STUDIA UBB CHEMIA, LVI, 3, 2011 (p. 15 - 26)

PREPARATION, CHARACTERIZATION AND SOLID STATE NMR INVESTIGATION OF A DYE-CONTAINING SMECTITE CLAY

SILVIA BORSACCHI[a,b *], MARCO GEPPI[a,b], LUCIA RICCI[a], ANGELA CARDELLI[a], GIACOMO RUGGERI[a]

ABSTRACT. This paper presents the preparation and characterization of the smectite clay Laponite modified by intercalation of dimethyldioctadecylammonium chloride and the cationic dye methylene blue. The modified clay (Laponite Blue) has been characterized by FT-IR, X-Ray diffraction, thermogravimetric analysis, SEM and solid state NMR. The exploitation of several characterization techniques and of an extended multinuclear and multi-technique solid state NMR approach allowed us to obtain detailed information on the intercalation of the dye in the clay and the structural and dynamic properties of the organic-inorganic interface between the clay surface and the organic modifiers. Laponite Blue appears interesting for the future preparation of polymer nanocomposites with good mechanical and barrier performances as well as exploitable optical properties.

Keywords: *Laponite, methylene blue, cation exchange, MAS NMR, CP dynamics*

INTRODUCTION

Methylene blue (MB) is an interesting widely used cationic dye. Its optical properties change depending on polarity, composition or pH of the surroundings [1]. It has been successfully used in combination with clays; for example Sumitani et al. have studied an organic/inorganic hybrid compound consisting of methylene blue, a cationic surfactant and a reductant intercalated into saponite. Authors have found that methylene blue is a good oxygen indicator which changes colour in oxidative environment [2]; this system represents an ideal oxygen optical sensor for food packaging [3]. Furthermore, an analytical use of methylene blue deals with its absorption by clay minerals for determining both their cation exchange capacities and surface areas.

Here we present the preparation, characterization and solid state NMR investigation of Laponite, a synthetic layered silicate similar in structure and composition to the natural smectite hectorite (empirical formula $Na^{+}_{0.7}[Si_8Mg_{5.5}Li_{0.3}]O_{20}(OH)_4]^{0.7-}$ [4, 5]), modified by exchange reaction with dimethyldioctadecylammonium chloride ("$2C_{18}$"), and methylene blue ("MB") ("Laponite Blue"). Laponite platelets (diameter of 25 nm and height of 0.92 nm)

[a] *Dipartimento di Chimica e Chimica Industriale, Università di Pisa, v. Risorgimento 35, 56126 Pisa, Italy, silvi@ns.dcci.unipi.it*

[b] *I.N.S.T.M. Consorzio Interuniversitario Nazionale per la Scienza e Tecnologia dei Materiali, Firenze (Italy)*

are constituted by a sheet of magnesium ions in octahedral coordination with oxygen anions and hydroxyl groups and two outer tetrahedral silica sheets. The isomorphic substitution of some magnesium cations with lithium cations and the presence of some vacant positions, give rise to a partial negative charge, which is balanced by sodium cations absorbed on the platelets surface ("Laponite RD"), where a quite large amount of water is also physisorbed [6]. Sodium cations can be exchanged with organic cations, such as alkylammonium surfactants, so obtaining "organoclays" which are extensively used with apolar polymeric matrices (typically polyolefinic) for the preparation of nanocomposites exhibiting very good mechanical and barrier properties [7, 8, 9]. In this field, the intercalation of a dye in an organoclay can be helpful for obtaining a deeper interpretation of the complex mechanism of intercalation/exfoliation of the clay in a polymeric nanocomposite, and nanocomposites with interesting optical properties can also be prepared.

Laponite Blue has been here prepared and characterized by means of FT-IR, TGA, X-Ray powder diffraction, SEM and multinuclear solid state NMR. Spectroscopic techniques have been widely used to study the behaviour of the organic molecules adsorbed on clay surfaces [11, 12, 13, 14, 15, 16, 17]. In particular solid state NMR, thanks to the wide choice of observable nuclei and exploitable nuclear properties, is a very powerful technique for the characterization of organic-inorganic complex materials [18, 19] and it has been extensively applied to the study of modified clays [6, 17, 20, 21].

