Synthesis of superhydrophobic montmorillonite by edge covalent bonding with monofunctional alkoxysilane

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We report the synthesis of superhydrophobic clay minerals by grafting a monofunctional alkoxysilane -trimethylethoxysilane on different organomodified montmorillonites. The structure of the montmorillonites was changed as evidenced by TGA, FTIR, DLS and X-Ray fluorescence analyses that confirmed the successful functionalisation.

1. Introduction

Nanoparticles are now the most important part of the nanomaterials market. After more than 20 years, the diversity of scientific, technological advances and innovations in processing and product development, are incredible. Originally, used to reduce the cost of materials, these filler proved to be very good reinforcing agents. Filling minerals, metals, fibers, etc. added to polymer matrix and dispersed on nanometric level, have shown significant improvements, often with several orders of magnitude of properties such as thermal stability, strength, barrier properties to gases and liquids, fire resistance, adhesive, storage of biologically active substances and not least recyclability, etc.. [1-11].

Today, a lot of reinforcement materials and polymer matrices are known; these are able to respond to the most exigent pretensions. After the geometric shape of the dispersed phase, we can classify: particles (usually spherical shape), fibers (most often cylindrical or tubular), layers (in general prismoidal form with a ratio of length and height very large, over 10^2) [12 -17].

Since the reinforcement efficiency is strongly related to their aspect ratio, platelet like fillers have drawn special interest. Layered silicates, especially montmorillonite type, are frequently used in the synthesis of nanocomposites. The major problem is the dispersion of the hydrophilic clay mineral into hydrophobic matrices. Because silicates are hydrophilic, the layers are not very well dispersed into hydrophobic materials. Our purpose is to modify the silicates surface, to turn into hydrophobic, these issues may contribute to a high degree of silicate exfoliation, and so special properties beyond the traditional can be obtained.

To increase the compatibility between the silicate and the matrix, the surface of clay mineral has to be modified. There are two ways to modify the layered silicates, either by: a)ion exchange with organic cation or by b) covalent bond formation (grafting) on the edges.

"Broken" edges from the end of the silicate lead to the formation of hydroxyl groups, therefore, to eliminate their contribution these can be reacted (blocked) with alkyl chlorosilanes or alkoxysilanes [15-18]. Modification with monofunctional silanes is essential because the polyfunctional alkylsilanes (di, tri, chloro or alkoxy) can restict the dispersion of the clay mineral due the polycondesation reaction [18, 19].

The possibility of obtaining superhydrophobic silicate by functionalisation at the ends of organophilic silicate (edge covalent bonding) with monofunctional alkoxysilane ([trimethyl ethoxysilane (TMES)), will be studied.

As the reaction between the OH groups and alkoxy groups from alkoxysilanes eliminates one molecule of alcohol, the montmorillonite contains at the edges three methyl groups bonded on silicon atom.

Schematic representation of the modified silicates, intended to be obtained, is illustrated in Fig. 1.
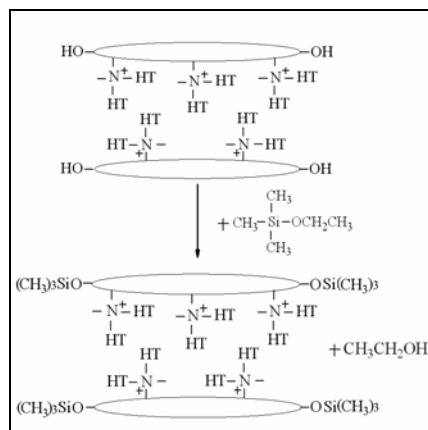

Fig. 1. Schematic diagram of the trimethylsilylation of organomodified montmorillonites.

2. Experimental

Materials

The clay minerals were provided by Southern Clay Products Inc. and are used in organomodified form with different ammonium salts (methyl, tallow, bis-2-hidroxyethyl)-(Cloisite® 30B; 90 meg/100g), (methyl, dihydrogenatedtallow)-(Cloisite® 93A; 90 meg/100g). The montmorillonites were vacuum dried at 60°C before use.

Trimethylethoxysilane (TMES) was used as supplied (Fluka). The solvent (dichlormethane) was purified by distillation before use.

Procedures

The modified montmorillonite was synthesized as follows: 4g clay mineral and 250 ml CH_2Cl_2 were introduced in the reaction flask and ultrasonicated for 10min. in an ice bath. The mixture was kept under nitrogen atmosphere and the temperature was raised to 40°C. 3.1 ml trimethylethoxysilane was added. The system was kept under stirring for three days (8 h/day), at 40°C. The grafted montmorillonite was washed with 300 ml CH_2Cl_2, ultra centrifuged and dried in the vacuum oven at 60°C before use.

Measurements

Particle hydrodynamic diameters were determined by Dynamic Light Scattering (DLS) with Zetasizer Nano ZS, ZEN3600. The samples were diluted with dichlormethane (0.02%).

