These unique properties of sc CO<sub>2</sub> have yet been exploited for the processing of polymer blends and nanocomposites<sup>7,8</sup>. Nevertheless, their use as a process for the modification of natural clays, while being recently patented<sup>9</sup>, has never been illustrated in the scientific literature.

In this work, we present the preparation of three types of nanoclays in supercritical carbon dioxide : firstly, nanoclays based on commercial alkyl ammonium salts, in order to compare our process with the classical water process, secondly alkyl phosphonium-based nanoclays to improve the thermal stability compared to the equivalent ammonium-based nanoclays and thirdly, nanoclays modified with functional phosphonium salts to enhance the compatibility with specific polymer matrices.

## MATERIALS AND METHOD

All the surfactants (Table 1) were purchased from Sigma-Aldrich Co. and were used as received. Commercial natural montmorillonite (MMT) known as Cloisite<sup>®</sup> Na<sup>+</sup> (cationic exchange capacity or CEC of 92.6 meq/100g) was supplied by Southern Clay Products (Rockwood Additives Ltd.). Carbon dioxide was obtained from Air Liquide Belgium (purity 99.995 %).

**Table 1 :** Surfactants used for the organomodification of montmorillonite clay

Name	Code	Ph.state (25°C)	MW (g/mol)
tetrabutylammonium chloride	TBACl	solid	277.93
tetraoctylammonium bromide	TOABr	solid	546.81
didodecyldimethylammonium bromide	DDDMABr	solid	462.65
tetrabutylphosphonium chloride	TBPCl	solid	294.89
tetraoctylphosphonium bromide	TOPBr	solid	563.78
trihexyltetradecylphosphonium chloride	THTDPCl	liquid	519.31
(2-hydroxyethyl)triphenylphosphonium bromide	HETPPBr	solid	389.27
(4-carboxybutyl)triphenylphosphonium chloride	CBTPPCl	solid	443.31
(2-hydroxybenzyl)triphenylphosphonium bromide	HBTPPBr	solid	451.34

Unmodified clay (MMT or HCT) and a slight excess of surfactant (1.1 equivalents relative to CEC) were poured into a 50 ml high pressure reactor. In case of functional salts, 1 ml of ethanol was added as a co-solvent. The temperature and the CO<sub>2</sub> pressure in the reactor were then adjusted and maintained at the desired values (typically 40°C and 200 bar). After 2 hours of reaction, the reactor was slowly depressurized. The resulting organoclay was characterized before and after being washed with acetone and dried.

X-ray diffraction (XRD) was carried out with a powder diffractometer Siemens D5000 (Cu K $\alpha$  radiation with  $\lambda = 0.15406$  nm, 50 kV, 40 mA, Ni filter) at room temperature, in order to investigate the interlayer distance of the clays, before and after washing.

Thermogravimetric analysis (TGA) was used both to determine the organic content of the prepared nanoclays after washing and to evaluate their thermal stability, using a TA Instrument TGA Q500 thermal analyser at a heating rate of 10°C per min, under N<sub>2</sub> flow, typically from room temperature to 600°C.

