

# SC CO<sub>2</sub> AS AN EFFICIENT SOLVENT FOR THE MANUFACTURE OF SPECIALTY ORGANOCLAYS: FROM LAB PREPARATION TO PRE-INDUSTRIAL PRODUCTION

Detrembleur C.\*, Naveau E., Calberg C., Alexandre M., Jérôme C.

Centre for Education and Research on Macromolecules (CERM), University of Liège, Sart-Tilman, B6a, B-4000 Liège, Belgium  
christophe.detrembleur@ulg.ac.be - fax : +3243663497

## ABSTRACT

Although the nanoclay particles market is continuously growing, the difficulty to disperse them in specialty polymers remains a major restraint. In order to increase the compatibility between fillers and matrices, the variety of clay organomodifiers has to be extended, in particular to non-water soluble surfactants.

In this context, our team has developed the use of supercritical carbon dioxide (scCO<sub>2</sub>) as solvent for the organomodification of clays. Indeed, scCO<sub>2</sub> has excellent transport properties and solubilises a large number of surfactants, among which fluorinated and silicon surfactants. The process is simple, environmentally friendly and easy to transfer to the industrial scale. Indeed, typical experimental conditions are a temperature of 40°C and a pressure of 100 bar for 2 hours. After reaction and depressurization, dry clays are directly obtained. Using this process, three types of organoclays were prepared: fluorinated nanoclays, siliconated nanoclays and high temperature stable nanoclays (up to 260°C). Their production has been scaled up to kilograms thanks to our lab's pilot plant, while their dispersion in specialty polymers is studied in collaboration with industrial partners. Finally, these organoclays are commercialized through the spin-off FINECLAY.

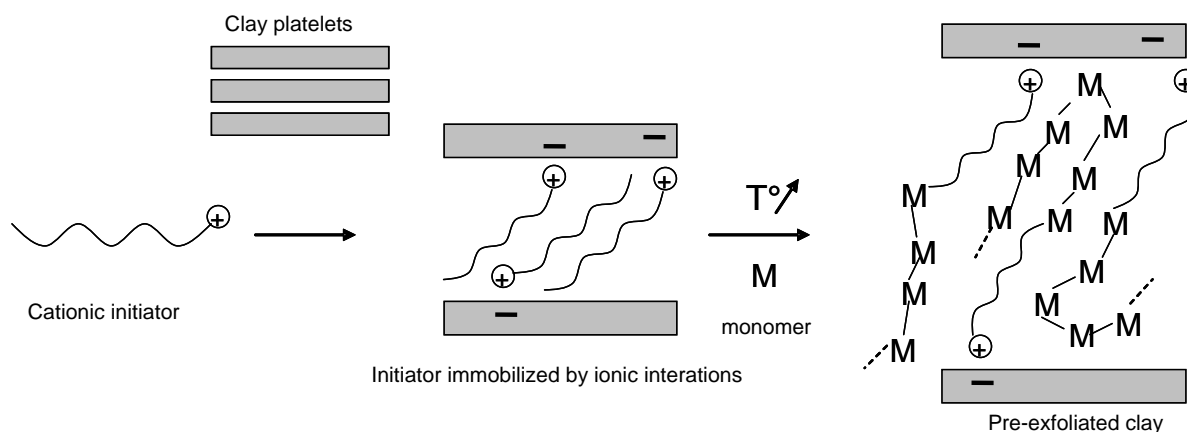
## INTRODUCTION

The nanoclay particles market has an annual growth of 20.3 %, according to a recent nanocomposites market study by Frost and Sullivan<sup>1</sup>. However, the low number of organoclay producers remains a major restraint. Indeed, due to the incompatibility between the clay, hydrophilic, and the polymer, hydrophobic, an organo-modification of the clay is necessary to ensure a fine dispersion of these nanofillers<sup>2</sup>. This is classically done by an ionic exchange reaction, between the sodium ions of the clay and quaternary ammonium cations (organic modifiers). This exchange is well-known in water<sup>3</sup>, however, in order to enlarge the variety of organic modifiers, our lab has demonstrated that it could be done in supercritical carbon dioxide (sc CO<sub>2</sub>) due to its excellent transport properties<sup>4</sup>. The process is simple, environmentally friendly and easy to transfer to the industrial scale. Moreover, as CO<sub>2</sub> is a gas at ambient temperatures, the tedious drying procedure associated with water is circumvented and the recovered product is free of residual solvent upon depressurization.

Using this process, several alkyl phosphonium salts have been successfully exchanged in montmorillonite and hectorite clay, yielding particularly thermally stable organoclays, suitable for the preparation of nanocomposites by melt blending<sup>5</sup>. These organoclays have already been prepared in large quantities in our pilot plant, with very convenient conditions.

Then the process was extended to the ionic exchange of functional surfactants such as monomers or initiators in order to induce polymer grafting from the clay platelets and so to produce pre-exfoliated organoclays by *in situ* radical polymerisation in sc CO<sub>2</sub>.

