

## NEW ETFE NANOCOMPOSITES BASED ON FLUORO-MODIFIED NANOCCLAYS

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**Keywords:** Fluorinated ammonium salts, fluorinated organo-modified montmorillonites, nanocomposites, ETFE

### Abstract

Three ETFE nanocomposites, containing 1.5% wt in inorganic part, were prepared using melt blending technology. Thermal stability was investigated by thermogravimetric analysis: the decomposition temperature increased of about 20°C. Chemical properties were evaluated by FTIR spectra and the degree of exfoliation was estimated by XRD patterns. Surface characterization through contact angle measurements showed peculiar effects.

### 1 Introduction

The field of polymer/clay nanocomposites is a new route developed in the last decade for preparing polymers with enhanced properties (increased modulus, thermal stability, better barrier properties, chemical resistance) [1]. The presence of fluorinated moieties inside polymeric matrices is known to improve significantly the chemical and thermal resistance of the pristine materials, being fluoro-polymers suitable for high performance industrial applications. One of the most used fluoro-polymer is ethylene-tetrafluoro-ethylene copolymer (ETFE) which shows the superior characteristics of both polyethylene (PE) and poly(tetrafluoro-ethylene) (PTFE) since it has the excellent processability of PE and the chemical resistance of PTFE. In this respect, the introduction of fluorinated surfactant with perfluoroalkyl chain, in the ETFE matrix, has attractive features: better thermal stability, water- and oil-repellency and low surface tension, caused by stiff perfluoro chains [2]. Furthermore, layered clay with cation exchange ability is interesting as a host material serving a 2-dimensional space to give a regular array of the cationic surfactant. In the present work we describe the modification of montmorillonite with partially fluorinated ammonium salts which are characterized by different fluorinated chain length ( $R_F = 4, 6$  and 8 carbon atoms) as depicted in Figure 1.

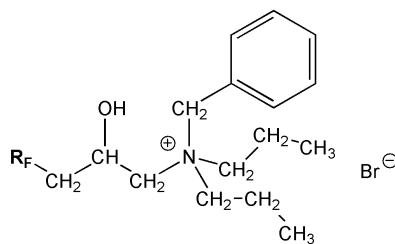


Figure.1. Chemical structure of the fluorinated surfactants

## 2 Materials and testing methods

*2.1- Materials.* Purified Na-montmorillonite (Dellite HPS) having a cation exchange capacity (CEC) of 128 meq/100 g, was purchased from Laviosa Chimica Mineraria S.p.A. Repro ETFE CONflon 7000 has been purchased by Convena. The salts  $[\text{R}_F\text{-CH}_2\text{-CH(OH)-CH}_2\text{N(CH}_2\text{CH}_2\text{CH}_3)_2(\text{CH}_2\text{Ph})]\text{Br}$  ( $\text{R}_F\text{N}^+$ ) ( $\text{R}_F = \text{C}_4\text{F}_9, \text{C}_6\text{F}_{13}, \text{C}_8\text{F}_{17}$ ) have been prepared according to procedures reported in the literature [3].

*2.2. Preparation of  $\text{R}_F\text{N}^+$ -MMT and of  $\text{R}_F\text{N}^+$ -MMT ETFE nanocomposites.*  $\text{R}_F\text{N}^+$ -MMT was prepared from Na-MMT (Dellite HPS) by ion exchange reaction using  $\text{R}_F\text{N}^+$  in water. 5.0 g (8.4 meq) of Dellite HPS were dispersed in 100 ml of hot deionized water (80 °C) under stirring for 24 h. 8.4 mmol of  $\text{R}_F\text{N}^+$  were dissolved in 100 ml of hot deionized water (80 °C) and slowly added to the Dellite HPS suspension under continuous and vigorous stirring. The reaction mixture was stirred at 80°C for 48 h. The resulting  $\text{R}_F\text{N}^+$ -MMT suspension was centrifuged at 10 000 rpm for 30 min and the solid separated. It was washed with water (4 x 50 ml) until free from halide (as tested using  $\text{AgNO}_3$  solution), centrifuged and obtained as a solid material which was dried under vacuum at 30 °C for 24 h and milled.

The ETFE nanocomposites, containing 1.5% wt in inorganic part, were prepared using melt blending technology (Plastograph Brabender).

*2.2. Physical and chemical characterization.* FTIR spectra were obtained on a Nicolet spectrophotometer Avatar 320 as KBr pellets and using an ATR equipment. For each sample 32 scans were recorder in the spectral range 4000-650  $\text{cm}^{-1}$  in the transmittance mode with a resolution of 4  $\text{cm}^{-1}$ . Thermogravimetric analyses (TGA) were performed on a TGAQ 5000 thermogravimeter analyzer, TA Instrument, under air atmosphere with heating rate of 20°C  $\text{min}^{-1}$  from 25 to 900°C and at constant temperature of 250°C for 15 min.

Powder X-ray diffraction (XRD) analyses of the samples were carried out with a Philips powder diffractometer X'Pert MPD using PW3123/00 curved Cu-filtered  $\text{Cu-K}\alpha$  radiation at a generator voltage of 40kV and a generator current of 30 mA. The diffractograms were scanned in the  $2\theta$  range from 1.5° to 30° at 0.01°/s rate in continuous scan. The powder was charged in a standard Philips aluminium sample-holder. The powder's area was 2 cm x 1.5 cm; height 2 mm.

