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Bionanocomposites Based on the Megamolecular Polysaccharide Sacran and Clay Minerals

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INTRODUCTION

Bionanocomposites are a novel group of organic-inorganic hybrid materials based on the assembly of natural polymers and inorganic solids, such as clays, through nanoscale interactions between both components (Darder et al., 2007). Similarly to conventional nanocomposites, bionanocomposites exhibit improved structural and functional properties, while offer biocompatible and biodegradable character associated with the biopolymer (Darder et al., 2007; Ruiz-Hitzky et al., 2008 and 2009). Therefore, these materials of bio-hybrid nature can receive the most diverse applications such as adsorbents, drug delivery systems in biomedicine and components in electrochemical devices, among others. Initially, the research in this area focused on the combination of lamellar or fibrous clays of various natures with the most abundant polymers in the biomass (cellulose, chitosan, starch), but it is now expanding with the search of alternative natural sources of polymer. Amongst them, sacran is an interesting biopolymer compound for developing novel clay-based bionanocomposites. This extracellular polysaccharide extracted from the cyanobacteria *Aphanothece sacrum* is an anionic megamolecule of extremely high molecular weight (about 1.6 × 10^7 $gmol^{-1}$), provided with both carboxylate (22 mol%) and sulfate groups (11 mol%). Its chains can self-orientate forming double helixes or even huge domains of liquid crystals at given concentrations (Okajima et al., 2009).

The aim of the present communication is to introduce novel bionanocomposites based on the assembly of sacran to sepiolite microfibrous clay and montmorillonite layered clay, investigating the main interactions between both components.

MATERIALS AND METHODS

Sacran (SCR) was extracted from frozen samples of the cyanobacteria *A. sacrum* by a previously reported method (Okajima et al., 2008). Sepiolite (SEP) from Vicálvaro (Spain), commercialized as Pangel S9, was provided by TOLSA SA; Cloisite®Na (Clois-Na) was purchased from Southern Clay Products.

For the preparation of sacran-sepiolite bionanocomposites, solutions with different sacran concentration were prepared in 50 mL of water by means of an ultrasound tip (VC750 Sonics Vibra Cell, operating at 20KHz) using a tip of 13 mm, with intermittent pulses of 10 s followed by a standby step of 10 s and a total applied energy of 10 kJ to obtain sacran solutions with concentration ranging between 0.2 and 12.6 gL^{-1}. Sepiolite suspensions were prepared in water applying magnetic stirring. Sepiolite dispersions (50 mL) were gradually added to each sacran dispersion, forming a single batch that is kept under constant stirring for 48 h at 30 ºC (± 2 ºC) in an incubator shaker at 100 rpm. The resulting final suspension was placed on a glass plate, dried at room temperature and atmospheric pressure, achieving transparent and self-standing bio-hybrid films.

For the preparation of sacran-montmorillonite bio-hybrid materials, sacran solutions were prepared as reported above. Suspensions of montmorillonite of different concentrations (0.2 - 3gL^{-1}) were prepared under ultrasonication, applying a total energy of 15kJ. The sacran solution was added to each montmorillonite suspension; the resulting samples were homogenized by ultrasonication (10 kJ) and dried in an analogous way to that described for sacran materials based on sepiolite.

The characterization of the bionanocomposites materials was carried out by CHNS elemental analysis (PerkinElmer 2400 series II CHNS/O elemental analyzer); X-ray diffraction (XRD) data was collected in a BRUKER D8-ADVANCE diffractometer (scan step of 2º min^{-1} between 2 to 70º), FTIR (Bruker IFS 66v/S Spectrometer with 2 cm^{-1} resolution) and thermal analysis (SEIKO SSC/5200 equipment), using air atmosphere (100 ml/min) from room temperature to 1000 ºC at 10 ºC min^{-1} heating rate. The specific surface of the materials were determined applying the BET (Brunauer-Emmett-Teller) method, from the adsorption/desorption of N_2 at 77 K (Micromeritics Flowsorb II 2300). Surface morphology was observed in FE-SEM equipment FEI-NOVA NANOSEM 230. Mechanical properties of the film samples were evaluated with a Model 3345 Instron Universal Testing Machine (Instron Engineering Corporation Canton, MA, USA) according to the D 882-88 ASTM standard method.

RESULTS AND DISCUSSION

The amount of sacran retained by sepiolite and montmorillonite was determined from the results of elemental chemical analysis. The adsorption isotherms at 30 ºC obtained for both clays show that the amount of adsorbed sacran increases with increasing initial concentration of the polysaccharide solution defining H-type isotherms, which indicates a great affinity of the polysaccharide for these clay substrates. These isotherms present a plateau region from 100 mgL^{-1} equilibrium concentrations, which corresponds to values of about 4.5 g and 8.5 g of sacran adsorbed per 100 g of SEP or Clois-Na, respectively. In the case

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of sacran-sepiolite bionanocomposites, this plateau may indicate that sacran reaches a complete coverage of the surface of the fibrous silicate, probably in a monolayer type conformation. In contrast, for the sacran bio-hybrids based on montmorillonite, the existence of only a plateau may indicate the existence of only one type of adsorption sites mainly with the polysaccharide intercalated in the interlayer region, as occurs in similar polysaccharides bearing positive charges (Darder et al., 2007).