**Figure 1** : Schematic representation of polymer grafting from the clay platelets



In our presentation, we will review the principles of sc CO<sub>2</sub> ionic exchange process with classical alkyl surfactants and detail the scaling-up of the process, before moving on to the prospects of *in situ* preparation of nanocomposites in a one pot process in sc CO<sub>2</sub>.

## MATERIALS AND METHODS

Cloisite<sup>®</sup> Na<sup>+</sup> (montmorillonite from Southern Clay Products) and a stoichiometric amount of trihexyltetradecyl phosphonium salt (Cytec Industries) were poured into a high pressure reactor. 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 vessel was slowly depressurized. The resulting organoclay was characterized by XRD and TGA before and after being washed with acetone and dried.

## RESULTS

Trihexyltetradecyl phosphonium salt was successfully exchanged in Cloisite Na<sup>+</sup>, with an interlayer distance of 2.7 nm and an exchange yield of 84 % (Table 1). Very similar results were obtained for the scaling-up to a 50 L high pressure reactor, confirming that the supercritical carbon dioxide process is easy to transfer to industrial scale with a high reproducibility. Moreover, the vessel can be filled up to 75 % of its height, without hindering the exchange reaction (tested on the 250 ml reactor).

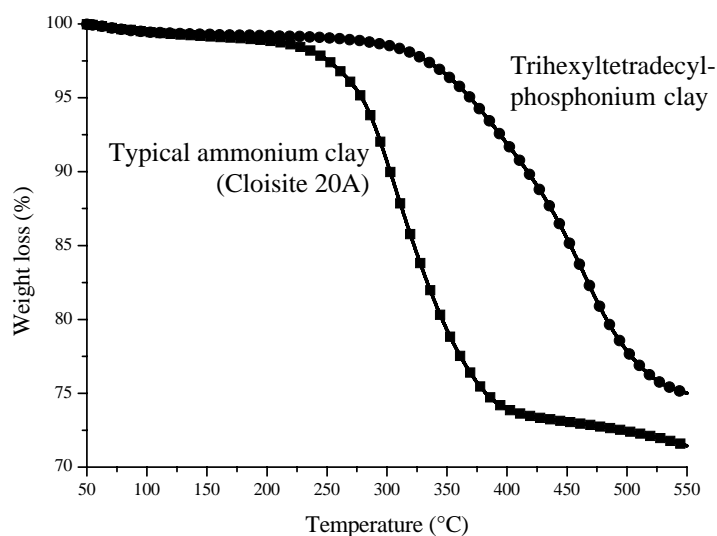
The thermal stability of this new organoclay was of 240°C, which represents a gain of 60°C compared to typical commercial nanoclays.

This organoclay is particularly well-suited for dispersion by melt blending in high temperature-processed polymers such as polyamide, polycarbonate or polyolefins.

**Table 1** : Results of the organo-modification of Cloisite Na<sup>+</sup> with trihexyltetradecyl phosphonium chloride in supercritical carbon dioxide

Amount of clay	Reactor volume	d <sub>001</sub> spacing (nm)		Exchange yield (%)
		bef. wash.	after. wash	
4 g	50 ml	2.7	2.5	84
40 g	250 ml	2.5	2.4	86
4 kg	50 L	2.6	2.4	81

**Figure 2** : Comparison of thermal stability of our phosphonium-modified clay with a commercial organoclay



## CONCLUSION

Supercritical carbon dioxide is an efficient process to produce thermally stable organoclays at pilot scale. Several kilograms of such organoclays are already available and the preparation of nanocomposites by melt blending is in progress in collaboration with industrial partners. This convenient process may be extended to the preparation of pre-exfoliated organoclays by *in situ* polymerisation in sc CO<sub>2</sub> from functional surfactants-modified clays.

## ACKNOWLEDGMENTS

E. Naveau is grateful to the Région Wallonne for financial support in the frame of 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 (IAP VI/27) Belgian Science Policy. C.D. is “Senior Research Associate” by the Fonds National de la Recherche Scientifique (F.N.R.S.).

## **REFERENCES :**

- [1] FROST AND SULLIVAN, World Polymer Nanocomposites Markets, **2007**
- [2] ALEXANDRE, M., DUBOIS, P., Materials Science and Engineering, vol. 28, **2000**, p. 1
- [3] NAVEAU, E., DETREMBLEUR, C., JEROME, C., ALEXANDRE, M., Recent Patents on Materials Science, vol. 2, **2009**, p.43
- [4] STASSIN, F., CALBERG, C., JEROME, R., PCT Int. Appl., WO 2004/108805, **2004**
- [5] NAVEAU, E., CALBERG, C., DETREMBLEUR, C., BOURBIGOT, S., JEROME, C., ALEXANDRE, M., Polymer, **2009**, doi : 10.1016/j.polymer.2009.01.040