## 3 Results and Discussion

*3.1. Preparation and characterisation of  $\text{R}_F\text{N}^+$ -MMT.* The organomodified-MMT was prepared by exchange of the interlayer  $\text{Na}^+$  cations with the ammonium cations  $[\text{R}_F\text{-CH}_2\text{-CH(OH)-CH}_2\text{N(CH}_2\text{CH}_2\text{CH}_3)_2(\text{CH}_2\text{Ph})]$  ( $\text{R}_F\text{N}^+$ ) ( $\text{R}_F = \text{C}_4\text{F}_9, \text{C}_6\text{F}_{13}, \text{C}_8\text{F}_{17}$ ) accordingly to the synthetic procedure previously described in order to obtain the intercalation of organic cations into the MMT layers. The FT IR spectra of the purified Dellite-HPS shows bands at 3625 and 3447  $\text{cm}^{-1}$  due to -OH stretching modes of Al-OH and Si-OH of MMT structure. The band at 1035  $\text{cm}^{-1}$  is attributed to Si-O stretching (in-plane) vibration for layered silicates. The peaks at 915, 870 and 839  $\text{cm}^{-1}$  are attributed to AlAlOH, AlFeOH and AlMgOH bending vibration. In the FT IR spectrum of  $\text{R}_F\text{N}^+$ -MMT peaks at 3057 and 2983  $\text{cm}^{-1}$  due to the vibrations of the CH moieties in the aromatic and aliphatic groups of the organic system and absorptions in the range 1210-1240  $\text{cm}^{-1}$  due to the vibrations of the CF groups are present, too.

The XRD patterns of  $\text{R}_F\text{N}^+$ -MMT after drying at 30°C show a  $d_{\text{spacing}}$  value which depends on the  $\text{R}_F$  chain length; in particular in the case of  $\text{R}_F = \text{C}_8\text{F}_{17}$  the first order peak at 3.41°

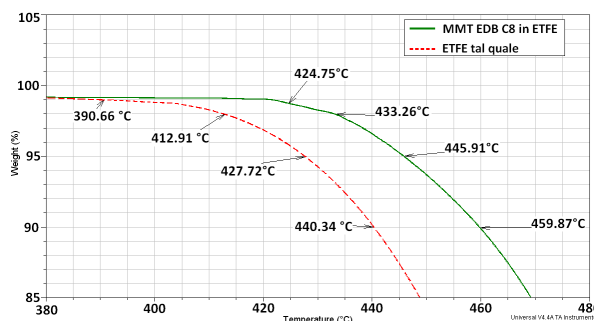
corresponding to a basal  $d_{\text{spacing}}$  of 2.55 nm must be compared with value of 0.91 nm of the pristine MMT.

It is noteworthy that very few examples are reported in the literature concerning the intercalation of cationic fluorinated surfactants into interlayer space of montmorillonite [4] and in most cases they are synthetic clay minerals where the fluorine has been introduced by means of chemical treatments which involve distinct structural changes [5]. On the contrary, the method here described appears to be of general application allowing the introduction of a wide variety of fluorinated ammonium cations by varying the fluorinated length chain and the N-bonded aliphatic or aromatic moieties, thus tuning the physical and chemical properties of the modified clay.

**3.3. Preparation and characterization of  $R_F N^+$ -MMT ETFE nanocomposites.** Reasonably due to the compatibility between the ETFE polymer and the  $R_F N^+$ -MMT organo-modified clay, a good dispersion of the clay into the polymer is obtained under the experimental conditions used, as shown by the morphological characterization obtained by ESEM. The FTIR spectra of the  $R_F N^+$ -MMT ETFE nanocomposites are characterized by the presence of the absorption of the ETFE polymer (1452, 1248, 1163 and 1038  $\text{cm}^{-1}$ ) together with the signals of the organo-modified MMT.

X-ray diffraction data for the  $R_F N^+$ -MMT ETFE nanocomposites show a moderate intercalation as indicated by the small increase of the interlayer (2.90 nm in the case of  $R_F = \text{C}_8\text{F}_{17}$ ).

A portion of the TGA curve of the  $R_F N^+$ -MMT ETFE nanocomposite ( $R_F = \text{C}_8\text{F}_{17}$ ) is reported in Figure 2. It shows that the onset of decomposition, which is assumed to be the temperature at which 2wt% weight loss has taken place, occurs at about 430°C, at a temperature about 20°C higher with respect to the starting ETFE.



**Figure 2.** A portion of the TGA curves of ETFE and  $R_F N^+$ -MMT ETFE nanocomposite ( $R_F = \text{C}_8\text{F}_{17}$ )

Surface characterization through contact angle measurements showed peculiar effects: a constant increasing of the surface tension dispersive component with respect to neat ETFE (from 6 to 12 mN/m) and an unexpected decreasing of the polar component shortening the fluorinated chain with a very low value (3.72 mN/m) in the case of  $R_F = \text{C}_4\text{F}_9$ . In this respect fluorinated nanoclays could be exploited for the formulation of oleophobic-hydrophilic new nanocomposite polymeric materials. Further characterizations are in progress.

## References

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