

# PREPARATION AND CHARACTERIZATION OF KAOLINITE INTERCALATED NANOCOMPOSITES

**Jose PASCUAL-Cosp**<sup>1</sup>, Mónica Benítez-Guerrero<sup>1</sup>, Francisco Corpas<sup>2</sup>, Ramon Artiaga<sup>3</sup>, Antonio Ramírez del Valle<sup>1</sup>.

<sup>1</sup>Universidad de Málaga, Málaga, SPAIN

<sup>2</sup>Universidad de Jaén, Linares, SPAIN

<sup>3</sup>Universidad de A Coruña, Ferrol, SPAIN

Preparation of hybrid organic-inorganic materials by intercalation of organic molecules in kaolinite brings about the possibility of availability of new materials with special functionalities. Its intimately assembled structure may give them new unique properties, as a combination of the silicate and organic component ones. These modified nanoclays can be used in industrial applications such as chromatography columns, selective catalysts, catalyst supports, high performance sorbents, ion exchangers, membranes, optical and electrochemical mechanisms and enzyme and dye supports in polymer and composites. Some of these applications are not sufficiently exploited. Technical applicability of these materials is controlled by the reactivity in the intercalation, thermal stability and the quality of the final products.

Preparation, characterization and study of the thermal behavior of various kaolinite nanocomposite intercalates are covered in this work, making use of kaolinite-polypyrrole nanocomposites as example.

The kaolin used in this work comes from Poveda de la Sierra, in Guadalajara, Spain. Its kaolinite content is above 95 %, with small amount of micas and quartz.

The composite kaolinite-polypyrrole is obtained by polymerization of pyrrole in a kaolinite-pyrrole complex. Oxidant compounds as iron(III) chloride ( $\text{FeCl}_3$ ), ferric sulfate ( $\text{Fe}_2(\text{SO}_4)_3$ ) and ammonium persulfate ( $(\text{NH}_4)_2\text{S}_2\text{O}_8$ ) are usually employed to accelerate the reaction. In this work, the polymerization was carried out without additives, at room temperature and pressure, under natural light. Although this way lasts more than when using accelerants, it allows for obtaining higher rates of intercalates.

It can be observed in Fig. 1 that the spacing obtained at the 001 basal reflection was reduced to 11.40 Å in the polymer composite, while in the monomer complex it was 14.20 Å. It is due to the re-orientation of the pyrrole molecules produced by the polymerization at the inter-laminar spacings and

to an important decrease of the inter-laminar species (I. A. I.= 70%). The main peak keeps the original symmetric and intense shape presented by the kaolinite-pyrrole complex. Equally spaced distribution and ordered stacking were also retained, with six diffractions attributed to the intercalated compound. Basal reflections of the kaolinite can also be observed, originated by the de-intercalated fraction produced by the polymerization process. Another consequence of the polymerization is an increase of the adsorbed reactant, which produces an increase of the diagram background. A difference with respect to the kaolinite-pyrrole complex is that the new one, with excess of reactant, is stable for months, what was confirmed by the fact that no changes were observed in the DRX plot.

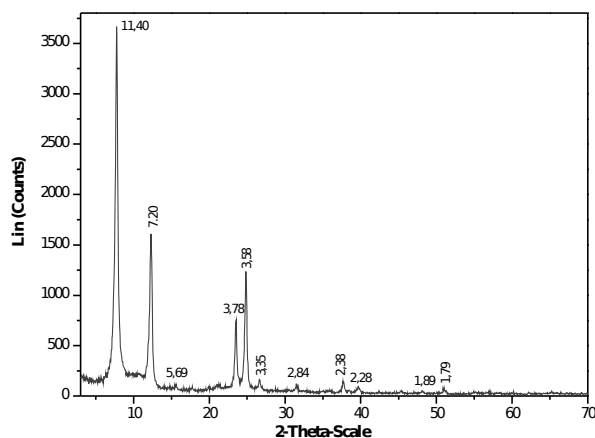


Fig. 1. DRX plot obtained from the kaolinite-polypyrrole composite.

The formation of a kaolinite-polypyrrole intercalated nanocomposite was also confirmed by FTIR analysis. The decrease of the intercalated material originated by the “in situ” polymerization produced an increase of intensity in the IR bands associated to OH vibrations in the inner surface of the laminae ( $\nu_1$ ,  $\nu_2$ ,  $\nu_3$ ), as can be observed in Fig. 2. The  $\nu_2$  band was not appreciable in the case of the monomer complex. The band at  $3618\text{ cm}^{-1}$ , which is

assigned to the inner hydroxyl group, did not experience any change.

