ENHANCEMENT OF LAYERED NANOCLAY PROPERTIES BY MEANS OF A TREATMENT WITH SUPERCRITICAL CARBON DIOXIDE

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Nanocomposite polymeric materials are a new generation of plastic materials with interesting final application properties for diverse industrial sectors. Nowadays, nanocomposites tend to use silicated layered nanoclays, that present two main problems: high price, due to low efficiency of processing; and low final efficiency in nanocomposites, due to dispersion limitations. Thus, research still looks for new nanoclay processing to optimise final prices and to increase final nanoclay yield in nanocomposites.

In this context, supercritical fluid technology may play an interesting role as an alternative for nanoclay modifying/processing. Under supercritical conditions, SCF´s may diffuse and enter into the interstitial silicate spaces. This way, SCF´s may be used to optimise the separation of nanoclays or as a reaction medium to apply functional chemical groups to change their properties.

Experimental test were performed with bentonite samples at two supercritical facilities, at pressures up to 270 bar and temperatures up to 55 ºC. SC-CO_2 treated bentonite samples with very different properties from those of the original non-treated material were achieved. The most significant change was observed in the absorbed water (TGA) and FTIR measurements. Treated bentonite samples exhibited higher specific surface, lower interlaminar water, and higher viscosity were achieved in water suspensions of nanoclays.

INTRODUCTION

Nanocomposite polymeric materials are a new generation of plastic materials with interesting final application properties for diverse industrial sectors. These materials are base on adding new mineral nanometric additives that provide enhanced properties to the plastic materials. These properties derive from their morphology and molecular structure. These new nanocomposite materials have a series of technological advantages such as better mechanical properties, better barrier and ignifuge properties, better environmental, abrasive and solvent stability. On the other hand, other properties are not diminished such as transparency, impact resistance, and density. These materials are very interesting for packaging, automotion, implants, aerospace, electrics, electronics, etc. [1, 2]. Nowadays, nanocomposites tend to use silicated layered nanoclays, although other fibrilar ones also exist. Layered nanoclays present two main problems: high price, due to low efficiency of processing; and low final efficiency in nanocomposites, due to dispersion limitations. Thus, research still looks for new nanoclay processing to optimise final prices and to increase final nanoclay yield in nanocomposites.

In this context, supercritical fluid technology may play an interesting role as an alternative for nanoclay modifying/processing. SCF´s show special transport and thermodynamic properties such as high diffusivity and low surface tension. Under supercritical conditions, they may diffuse and enter into the interstitial silicate spaces. This way, SCF´s may be used to optimised the separation of nanoclays or as a reaction medium to apply functional chemical groups to change their properties.

MATERIALS AND METHODS

Experimental test were performed with bentonite samples, previously pre-treated in order to prepare nanoclays and to ease result assessment. In brief, these bentonites were conditioned by a wet procedure and purified by sieving, rejecting typical impurities (figure 1). At the end, an homogeneous product was obtained.

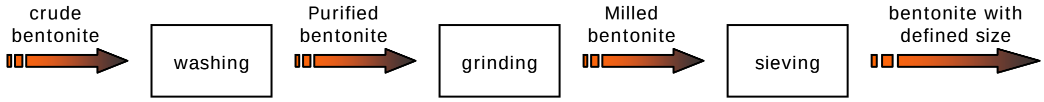

Figure 1. Nanoclay conditioning

Experimental test were performed with homogenous prepared bentonite samples at FSC500 supercritical plant (figure 2).

