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Thermal and morphological characterisation of organically modified sepiolite

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Abstract

In this paper the study of the morphological and thermal characterisation of pristine and organically modified sepiolites is performed. Sepiolites modified by means of two functionalization processes were studied: adsorption, of quaternary ammonium salts or amines, or grafting of silane reagents. By means of XRD the characteristic diffraction peaks of sepiolite structure were observed in every sample confirming that no structural changes occurred in the mineral lattice upon functionalization. As sepiolite is a non swelling clay organophilization takes place mainly by surface modification, maintaining its crystalline structure. SEM and HRTEM confirmed that the typical acicular morphology of sepiolite was maintained after modification, although the organically modified needles show a more irregular surface pattern. The study of the thermal behaviour of the organically modified sepiolites was performed by thermogravimetric analysis which shows a complex multi-step degradation process due to the overlapping of sepiolite dehydration processes and organic modifier volatilization.

Keywords: Sepiolite; Organic functionalization; Organo silane; TGA; HRTEM

1. Introduction

In the last few years much interest has been devoted to the synthesis and characterization of polymer clay nanocomposites (PCN) [1–12]. Most critical issues in PCN synthesis are the hydrophilic nature of clays and the strong solid–solid interactions in-between the clay layers that prevent their dispersion in the polymer.

In this respect the needle-like morphology of sepiolite seems to lead to processing advantages due to the better wettability of this inorganic filler by non polar polymers [13]. Furthermore, the higher surface area of sepiolite ($384 \pm 7\ m^2/g$) and lower contact area between needles as compared to the surface area of layered phyllosilicates ($82 \pm 1\ m^2/g$) [14] and contact area between clay layers can favour sepiolite dispersion.

Sepiolite is a hydrated magnesium silicate with the half unit-cell formula: $Si_{12}O_{30}Mg_8(OH)_4 \cdot (H_2O)_4 \cdot 8H_2O$. The sepiolite structure is constituted by a magnesium octahedral sheet in-between 2 layers of silica tetrahedrons which extend as a continuous layer with an inversion of the apical ends every six units. This inversion produces a discontinuous octahedral sheet which allows for the formation of rectangular section, tunnel like pores (Fig. 1), parallel to the fibre axis [15–19].

These nanostructured tunnels measure approximately $3.5 \times 10.6\ Å^2$ in cross section, and they are completely filled by zeolitic water $[H_2O]_{zeol}$ under ambient conditions. The terminal Mg^{2+} cations that are located at the edges of the octahedral sheets complete their coordination with two molecules of structural water $[H_2O]_{coord}$, which are in turn hydrogen-bonded to zeolitic water molecules located within the nanopores of the magnesium silicate.

The acicular morphology of sepiolites and their very high surface area improve adhesion/compatibility with polymeric matrices and provide an excellent reinforcing

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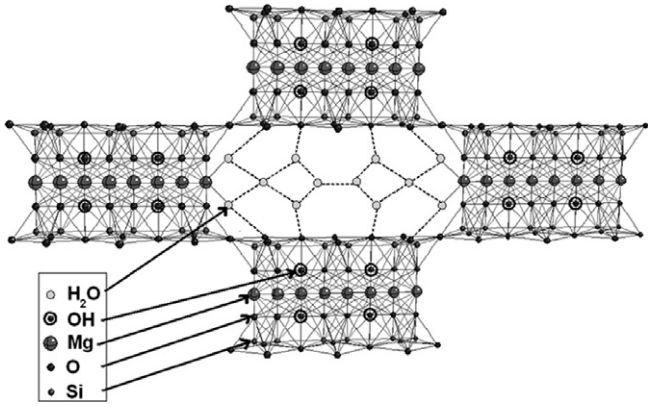


Fig. 1. Sepiolite structure: projection onto the (0 0 1) plane.

effect on polymers [20–26]. Furthermore, surface treatment of sepiolite with specifically designed organic surfactants [27–30] can enhance sepiolite compatibility with polymers.

These properties are mainly attributed to the large concentration of surface silanols, spaced every 5 Å along the length of sepiolite needle, that are easily available for coupling reactions with both polymers and organic surfactants. Moreover this very high density of silanol groups suggests that also other forces such as hydrogen bonding and Van der Waals interactions are largely involved in the adsorption phenomena at the interface.

Recent studies on thermal stability of polymer/sepiolite systems have shown a strong catalytic effect on thermal degradation of polyolefins attributed to the large presence of silanols on sepiolite surface [31].

Current studies in our laboratories have shown that the accurate functionalization of sepiolite surface via mercaptosilane grafting can avoid the catalytic effect on PP thermal degradation [32,33], keeping or slightly increasing the mechanical reinforcement typical of sepiolite [33].

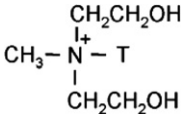
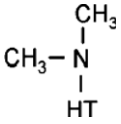
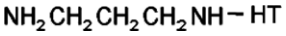
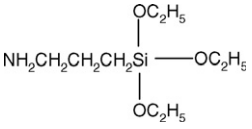
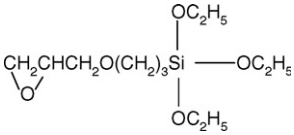
The aim of this paper is to study the thermal behaviour of sepiolites modified by two different functionalization processes: adsorption and grafting.

2. Materials and methods

Organophilic sepiolites (Table 1) were obtained from pristine sepiolite by means of specific physico-chemical purification, micronization and chemical modification processes developed and patented by Tolsa (Spain).

The micronization leads essentially to disagglomeration of the bundles of microfibres thus enhancing sepiolite surface area. Two different processes of functionalization are

Table 1
Surface treatment of sepiolites used

Code	Sample	Functionalization type	Organic modifier
S1	Pristine sepiolite		
S2	Sepiolite MT2EtOH	Adsorption	
S3	Sepiolite 2MHT	Adsorption	
S4	Sepiolite diamine	Adsorption	
S5	Sepiolite aminosilane	Grafting	
S6	Sepiolite epoxysilane	Grafting	
S7	Sepiolite mercaptosilane	Grafting