



Synthesis of nanocomposite films from wheat gluten matrix and MMT intercalated with different quaternary ammonium salts by way of hydroalcoholic solvent casting

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ARTICLE INFO

Article history:

Received 4 June 2009

Received in revised form 9 November 2009

Accepted 9 November 2009

Keywords:

A. Polymer–matrix composites

A. Nano-structures

B. Delamination

E. Casting

ABSTRACT

Protein-based nanocomposites consisting of wheat gluten matrix (WG) and montmorillonite (MMT) modified with quaternary ammonium salts (QA) were developed by hydroalcoholic solvent casting. A simple clay-modifying method using five QA salts of different molecular lengths composed of 4, 5, 16, 40 and 72 carbon atoms, represented by C₄N, C₅OHN, C₁₆N, C₄₀N and C₇₂N, was used for mineral intercalation. XRD analysis of composites containing Na–MMT, C₁₆N–MMT, C₄₀N–MMT, and C₇₂N–MMT indicated the diffraction peaks corresponding to the interlayer spacing were absent, demonstrating that these particles were significantly dispersed in the WG matrix. Concentration and dispersion of MMT in the WG protein were the main factors affecting on permeability to water vapor P_{wv} through the films. There was a decrease of P_{wv} when either the raw or the modified MMT was added. The more prominent decrease of the P_{wv} was found for dispersed mineral particles, such as C₁₆N–MMT, C₄₀N–MMT, and C₇₂N–MMT.

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1. Introduction

Polymer nanocomposites have received considerable attention over the last decade [1–7]. The incorporation of nanoclays such as montmorillonite (MMT) in polymer matrix is an interesting way to improve material properties such as, barrier, mechanical and controlled release properties [8–12]. In view of this, the number of researches on protein-based materials increases as a result of the present interest for renewable and biodegradable materials in non-food applications [13–15]. The complexity of proteins and the diversity of their different fractions can be used to develop materials with original functional properties that differ markedly from those of standard synthetic plastics materials. Most of them have a good film-forming capacity, due to their good gas barrier properties, such materials are highly suitable for different types of purposes, and also present the opportunity to be biodegradable and compostable which constitute very appealing functionalities [16–23]. The choice of polymer such as protein issue from wheat gluten for film processing is advantageous because

it can be modulated as a function of the nature of polymer and the conditions of material shaping [16–24]. When clay particles are widely dispersed in a polymer matrix, the resulting composite exhibits physical and/or chemical property that make them attractive for a variety of industrial applications. However, to realize the benefits of a polymer/nanocomposite, the clay particles should be exfoliated inside the polymer matrix. Therefore, the key to develop polymer matrix that exhibits unique physical and/or chemical property is reaching of clay dispersion at nanoscale (exfoliation). However, the incompatibility between the clay particles and the gluten matrix hinders exfoliation of MMT at the nanoscale level. A possible alternative is to produce modified organically cation-exchanged clays by modifying the nature of MMT and substituting the cation in the layer galleries of layers with cationic–organic surfactants. With the idea of establishing possible changes on the functional properties of the WG-based nanocomposites, quaternary ammonium compounds were selected on basis of their different chain lengths of quaternary ammonium composed of 4, 5, 16, 40 and 72 carbon atoms in the alkyl chain. The following notation was used to identify intercalating agents: tetramethylammonium (C₄N), dodecylethyltrimethylammonium (C₁₆N), (2-hydroxyethyl)trimethylammonium (C₅OHN), tetrakis(decyl)ammonium (C₄₀N) and tetraoctadecylammonium (C₇₂N).

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2. Experimental part

2.1. Materials

Na–MMT (nanofil[®] EXM 757) with cation binding capacity of 80 meq/100 g and particle size distribution ranging from 5 μm to 10 μm . Wheat gluten was purchased from Amylum (Belgium). Tetramethylammonium bromide ACS reagent $\geq 98.0\%$ ($\text{C}_4\text{H}_{12}\text{BrN}$) was purchased from Sigma–Aldrich Company. Dodecylethyldimethylammonium bromide purum $\geq 98.0\%$ ($\text{C}_{16}\text{H}_{36}\text{BrN}$), (2-hydroxyethyl)trimethylammonium chloride $\geq 97.0\%$ ($\text{C}_5\text{H}_{14}\text{NClO}$), tetrakis(decyl)ammonium bromide puriss $\geq 99.0\%$ ($\text{C}_{40}\text{H}_{84}\text{BrN}$) and tetraoctadecylammonium bromide purum $\geq 98.0\%$ ($\text{C}_{72}\text{H}_{148}\text{BrN}$) were purchased from Fluka Company. Absolute ethanol and 95% ethanol were purchased from Alcool Pétroleo Chimie Industrie (France).

