Nanoclay surface modification with novel phosphorous compounds for enhanced fire retardant properties of PVC nanocomposites

Gemma Ibarz Ric[1], Carlos Sáenz Ezquerro[1], Cristina Crespo Miñana[1], Javier Sacristán Bermejo[2], Mari Carmen Maestre Casas[2], Constantino Raspi[3]

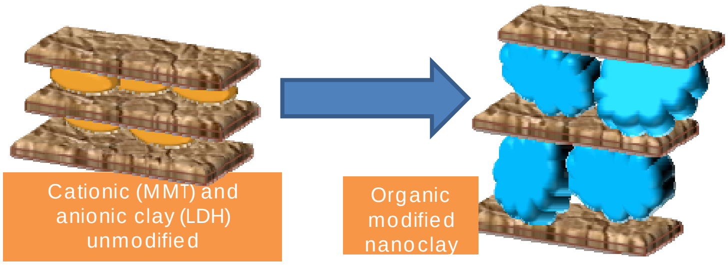
[1]*Aragon Institute of Technology, María de Luna 7-8, Zaragoza, Spain*
[2]*Acciona Infraestructuras R&D Department, C/ Valportillo Segunda, Nº8, Polígono Industrial Alcobendas, 28108 Alcobendas (Madrid), Spain*
[3]*C.G.S. di Coluccia Michele & C. sas, Borgo Stretto 10, 56127 Pisa, Italy*
gibarz@ita.es

Abstract
Due to the recent changes in REACH (Registration, Evaluation, Authorization and Restriction of Chemicals) European regulations, the use of halogen based compounds as flame retardant additives is no longer allowed. For this reason, the main aim of the NANOCORE project is to develop a technology to obtain a polymer foam core material by using modified nanoparticles in conjunction with synergistic non-toxic flame retardants, to develop a new FR system, for its use in PVC-based polymer foams for sandwich core materials.
One of the goals of the project that has been first addressed is the development of a process of modifying cost-efficient commercially available nanoparticles with non-halogenated fire retardant compounds. In this work we present the surface modification of nanoparticles (commercially available montmorillonites and layered double hydroxides) with different phosphorous-based compounds (Scheme 1).
The techniques that were used to characterize the modification of the particles were: Fourier Transformed Infrared Spectroscopy (FTIR), thermogravimetric analysis (TGA) and wide angle X-Ray diffraction spectroscopy (WAXRD), where it was observed that the intercalation of organic compounds within the interlayer region of cationic and anionic nanoclays produced the expansion of the interlayer distance (Figure 1). Moreover, reproducibility and preliminary upscaling of the fabrication, which is essential for the later industrial fabrication, has been also effectively achieved.
After surface modification, the nanoparticles were physically blended with polymer by melt mixing at 170ºC. The resulting nanocomposites were examined by means of SEM, Limited Oxygen Index (LOI), TGA and cone calorimeter tests at lab scale. The results show that the fire risk, measured in terms of fire performance index (FPI) of all PVC nanocomposites consisting of 5% nanoclay content, is about 70% lower with respect to pristine PVC. In other words, the incorporation of nanoparticles into the polymer increases about 70% of the fire performance of the base material (Figure 2).
In conclusion, the data obtained show that the production of surface modified nanoparticles has been accomplished, and the resulting PVC nanocomposites exhibit enhanced fire properties when compared to the pristine polymer.