The solid synthesized samples were analyzed by TGA, FTIR and X-Ray fluorescence.

Thermogravimetric analyses (TGA) were carried out on a TA Q5000 IR unit under nitrogen flowing (60ml/min) at a scan rate of 20°C/min. The solid sample was first equilibrated at 100°C then heated up to 900°C.

The Fourier transform infrared (FTIR) spectra were registered with a Brucker TENSOR 37 instrument from KBr pellets.

X-Ray fluorescence (XRF) analyses were performed on a PW4025-MiniPal-Panalytical type EDXRF Spectrometer. The determinations have been carried out in helium atmosphere, Kapton filter, for a period of 300 sec., at 20kV voltage and automatically adjusted current intensity; for the construction of the cap a 3.6 μm Mylar film was used.

3. Results and discussion

There are works on silylation of clay minerals using montmorillonites or laponite with different alkyl chlorosilanes or alkoxysilanes. In this paper, two organomodified montmorillonites are reacted with a monofunctional alkoxysilane. The montmorillonites modified with organic groups were examined by TGA, FTIR, DLS and X-Ray.

TGA curves and its derivatives for the pure samples and the synthesized one are presented in Fig. 2. For the pure samples we can observe a major peak around 350 °C with a shoulder at higher temperatures that was ascribed to the thermal degradation of organically modified montmorillonites, attributed to the release of olefin and amine. In the region of 600 °C, the montmorillonites loose the structural hydroxyl water. The mass loss between 710 and 800°C was attributed to the dehydroxylation [20].

TGA curves of the synthesized samples show modifications of the mass loss in the temperature range 250-650 °C that corresponds to the decomposition of organic moieties of the silane. Major modification can be observed at around 400 °C and 600 °C, these are due the loss of the trimethylsilyl groups [20-22].
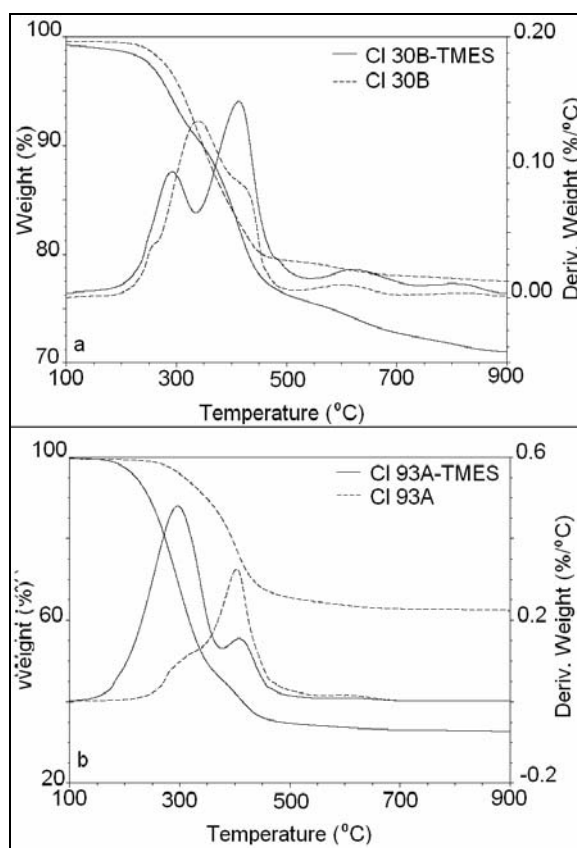

Fig. 2. Thermogravimetric analysis of weight loss as a function of temperature and its derivative for organomodified MMT and silane-modified MMT (a-Cl 30B; b-Cl 93A).

Table 1 summarizes the mass losses of the blank and synthesized samples in the range of 100-900 °C.

The difference between the mass loss in the range of 100-900°C of the blank (1) and synthesized sample (2) is equal with the amount of the TMES grafted if only edge modification is considered. Thus, the TGA results evidence the successful functionalisation of the organomodified montmorillonites. Though, it has to be

mentioned that self-condensation, partial face modification or ammonium salts losses during reaction, can occur [20].

Sample	Weight loss between 100-900°C (%)		(2)- (1) (%)
	- (1)	+TMES (2)	
Cl 30B	22.08	28.23	6.15
Cl 93A	37.22	66.97	29.75

FTIR analyses of the modified/unmodified Cl 93A revealed the specific peaks of the montmorillonites (Figure 2): 3635 cm−1 (OH vibration), around 2930 cm^{-1} (CH$_3$ stretching vibration from alkyl ammonium salts), 1045 cm^{-1} (Si–O stretching vibration) and 400–600 cm^{-1} (Si–O–Al bending vibration) (Fig. 3).
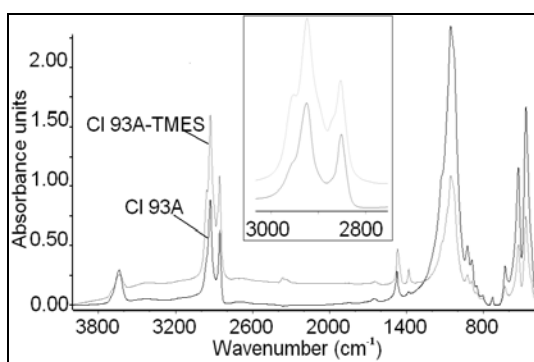

Fig. 3. FTIR spectra of Cl 93A and Cl 93A modified with TMES.