2.2. Intercalation of MMT

A cationic-exchange reaction between the layered silicates and the excess alkylammonium was used to prepare the organically modified MMT. The molar ratio of exchange capacity between the ammonium salts and MMT particles was 2 mMol g^{-1} whereas it corresponds to five times the exchange capacity of the host. The MMT-modifying mixture was prepared upon addition of 2.5 g Na–MMT into a hydroalcoholic solution consisting of 200 ml absolute ethanol–water (1:1), vigorously mixed by a magnetic stirrer with speed of 400 rpm for 1 h at 80 °C. After having been obtained a light-yellow suspension, 10 mMol quaternary ammonium salts was introduced into the MMT suspension, stirred for more 3 h at 80 °C. Then, the samples were taken out from flask and filtered immediately. The resultant products were washed with hydroalcoholic solutions of water–ethanol (1:1, volume ratio) for five times to remove unreacted quaternary ammonium molecules. The modified MMTs were then freeze-dried for 48 h. The C_xN –MMT label, in which subscript indicates the carbon number of QA, was used to identify the modified MMTs according to the molecule lengths of QA used: C_4N –MMT for tetramethylammonium bromide, C_5OHN –MMT for (2-hydroxyethyl)trimethylammonium chloride, C_{16}N –MMT for dodecylethyldimethylammonium bromide, C_{40}N –MMT for tetrakis(decyl)ammonium bromide and C_{72}N –MMT for tetraoctadecylammonium bromide.

2.3. MMT/WG nanocomposites processing

Twenty three milliliter of aqueous solution consisting of 0.02 g sodium sulfite was used to dissolve 15 g wheat gluten. Concentrated acetic acid was carefully dropped in it until pH 3.5 was obtained. The solution was then stirred by handling and reposed for 30 min. At the same time, MMT powders and 0.15 g glycerol were dispersed in 50 ml ethanol with the use of a high shear lab mixing (Silverson L4RT, England) for 10 min and an ultrason for 30 min. The MMT contents were always 0%, 2.5% and 5%, with respect to weight of WG. The MMT suspension was then incorporated to gluten solution and the weight of film-forming solution was adjusted to 100 g by addition of absolute ethanol, which corresponded to 62% in weight of the final solution. The mixing process was started off by applying a stirring speed of 10,000 rpm at room temperature for 15 min. The films were prepared by hydroalcoholic solvent casting onto a plastic plaque using a thin-layer applicator. After 2 h of air exposition, the WG-containing plaques were equilibrated at temperature of 20 °C and at relative humidity (RH) of 70% for 1 week.

2.4. FTIR–ATR analysis for MMT intercalation

FTIR–ATR spectra of Na–MMT and C_xN –MMTs were recorded using a Thermo FT–IR model Nicole 6700 spectrometer, equipped

with an ATR crystal diamond in the spectral range of 4000–800 cm^{-1} . The samples were analyzed as dry powders which have been kept in P_2O_5 for a week. Measures were performed in triplicate and a total of 64 scans were run for each spectrum to achieve the resolution of 4 cm^{-1} .

2.5. Wide-angle X-ray diffraction (WAXD) for modified MMT and nanocomposites

The changes on basal (d_{001}) spacing of the MMT, generated by either the organic modification with different intercalating agents or the nanocomposite formation, were analyzed by mean of a Philips Powder-Diffractometer equipped with a Ni-filtered Cu-K_α radiation. The XRD data of the MMT and organically modified MMT were collected in the range of $2\theta = 3^\circ$ – 25° at a scanning speed of 3° min^{-1} .

2.6. Scanning electronic microscopy (SEM) images

The morphology of C_{40}N –MMT–WG nanocomposite was visualized using a emission scanning electron microscope (JEOL JSM-6400F). Freeze-dried sample, introduced as film, was sputter-coated with a thin layer of platinum on their surface for visualization by SEM. Micrograph was obtained applying an accelerating voltage of 15 keV.

2.7. Measures of permeability to water vapor (P_{wv}) through the nanocomposite films

Cylinder-form glass cells filled up to 3/4 of its volume with distilled water was used as permeation cell. The 40 mm diameter nanocomposite films were closed tightly at the top of the permeation cell. After that, film-closed permeation cells were introduced into a desiccator fitted with an air-tight cover at 20 °C, in which silicagel was used as the desiccating agent. An air blower was coupled to inside desiccator cover to remove water vapor-saturated air surrounding the permeation cells, thus avoiding the water absorption back into cell. The weight loss of water-cell system, caused by the movement of water vapor outward, was determined at time intervals of 24 h. The values of P_{wv} were determined from:

$$P_{wv} = \frac{wx}{A\Delta t\Delta p} \quad (1)$$

where w is the slope of the weight loss versus time, x the film thickness, Δt the time of weight loss (s), A the area of water vapor-exposed film and Δp is the difference on external and internal water vapor pressures of the cell.

3. Results and discussion

3.1. ATR–FTIR analysis

Fig. 1 shows the FTIR spectra of C_4N , Na–MMT and C_4N –MMT in the spectral range of 4000–1250 cm^{-1} . The development of a prominent band at 1486 cm^{-1} in the spectrum of the C_4N –MMT was attributed to asymmetric C–H bending of terminal CH_3 groups coming from C_4N molecule, indicative of the MMT modification. The bands appearing at 3267 cm^{-1} in the same spectrum was attributed to stretching vibration of the structural O–H groups of the clay structure. These bands are indicative of the incorporation of C_4N molecules onto the layered gallery of the mineral.

Fig. 2 shows the FTIR spectra of C_5N , Na–MMT and C_5OHN –MMT in the spectral range of 4000–1250 cm^{-1} . The discrete band at 3222 cm^{-1} in the spectrum of the C_5OHN –MMT was assigned to

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