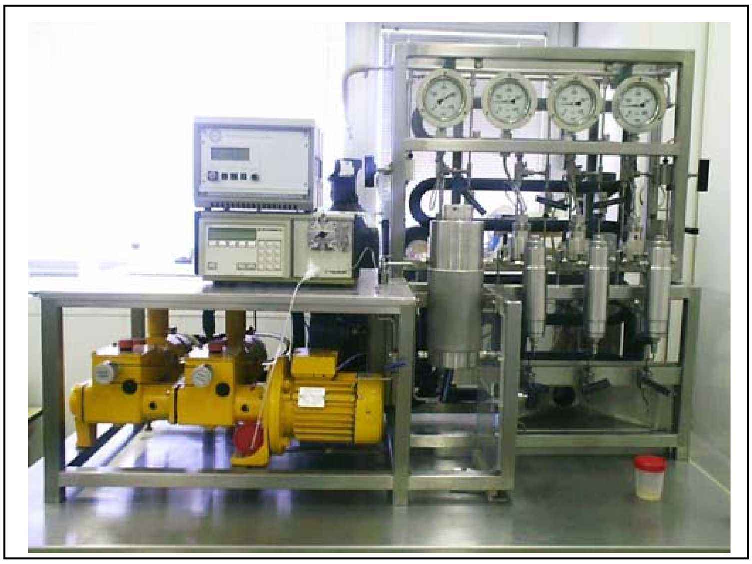

Figure 2. FSC500 supercritical CO_2 plant

This equipment, which has been describe in previous works (Berna *et al*., 2000) has a 0,5 L pressure vessel and three separators in series. It may operate at pressures up to 28 MPa, temperatures up to 343 K and flow rates up to 4 kg/h.

In order to assess results, a group of characterisation methods was identified in order to assess whether results may be interesting or not for already mentioned applications. This way, analytical procedures were adapted taking into account particular features of this kind of samples. SC-CO_2 treated bentonites were characterised through different assays, among them:

- Specific surface
- Water permeability
- Rheology assays
- Infrared Spectroscopy (FTIR)

RESULTS AND DISCUSSION

Experimental test were performed with bentonite samples at pressures up to 270 bar and temperatures up to 55 ºC, applying successive treatment cycles. Each cycle comprised three steps: pressurization, steady-state and depressurization. Main variables in these treatment tests were pressure, temperature and number of treatment cycles. Experimental conditions are presented in table 1.

Table 1. Conditions of supercritical CO_2 treatment tests

Operation conditions	Test 1	Test 2	Test 3	Test 4	Test 5
Amount of raw material (g)	150	150	150	150	150
Flowrate (kg/h)	4	4	4	4	4
Pressure (bar)	270	270	80	80	270
Temperature (ºC)	55	55	55	55	40
No of SC-CO_2 cycles (kg CO_2)	1	5	1	5	1

SC-CO_2 treated bentonite samples with very different properties from those of the original non-treated material were achieved, as it is shown in table 2.

Table 2. Characterisation results of supercritical CO_2 treatment tests

	Control	Test 1	Test 2	Test 3	Test 4	Test 5
Specific surface ± 0,2 (m^2 / g)	38,0	40,7	38,7	33,5	39,7	42,0
Water permeability	27	19	20	21	20	19
Viscosity at 200 s^{-1}						
Low shear stress, LS (MPa)	107 ± 1	82 ± 3	245 ± 5	50 ± 2	136 ± 4	172 ± 4
High shear stress, HS (MPa)	142 ± 3	174 ± 4	255 ± 5	189 ± 4	179 ± 5	204 ± 5

With respect to specific surface, a general increase was observed in all tests except test 3, the one with the lowest pressure and number of treatment cycles. The highest specific surface was achieved at 270 bar through one treatment cycle (test 1 and 5). Also, from a general point of view, SC-CO_2 treated bentonites exhibited similar permeability values, all lower than the original bentonite (non-SC treated, also called control)

With regard to viscosity, all samples exhibited higher values than control bentonite at high shear stress. At low shear stress, test 2, 4 and 5 viscosity values were larger than non-treated bentonites. Both highest viscosity values at low and high shear stress were observed in test 2. Shear stress curves at low and high shear stress are presented in figure 3. As it may be seen, a gel structure was got with bentonite treated under supercritical condition (high viscosity at low shear stress velocity and movement towards to shear stress value larger).