References

[1] Costa, F.R., Leuteritz, A., Wagenknecht, U., Jehnichen, D., Häußler, L., Heinrich, G., **2008**. Intercalation of Mg–Al layered double hydroxide by anionic surfactants: Preparation and characterization. *Appl. Clay Sci*. 38, 153–164.
[2] Moyo, L., Nhlapo, N., Focke, W.W., **2008**. A critical assessment of the methods for intercalating anionic surfactants in layered double hydroxides*. J. Mater. Sci.* 43, 6144–6158.
[3] De Paiva, L.B., Morales, A.R., Valenzuela Díaz, F.R., **2008**. Organoclays: Properties, preparation and applications. *Appl. Clay Sci*. 42, 8–24.
[4] Mittal, V., **2012**, Modification of montmorillonites with thermally stable phosphonium cations and comparison with alkylammonium montmorillonites. *Appl. Clay Sci.* 56, 103–109.
[5] Patel, H., Somani, R., Bajaj, H., Jasra, R., **2007**. Preparation and characterization of phosphonium montmorillonite with enhanced thermal stability. *Appl. Clay Sci.* 35, 194–200.
[6] Kiliaris, P., Papaspyrides, C.D., **2010**. Polymer/layered silicate (clay) nanocomposites: An overview of flame retardancy. *Prog. Polym. Sci.* 35, 902–958.
[7] Gong, F., **2004**. Thermal properties of poly (vinyl chloride)/ montmorillonite nanocomposites. *Polym. Degrad. Stab.* 84, 289–294.

Schemes and Figures



Scheme 1: Nanoclay surface organic modification

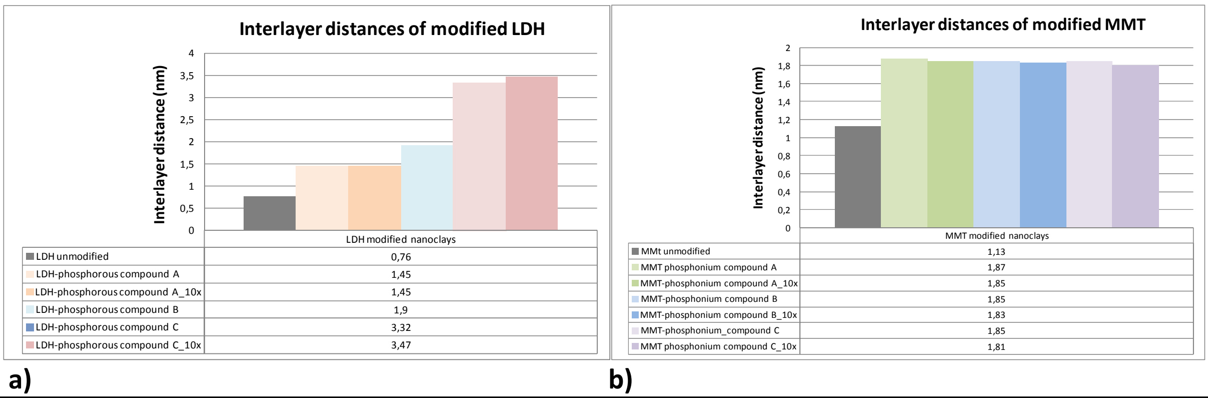


Figure 1: Interlayer distances d_{001} (nm) as measured by means of XRD of a) LDH after phosphorous compounds modification and b) MMT after phosphonium compounds modification. The values for upscaled samples (x10) are also included.

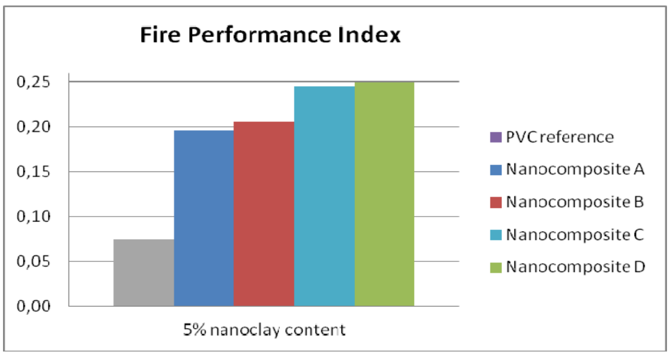


Figure 2: Fire performance index of different PVC nanocomposites with 5% of nanoclay content in comparison with the pristine PVC polymer.