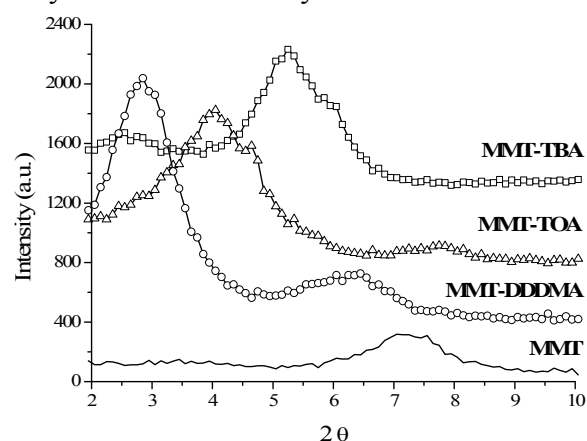
## RESULTS

### *Alkyl ammonium salts*

Clay organomodification was easily carried out in sc CO<sub>2</sub> for typically 2 hours by contacting the clays with a slight excess (1.1 eq relative to clay CEC) of the alkyl ammonium salts. After the treatment in sc CO<sub>2</sub>, the organomodified clays were analysed by X-ray diffraction (XRD). This technique enables us to determine the distance between two adjacent sheets of the silicate. The also called interlayer distance is calculated via Bragg's relation with the 2θ angle of the first diffraction peak (001) :  $d_{001} = \lambda / 2 \sin \theta$  (with  $\lambda = 0.154$  nm).

The diffraction patterns of the natural clay (MMT) and the various organoclays are represented in Figure 2. These scans show that replacing the sodium ions with large ammonium cations results in higher interlayer distances (lower 2θ angles). In other words, the montmorillonite gallery (initial d-spacing of 1.2 nm) expands as needed to accommodate more intercalated material. The expansion goes from 1.7 nm in the presence of tetrabutylammonium cations (MMT-TBA), to 2.2 nm with tetraoctylammonium cations (MMT-TOA) and to 3.1 nm with didodecyldimethylammonium cations (MMT-DDDMA).

**Figure 2 :** XRD patterns of montmorillonite clay modified with alkyl ammonium salts



Interestingly, the interlayer distance is proportional to the size of the cation. This relationship was previously demonstrated by Fornes et al<sup>10</sup> for exchange reactions in water. It is thus confirmed for the supercritical carbon dioxide exchange process.

In order to eliminate the excess of surfactant in the clay, organomodified clays were washed with acetone, a good solvent of the different ammonium salts. After this treatment, the interlayer distance of the product is maintained, as confirmed by XRD. The organic content remaining after the clay washing was quantified by thermogravimetric analysis (TGA). Indeed, the natural clay only loses a few percents of weight just below 550°C, whereas ammonium salts are completely degraded at this temperature. The weight loss between 100 and 550°C of the washed organoclays is then compared to the theoretical weight loss based on the cationic exchange capacity of the clay to calculate the yield of exchange reaction (Table 2).

**Table 2 :** Results of the organomodification of montmorillonite clay (MMT) with alkyl ammonium salts (after washing)

Organoclay	Surfactant	Org. cont. (wt %)	d <sub>001</sub> spacing (nm)	Exchange yield (%)
MMT-TBA	tetrabutylammonium chloride	14.5	1.7	78
MMT-TOA	tetraoctylammonium bromide	25.0	2.2	83
MMT- DDDMA	didodecyldimethylammonium bromide	22.7	2.9	87

A relatively high exchange yield is obtained with these alkyl ammonium salts. Compared to the water process, often requiring 24 hours of exchange reaction at a temperature of 80°C, the intercalation can be obtained in a short period of time (2 hours) and at a low temperature (40°C). Moreover, these organoclays can be directly used for the preparation of nanocomposites without any drying step. This process was then applied to non-water soluble phosphonium salts.

#### *Alkyl phosphonium salts*

The same procedure was followed to intercalate phosphonium salts between the layers of montmorillonite clay. For the sake of comparison, two alkyl phosphonium salts, tetrabutylphosphonium chloride (TBPCl) and tetraoctylphosphonium bromide (TOPBr) with the same structure as the previously described ammonium salts were chosen. The third selected salt, trihexyltetradecylphosphonium chloride (THTDPCl) is an ionic liquid, chosen for its long alkyl chain and its relatively low cost, essential for an industrial application.

XRD analysis of the organomodified clays showed again an intense diffraction peak at lower angles than that of the natural clay, indicating an intercalation of the different phosphonium salts in the clay. The d-spacing and exchange yield are presented in Table 3.