In this work the use of several characterization techniques and of different solid state NMR experiments, including ^{1}H, ^{13}C, ^{29}Si spectra and ^{1}H-^{29}Si Cross-Polarization dynamics experiments, and the comparison with unmodified Laponite (Laponite RD) and that exchanged with dimethyldioctadecylammonium chloride only ("Laponite-$2C_{18}$") allowed the obtainment of interesting and detailed information on the intercalation of the dye in Laponite Blue as well as on the structure and dynamic properties of the organic-inorganic interfaces.

RESULTS AND DISCUSSION

FT-IR analyses carried out on KBr pressed disk with the clay before and after the treatment confirm the occurred modification of Laponite with dimethyldioctadecylammonium chloride and methylene blue. Figure 1 shows the spectrum of Laponite Blue overlapped with that of Laponite RD. In the spectrum of Laponite Blue it can be observed the presence of typical absorption bands due to both $2C_{18}$ and MB at 2924 cm^{-1} and 2852 cm^{-1} (asymmetric and symmetric stretching of $-CH_2-$ in the alkyl chains of $2C_{18}$) and the weak band at 1603 cm^{-1} (see inset), attributed to aromatic ring vibration of MB.

The amount of $2C_{18}$ and MB in the clay could be quantified through thermogravimetric analysis. In the thermogram of Laponite Blue (Figure 2) a little weight loss is observable at about 75°C, attributed to water weakly bonded to the clay. A degradation step appears at about 345°C, which must be attributed to $2C_{18}$ and MB. By deconvolution procedure of the

derivative of TGA curve (inset in Figure 2), we have estimated the amount of $2C_{18}$ and MB in the clay (respectively 23.7 and 8.3 wt.%).

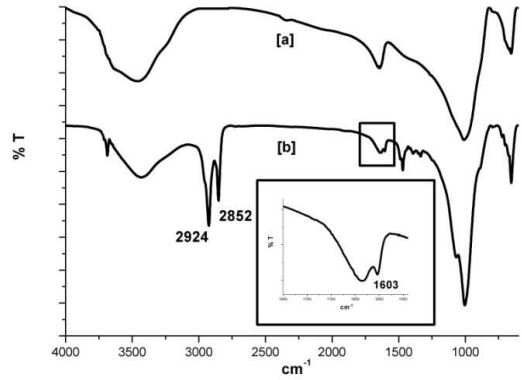

Figure 1. FTIR spectra of (a) Laponite RD and (b) Laponite Blue

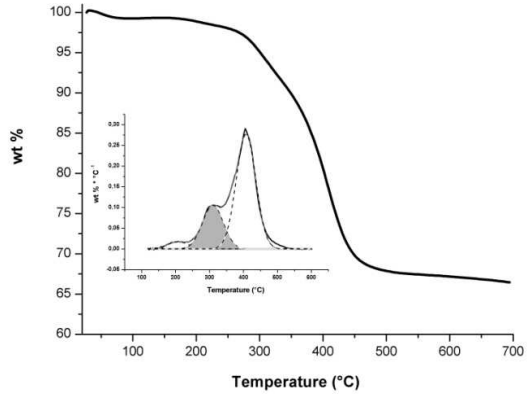

Figure 2. TGA thermogram of Laponite Blue with deconvolution of its derivative curve (inset)

Figure 3 shows the X-ray diffractograms of Laponite Blue, Laponite RD and Laponite-$2C_{18}$. It is evident an increase in the d-spacing (the spacing between two consecutive clay platelets) in passing from Laponite RD to both the modified clays. Furthermore, the d-spacing of Laponite Blue is larger than that of Laponite-$2C_{18}$, which can be attributed to the intercalation of both $2C_{18}$ and MB in the galleries between the clay platelets.

