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Structural and microstructural studies of montmorillonite-based multilayer nanocomposites

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ABSTRACT

Hypotheses: Montmorillonite, an abundant raw material, is a good candidate to obtain textured nanocomposites. However, the resulting structure of the composite depends on the dispersant used. This work aims at investigating the effect of organic polysaccharides, namely carboxymethylcellulose (CMC) or chitosan (Ch) differing by their side groups, on the resulting structure of montmorillonite-based nanocomposites.
Experiments: The effect of sodium hexametaphosphate and of two polysaccharide derivatives (carboxymethylcellulose and chitosan) combined with montmorillonite on the structure and microstructure of resulting composite films was investigated using particle size analysis, rheological measurements, thermogravimetric analysis, X-ray diffraction, scanning electron microscopy and flexural properties measurements of the textured films.
Findings: Results showed that the film structure and microstructure depend on the additive. The high organization (and resulting toughness) of the montmorillonite/sodium hexametaphosphate films results from an exfoliated then layered microstructure, whereas the addition of polysaccharide derivatives leads to the particle agglomeration. In this case, two mechanisms are in competition: surface adsorption and intercalation between exfoliated platelets.

1. Introduction

Natural bio-materials, for example mollusk shells natural nacres, are known for their remarkable mechanical properties which are difficult to reproduce synthetically. These composite materials exhibit outstanding combination of high strength, hardness and toughness, which are mainly attributed to their highly regular brick and mortar arrangement of aragonite and biopolymer layers [1,2]. The latter is acting as a mortar and its content is less than 5 wt% within the composite [3]. The thickness and length of aragonite platelets vary, depending on the mollusk species [3,4]. This alternatively piled structure has opened an inspiring route for material design, namely nanolaminated organic–inorganic composites where clay platelets can be used as a structural element. However, the aptitude of clay platelets to form well-organized structures also depends strongly on the attractive interactions existing between the different clay mineral surfaces. Attractive forces between platelet faces are necessary for the formation of a textured band-like structure, whereas attraction between faces and edges must lead to a card-house-like structure [5]. Montmorillonite, a clay mineral, has a broad variety of applications in industry and environmental protection [6]. In this mineral, charge defects in the silicate layers are compensated by alkali or alkali-earth cations (Ca^{2+}, Mg^{2+} and Na^{+}, etc.) located between oxide sheets. Montmorillonite platelets possess high aspect ratio (the oxide sheet thickness is higher than 1 nm, when the lateral dimension may vary from 30 nm to several microns or larger) and present a specific behavior in aqueous dispersion according to their basal faces charges [7,8]. These characteristics make montmorillonite, abundant raw materials, and a good candidate to obtain structured nanocomposites.

In this work, self-assembly of montmorillonite platelets in the presence of an excess of sodium cations is used to prepare ordered nanolaminated organic–inorganic composites with a brick-like structure similar to nacre. The mortar was charged organic polysaccharides, namely carboxymethylcellulose (CMC) or chitosan (Ch). These two polymers have attracted a great interest as multilayer materials due to their high abundance in nature (CMC is a derivative of cellulose from biomass and chitosan is derived from chitin which is present in cartilage, mollusk shells, nacre, insects...), their hydrophilic property, their film forming capacity,

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and more importantly their functional groups such as cationic amino (NH_2^+) groups present in chitosan or anionic carboxyl (COO^-) groups present in CMC, which provide an opportunity for chemical modification [9]. The specific surface area of the clay mineral was measured using Brunauer, Emett and Taylor (BET) method. Suspensions were characterized using rheological and particle size analysis. The multilayer nanocomposites obtained by evaporation of water from suspensions were investigated by SEM, thermogravimetric analysis (TGA), X-ray diffraction and flexural tests.

2. Experimental section

2.1. Materials

The clay mineral used for this experiment is a bentonite-type clay (M) supplied by "Comptoir Provençal des Argiles" (CPA, S.A., Hyères les Palmie, France). The mineralogical composition is approximately 60 wt% montmorillonite (noted MMT), 5 wt%. silica, 27 wt% illite, 1 wt% kaolinite and 3 wt% calcite. The specific surface area, estimated with the BET equation with nitrogen adsorption on raw material surface, is approximately 105 $m^2\,g^{-1}$ and the natural pH value of a clay mineral suspension in deionized water is 8.7. Sodium carboxymethylcellulose (CMC), Finnfix CMC-10, was obtained from CP Kelco (Atlanta, USA). Chitosan (Ch) (molecular mass: 350,000 $g\,mol^{-1}$, N-deacetylation degree 75–85%) was obtained from Sigma–Aldrich Chemicals (USA). Sodium hexametaphosphate (HMPP) from Sigma–Aldrich was used as exfoliation agent. All chemicals were used as received without further purification. The chemical structures of the additives are presented in Fig. 1.