**Table 3 :** Results of the organomodification of montmorillonite clay (MMT) with alkyl phosphonium salts (after washing)

Organoclay	Surfactant	Org. cont. (wt %)	d <sub>001</sub> spacing (nm)	Exchange yield (%)
MMT-TBP	tetrabutylphosphonium chloride	15.5	1.8	80
MMT-TOP	tetraoctylphosphonium bromide	21.8	2.4	72
MMT-THTDP	trihexyltetradecylphosphonium bromide	26.0	2.6	84

A slightly higher interlayer distance is obtained for the phosphonium salts compared to the same ammonium salts. This is related to the greater size of the phosphorus atom in comparison with the nitrogen atom. Overall, the exchange yields are very similar.

The gain of thermal stability of these organoclays was then evaluated by comparing the onset temperature of degradation from the derivated thermogravimetric curve (DTG), this is at the point where derivative weight change increases to > 0.01%/°C.

**Table 4 :** Onset temperature of degradation of the alkyl phosphonium- and ammonium-modified montmorillonite clays

Organoclay	Onset temp. of degradation
MMT-TBA	164°C
MMT-TOA	157°C
MMT-DDDMA	177°C
MMT-TBP	252°C
MMT-TOP	227°C
MMT-THTDP	241°C

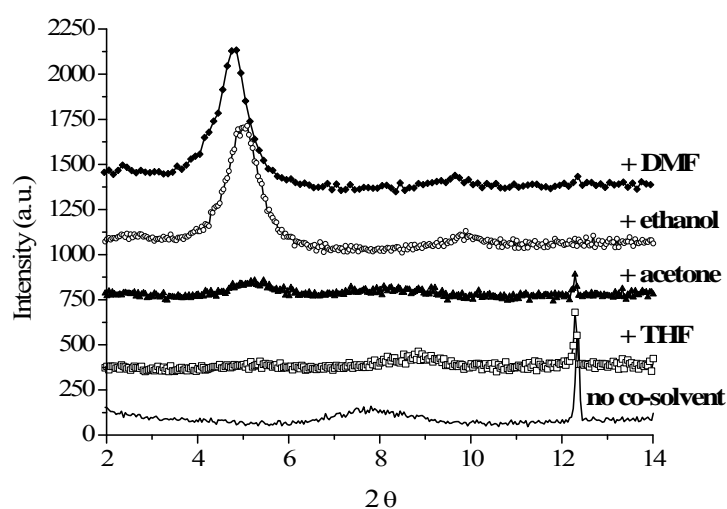
From the results presented in Table 4, it appears clearly that the degradation is delayed in case of phosphonium-modified clays. The gain in the thermal stability compared to ammonium-based organoclays goes from 60 to 80°C, which is a significant advantage when preparing nanocomposites by the melt blending method.

### Functional phosphonium salts

Following the same conditions, we tried to extend the range of surfactants used in this process to functional phosphonium salts. Three types of salts were tested : hydroxyethyltriphenyl phosphonium bromide (HETPPBr), carboxybutyltriphenyl phosphonium chloride (CBTPPCL) and hydroxybenzyltriphenyl phosphonium bromide (HBTPPBr). In these cases however, the organomodified clays showed a diffraction pattern corresponding to the superposition of both natural clay and phosphonium salt diffractograms. No intercalation was thus observed. Therefore, the addition of a co-solvent was necessary. A few solvents with different polarities were tested, respecting a 2 % volume compared to the capacity of the CO<sub>2</sub> vessel.

Based on the XRD analysis (Figure 3), it can be stated that no intercalation is detected in the case of acetone and tetrahydrofuran (THF), whereas the intercalation occurs with the most polar solvents, dimethylformamide (DMF) and ethanol. These solvents are thus efficient to enhance the polarity of sc CO<sub>2</sub>, even at a low concentration (2 % vol.). Ethanol, more environmentally-friendly, was chosen as co-solvent for the organo-modification of the other functional phosphonium salts. The results are presented in Table 5.