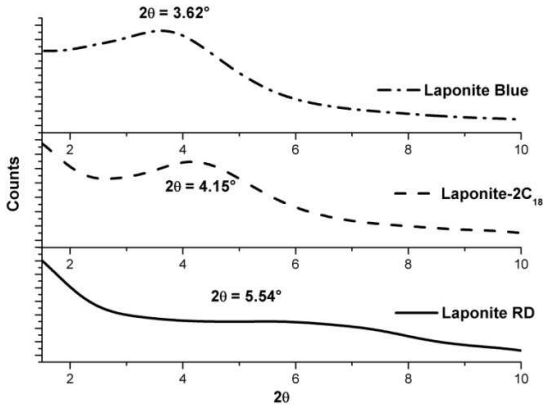

Figure 3. X-Ray diffractograms of Laponite RD, Laponite-2C_{18} and Laponite Blue

SEM micrograph highlighted a non-homogeneous distribution of the particles size in both Laponite RD and Laponite Blue (Figure 4). The surface of Laponite Blue appears rougher than that of Laponite RD, probably because of the treatment with 2C_{18} and MB.

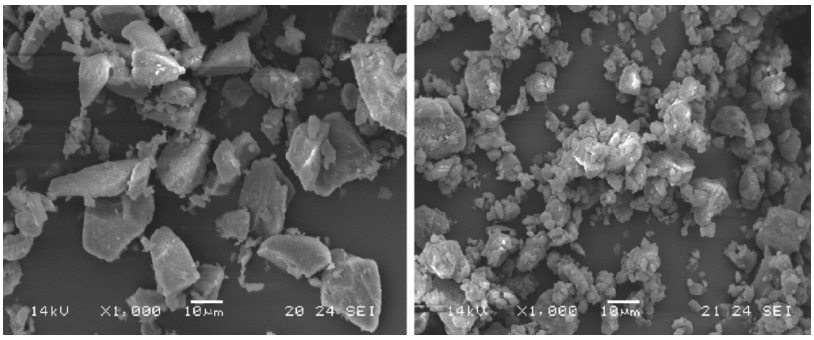

Figure 4. SEM micrograph of (left) Laponite RD and (right) Laponite Blue

Solid state NMR

In Figure 5 the ^{29}Si CP-MAS spectra of Laponite Blue, Laponite RD and Laponite-2C_{18} are shown. The most intense peak in all spectra, observed at -94.7 ppm, arises from Q^3 $\underline{Si}(OMg)(OSi)_3$ silicon nuclei of the tetrahedral sheets, while the small and broad signal centered at about -85 ppm must be attributed to not fully condensed Q^2 silicon nuclei, mostly present as $\underline{Si}(OMg)(OSi)_2(OH)$. In the two modified Laponite samples this signal clearly shows the presence of two components. In a previous work [6], we could assign the peak at -84.5 ppm to silanols present on the clay platelet edges,

while that at -86.5 ppm to those located onto the platelets surface. The scarce resolution of the Q^2 signal in the spectrum of Laponite RD can be attributed to the known presence of a large amount of physisorbed water, mostly removed in the organically modified samples, which gives rise to a noticeable heterogeneity of silanols environments, resulting in a distribution of isotropic chemical shift values. The ^{29}Si CP-MAS spectrum of Laponite Blue is substantially identical to that of Laponite-2C_{18}, indicating that, as expected, MB does not induce chemical modifications of the clay.

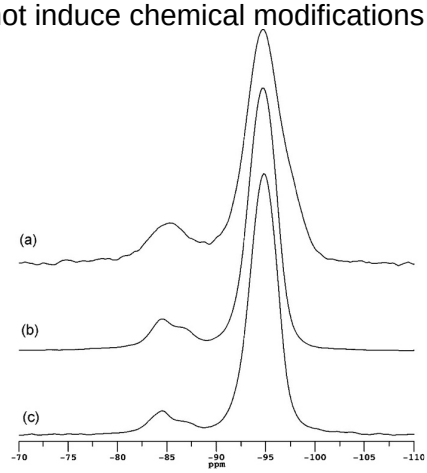

Figure 5. ^{29}Si CP-MAS spectra, recorded at a MAS frequency of 6 kHz, of (a) Laponite RD, (b) Laponite-2C_{18}, (c) Laponite Blue