2.2. Preparation of M suspensions

2.2.1. Suspensions with sodium hexametaphosphate (HMPP)

About 100 g of commercial raw material (M) with a particle size-fraction less than 100 μm was dispersed in 1 L of deionized water (W). The water over solid mass ratio is equal to 10. To obtain the Na^+ Ca^{2+} ions exchange and to favor the delamination of the bentonite particles, the sodium salt of HMPP was added. Two quantities of sodium salt were added, 5 and 10 wt% with respect to the amount of clay mineral. The corresponding suspensions are noted $M/HMPP^5$ and $M/HMPP^{10}$ respectively. The mixture was stirred for 2 h at room temperature. In order to separate as much as possible the montmorillonite clay particles from other minerals such as quartz and calcite, sonication (20 kHz, 750 W) prior to centrifugation (18,000 RCF for 10 min), was applied to the suspensions for 1 min. The pH value of the obtained suspensions, weakly dependent on the nature and the amount of dispersant, was always higher than 8, which is a necessary condition to obtain a stable montmorillonite suspension [10].

Multilayer nanocomposites were prepared according to a previously published procedure [5]. Following preparation, the supernatant, separated by centrifugation, was introduced in a flat bottom polyethylene vessel and maintained in an oven at a controlled temperature (30 °C). During the progressive evaporation of water, a sol–gel transition was observed, corresponding to a change from

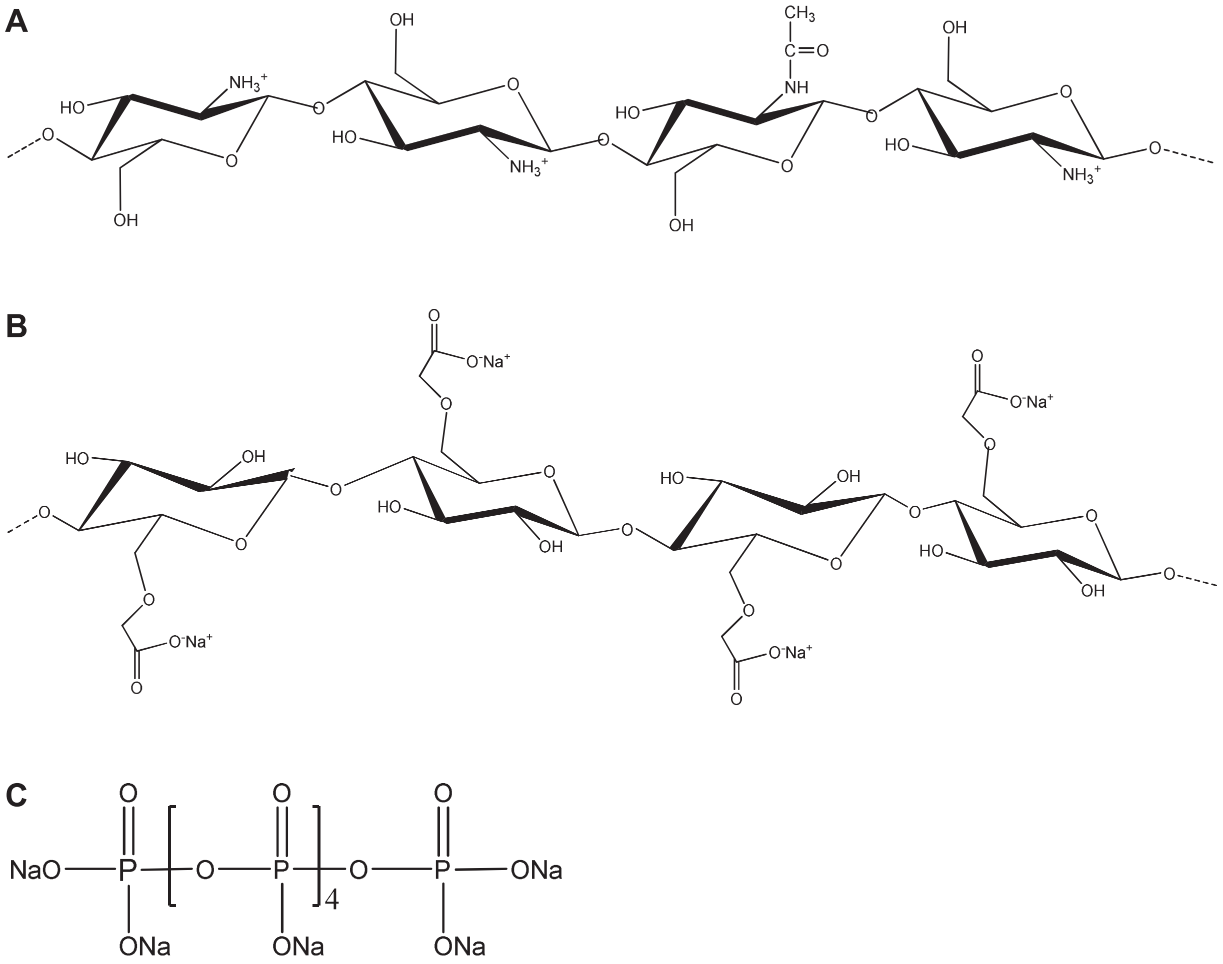

Fig. 1. Structure of (A) chitosan, (B) carboxymethylcellulose and (C) sodium hexametaphosphate.