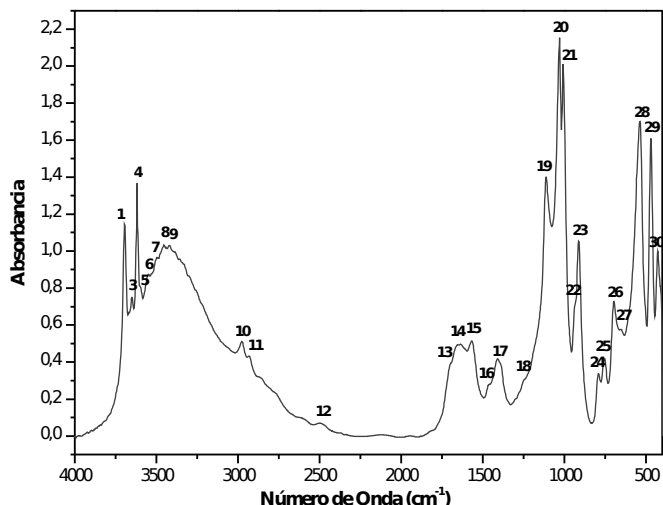


Fig. 2. FTIR spectrum obtained from the kaolinite-polypyrrole composite.

It can be also observed on the FTIR spectra that there is a band at  $3568\text{cm}^{-1}$  in the monomer complex. In the polymer complex that band is replaced by two new bands at  $3597$  and  $3549\text{cm}^{-1}$ , which can be assigned to the formation of two hydrogen bonds between the polypyrrole and the external hydroxyl groups. Other two new bands appear in the same region, centered at  $3498$  and  $3454\text{cm}^{-1}$ , which can be attributed to N-H vibrations. The appearance of these new bands and its different frequencies with respect to the ones in the monomer complex is due to the polymerization, corresponding the new frequencies to vibrations in the polymer chain. Finally, the  $3421\text{cm}^{-1}$  band corresponds to water hydroxyl groups vibrations. It appears at a higher frequency than in the kaolinite-polypyrrole complex because the polypyrrole-water interaction is weaker than the monomer-water one.

It can be observed in Fig. 3 that the morphology of the complex was dramatically distorted by the “in situ” polymerization. The laminae tend to form  $4\text{ }\mu\text{m}$  height compact stackings (tactoids). These tactoids are composed of nanocomposites dispersed in a polymer matrix. It can be observed in Fig. 4 that the size of the laminae packages is about  $40\text{-}60\text{ nm}$ . Due to structural tensions, the thickness of polymer layer joining the packages varies from  $20$  to  $80\text{ nm}$  depending on the location in the tactoid.

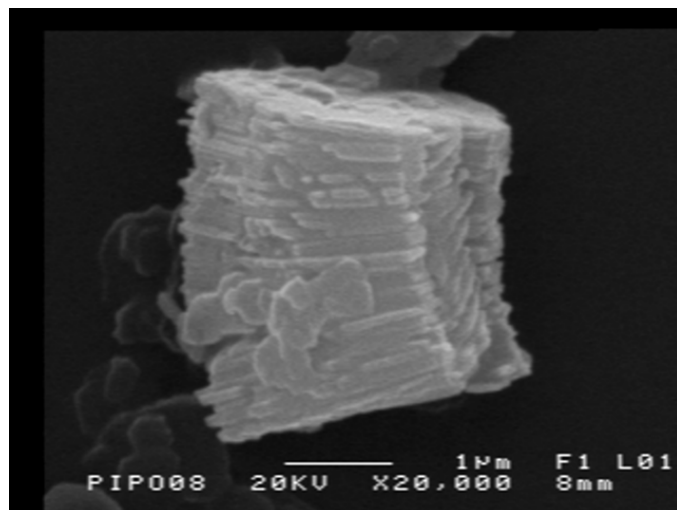


Fig.3. SEM picture.



Fig.4. TEM picture.

#### ACKNOWLEDGEMENTS

The second author wishes to thank the Spanish Consejo Superior de Investigaciones Científicas (CSIC) for the awarding of a JAE pre-doctoral grant. Likewise, the 4th author acknowledges the Spanish Ministerio de Educación y Ciencia for the provision of funds MTM2008-00166.

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