Interesting information can be obtained from ^{1}H-MAS spectra, which are shown in Figure 6. As already reported [6], in passing from Laponite RD to Laponite-2C_{18} the signal at 4.4 ppm, due to physisorbed water and hydrogen-bonded silanol protons, substantially disappears, as result of water removal; the signal due to Mg(OH) protons is still observed at 0.4 ppm and peaks at 1.6 and 1.8 ppm appear, arising from 2C_{18} alkyl chains and silanols not involved in hydrogen-bonds, respectively. The spectrum of Laponite Blue shows the same signals observed for Laponite-2C_{18}, confirming that the treatment with both 2C_{18} and MB still determines the removal of most of the physisorbed water and of silanol hydrogen-bonds. Signals of MB protons could not be observed probably due to the scarce amount of the dye and an intrinsic broadness of its signals, not efficiently removed by MAS. It is worth to notice that the spectrum of Laponite Blue shows a noticeable narrowing with respect to that of Laponite-2C_{18}. Even if the analysis of ^{1}H-MAS spectra is in general far from being straightforward, due to the complex effects of incomplete averaging of homonuclear dipolar couplings, the observed narrowing can be an indication of a larger mobility of the organic components in Laponite Blue with respect to Laponite-2C_{18}.

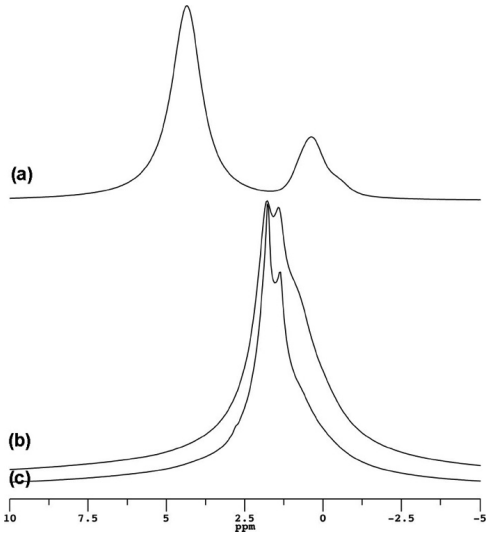

Figure 6. ^{1}H-MAS spectra, recorded at a MAS frequency of 6 kHz, of (a) Laponite RD, (b) Laponite-2C_{18}, (c) Laponite Blue

In order to obtain more detailed information on the organic-inorganic interface between Laponite and 2C_{18} and MB, ^{1}H-^{29}Si CP dynamics curves were experimentally built and analysed. This basic experiment, often used in the study of organic-inorganic multicomponent materials [17], consists in the registration of ^{29}Si CP-MAS spectra at different values of contact time (the time interval during which the ^{1}H magnetization is transferred to ^{29}Si nuclei); the peaks area is then plotted as a function of the contact time and the resulting trends fitted with suitable equations. For each peak, the values of the Cross-Polarization time, T_{SiH}, and of the ^{1}H spin-lattice relaxation time in the rotating frame, $T_{1\rho}$, both related to structural and dynamic properties of the interface, are obtained as best-fitting parameters. In Figure 7 the ^{29}Si CP-MAS spectra recorded at different values of contact time for Laponite Blue, Laponite-2C_{18} and Laponite-RD are shown.

The experimental trends of the three samples appear clearly different, suggesting differences in the properties of the interface between the clay and the intercalated protonated species (water in the case of Laponite RD).