Intercalation of sacran in the Clois-Na interlayer is confirmed by XRD (Fig. 1). A shift of XRD peaks towards lower 2θ values is observed in the bionanocomposites patterns, reaching 1.44 nm for the material with 17 wt% of clay content. For samples with low Clois-Na content, the diffraction peaks of the montmorillonite are absent. This fact may point out to a possible exfoliation of the clay, however a dilution effect of the clay cannot be disregarded.

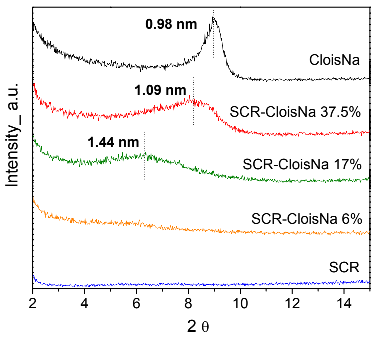

fig 1. : XDR patterns of pristine sacran and Clois-Na, and the bionanocomposites resulting from their assembly.

The interaction between sepiolite and sacran was investigated by FTIR spectroscopy. The spectra of the bionanocomposites show a decrease in the intensity of the band at 3720 cm^{-1}, assigned to the vibration of silanol groups (Si-OH) located at the external surface of the sepiolite, being proportional to the sacran content in the hybrid material. This behavior is attributed to a strong interaction through hydrogen bonding basically between the Si-OH groups of the silicate surface and the freely accessible sacran hydroxyl groups and also with other anionic functions of the biopolymer (carboxyl and/or sulfate) that produces a shift towards lower frequencies values. In contrast, the band related to the O-H vibrations of Mg-OH groups at 3680 cm^{-1} remains unaltered, because these groups located inside the structural blocks of sepiolite are inaccessible to the adsorbed species. In the FTIR spectra of resulting bionanocomposites, the characteristic bands sacran around 2920, 1420 and 1240 cm^{-1} attributed to ν_{CH} (C-H) of alkyl groups, ν_{CO} (COO), ν_{SO} (S=O) of SO_4 respectively, are also present. The morphology of the bionanocomposites was investigated using FE-SEM technique (Fig. 2). The sacran image (Fig. 2a) reveals a curious morphology consisting of thin layers and small fibrils. However, the images of sacran-sepiolite hybrid materials (Fig. 2b) show a quite different morphology. The bionanocomposites appear more compact, with the sepiolite fibers well integrated within the biopolymer matrix (Fig. 2b'). Such arrangement points out to a possible enhancement of the mechanical properties of these hybrid materials.

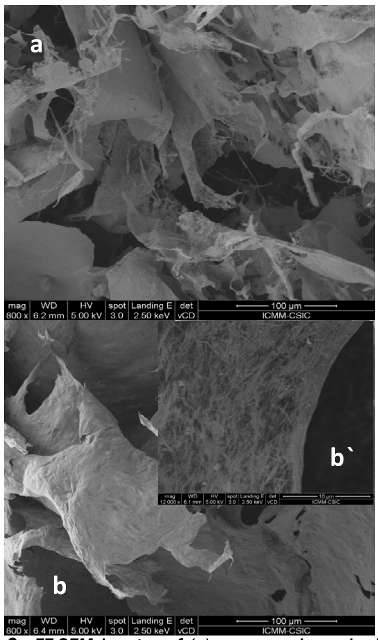

fig 2.: FE-SEM images of (a) sacran polysaccharide and (b) the bionanocomposite sacran-sepiolite with 17 wt% of sepiolite.

In this way, we have evaluated mechanical properties of these sacran-sepiolite bionanocomposites. The bio-hybrid films show good tensile moduli (E), presenting for instance 2.5 GPa for the bionanocomposite with 15% of sepiolite content. This value is very interesting because it represents about twice the value determined in pristine sacran materials (0.9 GPa). In addition, these materials exhibit resistance and integrity in aqueous solutions considerably increased in comparison to neat sacran films.

CONCLUDING REMARKS

The present work presents preliminary results on new bio-hybrid materials based on clay minerals of different morphology (sepiolite fibrous clay and montmorillonite layered clay) assembled to sacran, a novel polysaccharide extracted from cyanobacteria. Interestingly, this megamolecule is able not only to become associated with the external surface of sepiolite via its silanol groups but also to intercalate layered clays. These bionanocomposites can be processed as self-supporting films owing to the film-forming ability of sacran and show improved tensile properties due to presence of the clay. Considering the interesting colloidal and metal complexing properties of sacran (Okajima et al., 2010) these novel bionancomposites result very promising for a wide range of applications, from medical purposes to environmental remediation as heavy metal and lanthanide sorbents. Work is in progress to explore diverse applications.

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