**Figure 3** : XRD patterns of montmorillonite clay modified with hydroxyethyltriphenylphosphonium salt using different co-solvents



**Table 5** : Results of the organomodification of montmorillonite clay (MMT) with functional phosphonium salts (after washing)

Organoclay	Surfactant	Org. cont. (wt %)	d <sub>001</sub> spacing (nm)	Exchange yield (%)
MMT-HETPP	(2-hydroxyethyl)triphenyl phosphonium bromide	20.0	1.7	90
MMT-CBTPP	(4-carboxybutyl)triphenyl phosphonium chloride	20.6	1.8	75
MMT-HBTPP	(2-hydroxybenzyl)triphenyl phosphonium bromide	21.0	1.8	82

All of these three functional surfactants were successfully intercalated in sc CO<sub>2</sub> with the addition of ethanol as co-solvent, with a particularly high exchange yield in the case of HETPP.

Our sc CO<sub>2</sub> process for the modification of natural clays is thus very efficient for a large variety of surfactants, with the addition of a small quantity of a polar solvent in case of functional salts. Solubility measurements have still to be done to complete this study.

## CONCLUSION

As a conclusion, three types of organomodified-nanoclays were prepared using our supercritical carbon dioxide process. Alkyl ammonium and alkyl phosphonium salts were successfully exchanged in natural clay at low temperatures. The exchange reaction is very fast and the obtained nanoclays can be directly used to prepare nanocomposites. The phosphonium-modified clays present a gain in thermal stability up to 80°C compared to the ammonium-modified clays and are particularly well adapted for the melt processing of polymers at temperature between 180 and 250°C.

Phosphonium salts containing a hydroxy- or carboxy- function were also intercalated between the clay layers with a high exchange yield, using 2 % vol. of ethanol as a co-solvent to enhance the polarity of sc CO<sub>2</sub>.

Finally, this process is easily transferable to an industrial scale. Kilograms of such organoclays can now be obtained thanks to our lab's pilot plant (reactor of 50 L).

## ACKNOWLEDGMENTS

This work was financed by the Région Wallonne under the FIRST Spin Off program FINECLAY. CERM is also grateful to the Belgian Science Policy for general support in the frame of the Interuniversity Attraction Poles Program (PAI V/03-action P3). C.D. is "Chercheur Qualifié" by the Fonds National pour la Recherche Scientifique (F.N.R.S.) and E.N. thanks Prof. Rulmont for XRD measurements.

## REFERENCES :

- [1] ALEXANDRE, M., DUBOIS, P., *Materials Science and Engineering Reports*, Vol. 28, **2000**, p.1
- [2] LEBARON, P. C., WANG, Z., PINNAVAIA, T. J., *Applied Clay Science*, Vol. 15, **1999**, p. 11
- [3] USUKI, A., HASEGAWA, N., KATO, M., *Advances in Polymer Science*, Vol. 179, **2005**, p. 135
- [4] XIE, W., GAO, Z., PAN, W.-P., HUNTER, D., SINGH, A., VAIA, R., *Chemistry of Materials*, Vol. 13, **2001**, p. 2979
- [5] THOMASSIN, J.-M., PAGNOULLE, C., BIZZARI, D., CALDARELLA, G., GERMAIN, A., JEROME, R., *Solid State Ionics*, Vol. 177, **2006**, p. 1137
- [6] ZHAO, Q., SAMULSKI, E. T., *Macromolecules*, Vol. 36, **2003**, p. 6967
- [7] TOMASKO, D. L., HAN, X., LIU, D., GAO, W., *Current Opinion in Solid State and Materials Science*, Vol. 7, **2003**, p. 407
- [8] ZHAO, Q., SAMULSKI, E. T., *Polymer*, Vol. 47, **2006**, p. 663
- [9] STASSIN, F., CALBERG, C., JEROME, R., *PCT Int. Appl.*, **2004**, WO 2004/108805
- [10] FORNES, T. D., YOON, P. J., HUNTER, D. L., KESKKULA, H., PAUL, D. R., *Polymer*, Vol. 43, **2002**, p.5915