Q3 and Q2 signal areas vs contact time were fitted to equation 1 [21], or using its bi-exponential modification, when necessary.

$$I(ct) = M_0\left(e^{-ct/T_{1\rho}(^{1}H)} - e^{-ct/T_{SiH}}\right) \qquad \text{(eq.1)}$$

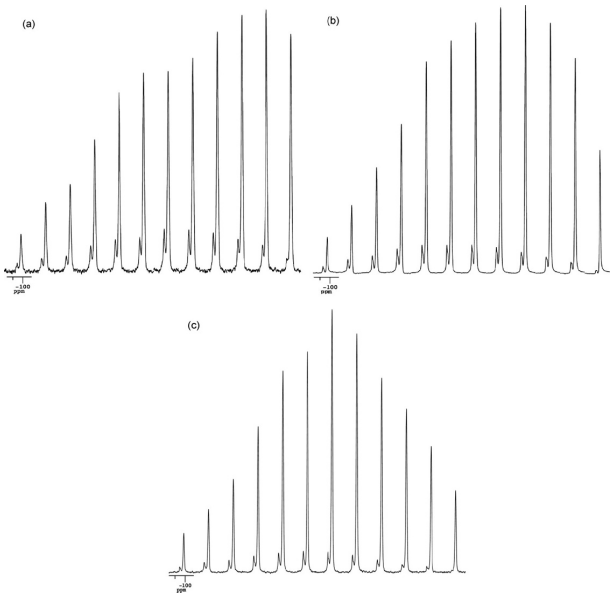

Figure 7. Selection of ^{29}Si CP-MAS spectra of (a) Laponite RD, (b) Laponite-2C_{18}, (c) Laponite Blue, recorded at a MAS frequency of 6 kHz and at the same contact time values, ranging between 0.1 and 20 ms

An example of fitted curve is reported in Figure 8, and the results of the analysis are summarized in Table 1.

T_{SiH} is a time constant related to the strength of the ^{1}H-^{29}Si dipolar couplings, being smaller for ^{29}Si nuclei more strongly coupled to protons. Stronger dipolar couplings arise either from a higher number of spatially close proton nuclei and a higher rigidity of the domain. In Laponite Blue the T_{SiH}'s of Q^2 silicon nuclei are smaller than that of Q^3, in agreement with the presence and the lack of directly bonded OH groups, respectively. While directly bonded OH groups will be the main source of magnetization for Q^2 silicons, fully condensed Q^3 silicons will receive magnetization mainly from protons of the intercalated organic species 2C_{18} and MB.

The interpretation of proton $T_{1\rho}$ values is more complex; in the solid state spin diffusion tends to average different intrinsic values of proton spin-lattice relaxation times in the rotating frame, related to differences in the molecular motions with characteristic frequencies of the order of kHz, to a single value. The measurement of a single $T_{1\rho}$ indicates that the sample is homogeneous approximately on a 10 Å spatial scale, while multiple partially averaged values are measured in samples heterogeneous on that scale. In Laponite Blue the detection of three different $T_{1\rho}$ indicates that the different

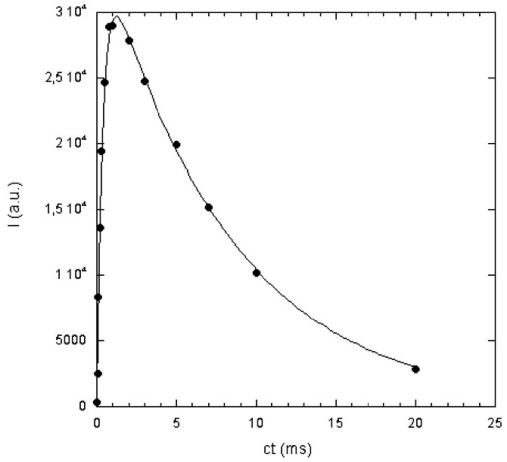

Figure 8. Fitting of the CP dynamics curve of the ^{29}Si signal at -86.5 ppm of Laponite-2C_{18}. On the *x* and *y* axes contact time values and signal areas are reported, respectively

protons (edge and surface silanol and organic ones) belong to domains with average dimensions larger than about 10 Å.

Table 1. T_{SiH} and proton $T_1\rho$ as obtained from the analysis of the CP dynamics curves of the different silicon nuclei in Laponite RD, Laponite-2C_{18} and Laponite Blue. In the cases in which multiple components were present their fractional weight is reported within parentheses.