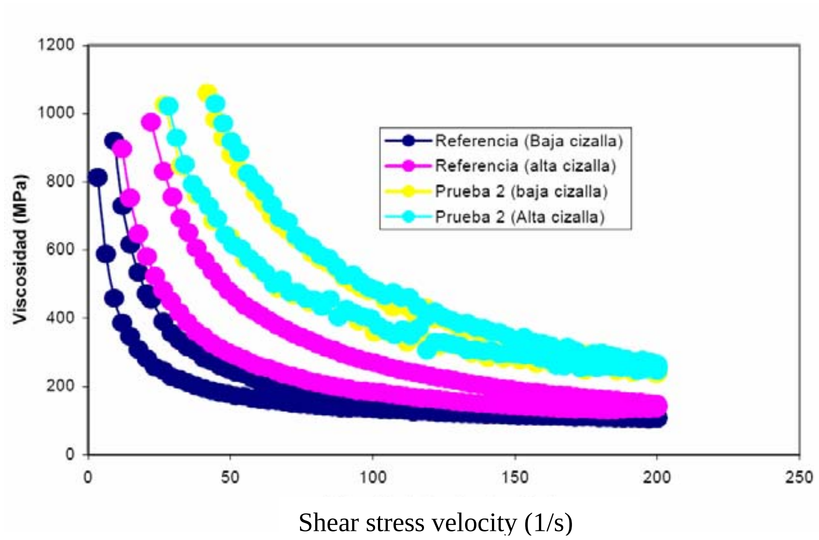

Figure 4. Viscosity curves as a function of shear stress velocity for control and test 2 bentonites

TGA curves are presented in figure 4. Significant differences were observed between original bentonites and SC-CO_2 treated ones. Two zones may be distinguished for result assessment: up to 500 ºC and up to 800 ºC.

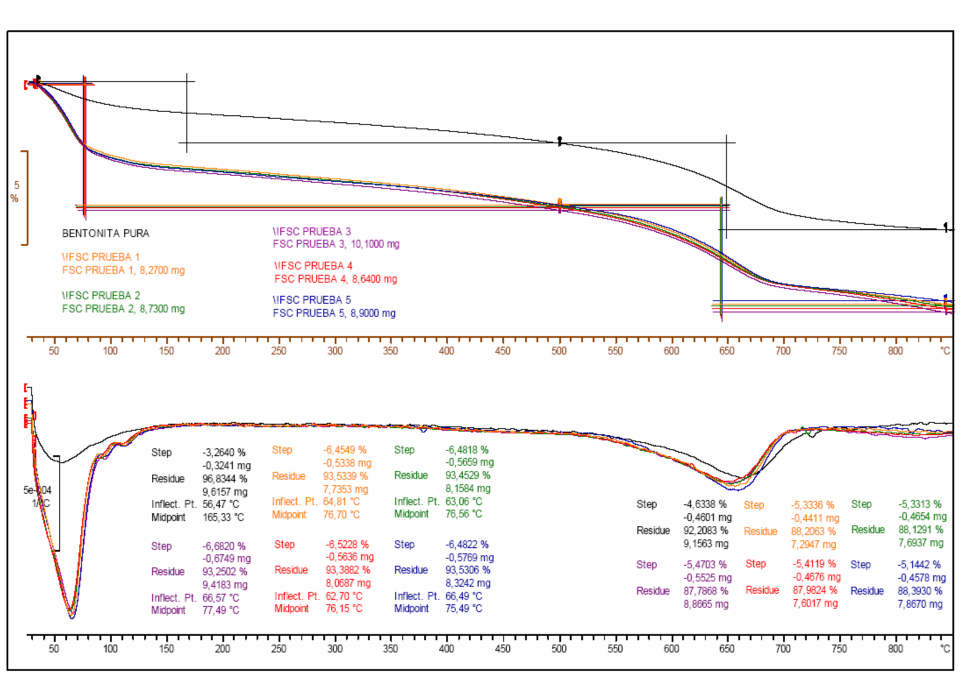

Figure 5. TGA and DTG curves for pure and SC-CO_2 treated bentonites

In the first zone, the amount of decomposed material increased with respect to the reference bentonite (from 3 up to 6 %) and decomposition occurred at a slightly higher temperature (65 ºC vs 55 ºC), which may indicate a stronger bond of decomposed substance to bentonites. Also, first derive curve (figure 5 bottom) presented two shoulders within the range 80-120 ºC. In the second zone, also the percentage of decomposed material was larger for treated bentonites than for original ones, although in this case the maximum loss of weight was observed at lower temperatures that at control bentonite. Nevertheless, this decomposition material percentage increase was slighter than that loss percentage growth observed in the first zone.