Because the peak of cuaternary ammonium salts overlaps with the peak of methyl at around 2955 cm^{-1} [21], we calculated the intensities ratios at 2957 cm^{-1} and 3633 cm^{-1} (MgOH); the samples were analyzed at the same concentration (0.3215%). It was observed that the ratio increases. This can only occur from the increase of trimethylsilyl groups resulted in the grafting process on the clay mineral (Table 2).

Table 2 FTIR Intensity ratio calculated for Cl93A-TMES sample.

Sample	ICH3 (λ=2957cm^{-1})	IMgOH (λ=3632cm^{-1})	ICH3/IMgOH
Cl 93A	0.9732	0.2984	3.26
Cl 93A-TMES	0.9446	0.2571	3.67

DLS measurements of the dispersed samples in dichlormethane are presented in Fig. 4. Before TMES grafting, montmorillonites lamellas are rich in Si-OH marginal groups. These groups exhibit a polar behavior towards the nonpolar medium (dichlormethane) that implies a preferential aggregation process of the dispersed particles.
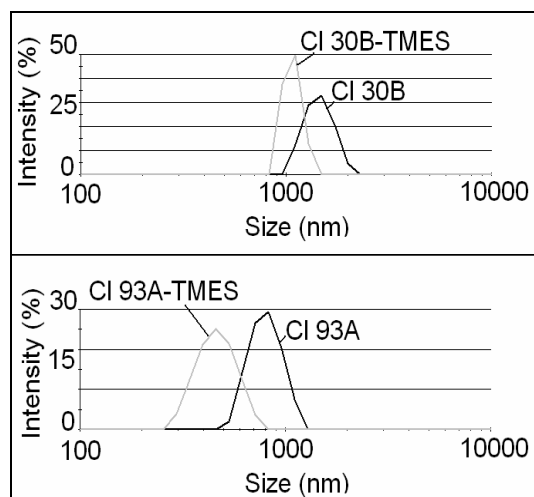

Fig. 4. Size distribution by DLS of the dispersed samples in dichlormethane.

After the reaction with TMES, the end groups modifies in -O-Si(CH$_3$)$_3$ which implies a more hydrophobic behavior therefore a lower aggregation tendency of the particles (as shown by the mean peak diameter - Table 3).

Table 3. DLS values of the dispersed sample in dichlormethane.

Sample	Mean peak diameter (nm)	
	-	TMES
Cl30B	1449	1073
Cl93A	806	468.4

In this context, we can state that the dispersability degree is increased by the elementary particles modification with methyl groups. These interactions correlated with the polarity differences could be an indirect evidence of TMES grafting.

X-Ray analyses proved also the modification of the montmorillonites. After the modification of the montmorillonites with TMES, the intensity of Si band decreased, in all of the cases (Fig. 5).
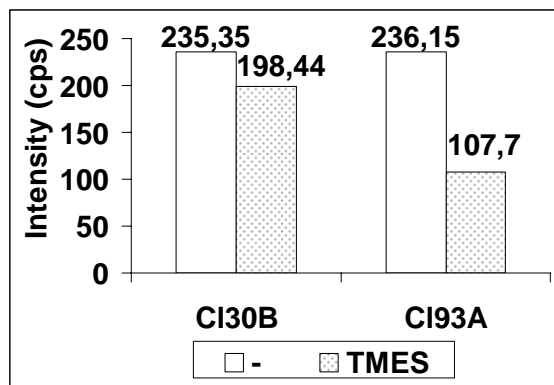
Fig. 5. Intensity of Si band obtained for pure and synthesized samples.

The presence of organic methyl groups at the montmorilonite surface, decrease the peak intensity. It is noticeable that the most remarkable decrease was recorded for Cl 93A-TMES sample, where the amount of grafted TMES was greater than for Cl 30B.

4. Conclusions

Two organomodified montmorillonites were reacted with a monofunctional alkoxysilane. The samples analyses indicated the successful functionalization of the organomodified montmorillonites. TGA analyses showed modification in the range of 250-600°C due the decomposition of trimethylgroups of the silylation agent. FTIR analyses revealed that the intensities ratio at 2957 cm^{-1} (CH$_3$) and 3633 cm^{-1} (MgOH) is greater for the synthesized sample. X-Ray showed that organic methyl groups grafted on the montmorilonite surface decrease the silicon peak intensity.

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