	Q^2				**Q^3**	
	T_{SiH} (ms)		**$T_{1\rho}$ ms**		**T_{SiH} (ms)**	**$T_{1\rho}$ms**
Laponite RD	0.90 ± 0.01		1.0 ± 0.1 (w=0.75±0.03) 13.0 ± 2 (w=0.25±0.03)		0.46 ± 0.06 (w=0.31±0.02) 7.3 ± 0.9 (w=0.69±0.02)	3.0 ± 0.5 (w=0.22±0.03) 30 ± 2 (w=0.78±0.03)
	Q^2 (-84.5 ppm)		**Q^2 (-86.5 ppm)**			
	T_{SiH} (ms)	**$T_{1\rho}$ ms**	**T_{SiH} (ms)**	**$T_{1\rho}$ms**		
Laponite-2C_{18}	0.37 ± 0.02	8.0 ± 0.4	0.47 ± 0.03	12.6 ± 0.8	0.73 ± 0.06	23 ± 3
Laponite Blue	0.45 ± 0.03	5.2 ± 0.3	0.53± 0.08	6.4± 0.9	0.74± 0.04	10.0± 0.6

The comparison with the results obtained for Laponite-2C_{18} allows us to gain some insights into the effect of the presence of MB. The T_{SiH} of Q^3 silicons is not modified by the presence of the dye, suggesting that MB is not located in close proximity of the clay platelets surface, where 2C_{18} cations would remain dominant, attracted by the surface negative charges of the clay. Moreover the $T_{1\rho}$ values measured in Laponite Blue are clearly smaller than those of Laponite-2C_{18}. This could be due either to a very small intrinsic $T_{1\rho}$ of MB, which, by spin diffusion, would strongly decrease all the other measured values, or, more likely, to an increase of mobility in the kHz regime of the most abundant alkyl chains, as already suggested by ^{1}H-MAS spectra.

At last it is interesting to observe the results obtained for Laponite-RD, which appears much different from those of the organoclays. The fitting of the curves required the use of two $T_{1\rho}$ components for both silicon signals and of two T_{SiH} for Q^3 ones, indicating a strong heterogeneity of silicon environments, which is probably due to the presence of a large amount of water interacting in different ways with the clay platelets surface. The T_{SiH} of Q^2 is larger than that detected in the organoclays, indicating that the physisorbed water makes the silanols environment on average quite mobile. The two values obtained for Q^3, the polarization of which mainly arises from water, again reflects the presence of water differently interacting with the clay and therefore showing different degrees of mobility. Moreover, the multiple values of $T_{1\rho}$ again indicate a noticeable distribution of different proton environments, as well as heterogeneity on a 10 Å scale.

Useful information on Laponite Blue could also be obtained from ^{13}C spectra. While the MB signals could not be easily observed, those of 2C_{18} were evident and the comparison with the spectrum of Laponite-2C_{18} was particularly useful. In Figure 9 the 20-45 ppm region of the ^{13}C CP-MAS spectra of the two organoclays is shown. The signals observed arise from 2C_{18} alkyl chains and in particular those at 33 and 31 ppm are attributed to methylene groups in all-trans conformation and experiencing fast interconformational jumps between trans and gauche conformations, respectively. It is evident that in Laponite Blue the relative intensity of the peak at 31 ppm is significantly larger, suggesting that a higher fraction of surfactant alkyl chains experiences a noticeable mobility, in agreement with what already highlighted by proton MAS spectra and $T_{1\rho}$ results.

CONCLUSIONS

A smectite clay, Laponite, doubly organically modified by intercalation of an alkylammonium surfactant and a dye, methylene blue, has been successfully prepared. The intercalation of the dye could be verified with several characterization techniques and quite detailed information could be obtained through different solid state NMR experiments, also by exploiting the comparison with the same clay without dye. The organic modification of the clay causes the removal of most of the physisorbed water, present in a large amount in the untreated Laponite, with consequent strong modification of the environment of the nuclei present on the clay platelets surface. The d-