With respect to FTIR, spectra belonging to tested samples confirmed differences in comparison to non-treated bentonites. Absence or reduction of peaks related to hydroxyl group was seen, which may reflect the removal or diminishing of absorbed water in the nanoclay. SC-CO2 presented two bands near 1400 cm^{-1} and a wide band between 2800 and 3000 cm^{-1}.

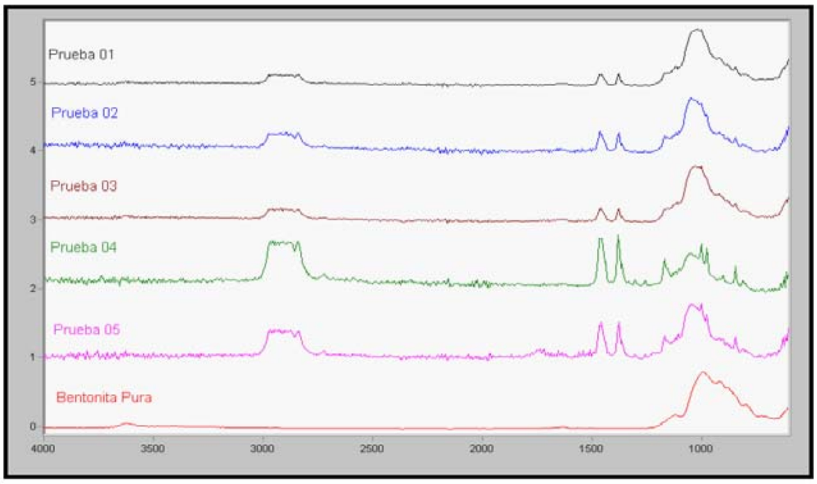

Figura 6. FTIR spectra of reference (original bentonite) and SC-CO_2 treated samples

This fact may be related to the presence of different types of chemical groups that exhibit vibrations within the observed bands (table 3). This way, as a hypothesis, SC-CO2 treatment may cause an important change in the bentonite plates, which also imply notable changes in the derived material properties. Several explanations have been proposed for this fact and further research is on its way to analysed them in depth.

Table 3. Potential vibrations within observed FTIR bands in SC-CO_2 treated samples

Band	Group	Comments
1380 cm-1		
Medium	C-H	rocking, aldehydes
Medium /wide (2 bands or more)	CO_2	asym str., acid carboxylic salts
Strong	SO_2	asym str., sulfonates R(RO)SO2
Medium-Strong	C-H	sym def, -CH3
Medium-Strong (2 bands)	C-H	sym def, C(CH3) 2
1460 cm-1		
Strong / wide	-N-C=S	vibration
Media	CH_2-	scissoring, alcanes
Media	CH_3	asym (bending) def
2800-3000 cm-1		
weak, very wide	-OH	str, ac. carboxylyc enlazados con puentes de hidrógeno
Strong	CH	*asym & sym str*, CH_3
Stgrong	CH	*sym str*, -CH_2- alcanes
Weak (2 bands)	CH	*str*, aldehidos
Weak (lots of bandas)	NH	*str*, quaternnaire ammonium salts
Medium	CH	*str*, -OCH_3

str: stretching / *def*: deformation / *sym*: symetric / *asym*: antisymetric

CONCLUSIONS

SC-CO_2 treated bentonite samples with very different properties from those of the original non-treated material were achieved. This way, as a hypothesis, SC-CO_2 treatment may cause an important change in the bentonite plates, which also imply notable changes in the derived material properties. The most significant change is observed in the absorbed water (TGA) and FTIR measurements. Treated bentonite samples exhibited higher specific surface, lower interlaminar water, and higher viscosity were achieved in water suspensions of nanoclays. These treated nanoclays, according to characterisation results, may be interesting to produce nanocomposite materials.

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