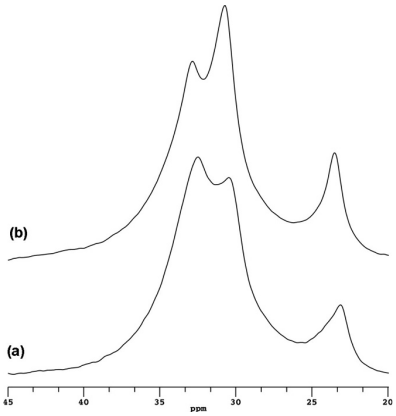

Figure 9. 20-45 ppm region of the ^{13}C CP-MAS spectra of (a) Laponite-$2C_{18}$ and (b) Laponite Blue, recorded at a MAS frequency of 6 kHz

spacing of the clay increases after the intercalation of the surfactant and a further increase is observed when the dye is added. Methylene blue seems to be dispersed among the surfactant chains, rather than directly adsorbed on the clay surface. The observed d-spacing increase is also associated with an increase of mobility of the $2C_{18}$ alkyl chains clearly detected in several NMR experiments, which can also indicate a partial disorder in the clay platelets arrangement induced by the intercalation of both the organic modifiers. The dye-containing Laponite here obtained could be used for the preparation of polymer nanocomposites potentially exhibiting not only the good mechanical and barrier properties provided by the clay but also the interesting optical properties of methylene blue.

EXPERIMENTAL SECTION

Materials

Laponite RD (supplied by Rockwood Additives, UK), is a synthetic clay of the smectite group. Laponite has been modified with dimethyldioctadecylammonium chloride (Fluka) and methylene blue (Fluka), whose chemical structures are shown in Figure 10. Figure 11 shows an image of the powder before (Laponite RD) and after (Laponite Blue) the modification. Laponite-2C18 was available from a previous work [6].

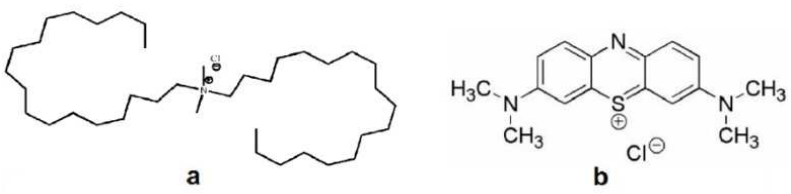

Figure 10. Structures of (a) dimethyldioctadecylammonium chloride and (b) methylene blue

Synthesis of Laponite Blue

In a three-neck flask equipped with magnetic stirrer, thermometer, dropping funnel and dropping cooling 2 l of H_2O was added. When temperature was at 60℃, 10.12 g of Laponite RD was constantly added under vigorous stirring.

The suspension was stirred for 2 hours. Afterwards, 500 cc of aqueous solution containing dimethyldioctadecylammonium chloride (4.59 g) and methylene blue (79.80 mg) was added.

The mixture was still stirred for 24 hours and then filtered under vacuum and washed with three portions of water (to remove all excess of both ammonium salts). The organoclay was freeze-dried, ground with ball mill and characterized (yield 79.7%).

Figure 11. Image of (left) Laponite RD and (right) Laponite Blue

Samples characterization

FT-IR spectra were recorded in a Perkin Elmer Spectrum One spectrometer on KBr pressed disk.

Thermogravimetric analysis (TGA) was carried out with a Mettler Toledo TGA/SDTA 851 calorimeter from 25 to 700 ℃ a t a scanning rate of 10 ℃/min in nitrogen atmosphere.

X-ray diffractograms were achieved on a Diffractometer D 500/501 Siemens mod Kristalloflex 810 with CuKα radiation (λ = 0.15406 nm).

Scanning Electron Microscopy (SEM) were recorded with a microscope Jeol JSM mod. T-300.

Laponite Blue was ground with Retsch ball mill.

Solid state NMR spectra were recorded on a a double-channel Varian InfinityPlus 400 spectrometer, equipped with a 7.5 mm cross-polarization (CP) - Magic Angle Spinning (MAS) probehead, working at 399.88 MHz for ^{1}H, 79.44 MHz for ^{29}Si, and 100.56 MHz for ^{13}C. ^{1}H, ^{13}C, and ^{29}Si 90° pulse lengths were always between 4.0 and 5.0 μs. ^{13}C and ^{29}Si spectra were recorded under high-power proton decoupling conditions. ^{29}Si CP-MAS spectra were recorded with a MAS frequency of 6 kHz, a recycle delay of 2 s, contact times variable in the range 0.1-20 ms and accumulating 4000 transients. ^{13}C CP-MAS spectra were recorded with a MAS frequency of 6 kHz, a recycle delay of 2 s, a contact time of 5 ms and accumulating 2000 and 33000

transients for Laponite-2C_{18} and Laponite Blue, respectively. ^{1}H-MAS spectra were acquired at a MAS frequency of 6 kHz, with a recycle delay of 2 s and accumulating 64 transients. TMS was used as a primary chemical shift reference for all nuclei, while hexamethylbenzene, 3-(trimethylsilyl)-1-propane-sulfonic acid sodium salt, and adamantane as secondary references for ^{13}C, ^{29}Si and ^{1}H, respectively. All of the experiments were performed at a temperature of 20 °C, controlled to within ± 0.1 °C.

ACKNOWLEDGMENTS

Fondazione Cassa di Risparmio di Pisa (POLOPTEL project) is acknowledged for partial financial support.

REFERENCES

1. J. Cenens, R. A. Schoonheydt, *Clays and Clay Minerals,* **1988**, *36*, 214.
2. M. Sumitani, S. Takagi, Y. Tanamura, H. Inoue, *Analytical Sciences,* **2004**, *20*, 1153.
3. A. Mills, *Chemical Society Reviews* **2005**, *34*, 1003.
4. N. J. Willenbacher, *Journal of Colloid and Interface Science,* **1996**, *182*, 501.
5. www.laponite.com (Rockwood Specialties).
6. S. Borsacchi, M. Geppi, L. Ricci, G. Ruggeri, C.A. Veracini, *Langmuir,* **2007**, *23*, 3953.
7. M. Alexandre, P. Dubois, *Materials Science and Engineering: R: Reports,* **2000**, *28*, 1.
8. S. Sinha Ray, M. Okamoto, *Progress in Polymer Science,* **2003**, *28*, 1539.
9. S.J. Ahmadi, Y.D. Huang, W. Li, *Journal of Materials Science,* **2004**, *39*, 1919.
10. P. T. Hang, G. W. Brindley, *Clays and Clay Minerals*, **1970**, *18*, 203.
11. A. Guerses, C. Dogar, M. Yalcin, M. Acikyildiz, R. Bayrak, S. Karaca, *Journal of Hazardous Materials,* **2006**, *131*, 217.
12. A. Al-Futaisi, A. Jamrah, R. Al-Hanai, *Desalination,* **2007**, *214*, 327.
13. C. A. P. Almeida, N. A. Debacher, A. J. Downs, L. Cottet, C. A. D. Mello, *Journal of Colloid and Interface Science,* **2009**, *332*, 46.
14. Q. Chen, W. T. Kerk, A. M. Soutar, X. T. Zeng, *Applied Clay Science,* **2009**, *44*, 156.
15. D. Ghosh, K. G. Bhattacharyya, *Applied Clay Science,* **2002**, *20*, 295.
16. M. Hajjaji, A. Alami, *Applied Clay Science,* **2009**, *44*, 127.
17. M. Geppi, S. Borsacchi, G. Mollica, C.A. Veracini, *Applied Spectroscopy Reviews,* **2009**, *44*, 1.
18. M. Geppi, S. Borsacchi, G. Mollica "Solid-state NMR of organic/inorganic multi-component materials" in Encyclopedia of Magnetic Resonance, Eds-in-chief R.K. Harris and R.E. Wasylishen, John Wiley, Chichester, DOI:10.1002/9780470034590. emrstm1014, published online **2008**.
19. J. Grandjean, *Clay Materials,* **2006**, *41*, 567.
20. D. Kubies, R. Jérôme, J. Grandjean, *Langmuir,* **2002,** *18*, 6159.
21. E.O. Stejskal, J. Schaefer, M.D. Sefcik, R.A. McKay, *Macromolecules,* **1981**,*14*, 275.