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Novel bionanocomposites of poly(vinyl alcohol) and modified chiral layered double hydroxides: Synthesis, properties and a morphological study

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ABSTRACT

The effect of novel modified layered double hydroxides (LDHs) on thermal and structural properties of poly(vinyl alcohol) (PVA) was investigated. Organically modified chiral LDH was prepared via ion exchange reaction of LDH in a solution of *N,N′*-(pyromellitoyl)-bis-L-phenylalanine diacid in distilled water. The modified Mg-Al LDH materials showed an increase in interlayer distance as compared to the unmodified Mg-Al LDH by X-ray diffraction (XRD). Bionanocomposites of PVA with the modified chiral LDH were prepared with different compositions of LDH by solution-intercalation method using the ultrasound-assisted technique. The effect of LDH contents on thermal, physicomechanical, and morphological properties of PVA films was investigated using XRD, Fourier transform infrared, thermogravimetric analysis (TGA), field emission scanning electron microscopy and transmission electron microscopy techniques. The TGA of the obtained bionanocomposites showed an increase in thermal stability. The uniform distribution of clay due to the intimate interaction between clay and polymer appeared to be the reason for the improved properties.

1. Introduction

Layered double hydroxides (LDHs), which are widely known as host–guest materials, are a significant class of naturally occurring minerals whose synthesis in the lab is easily accessible [1,2]. Such materials, also known as anionic clays, have the capability of anion swelling, making them very versatile. In addition to the rich intercalation chemistry that can be played with, it also shows a wide range of variations in its composition. This latter aspect is based on the versatility of the general formula $[M^{2+}{}_{1-x}\,M^{3+}{}_x\,(OH)_2](A^{m-})_{x/m}\cdot nH_2O$, where both M^{2+} and M^{3+} can be varied, and A^{m-} is usually a simple anion such as Cl^-, $NO_3{}^-$ or $CO_3{}^{2-}$. In its general formula, x measures the amount of M^{3+} relative to $(M^{3+}+M^{2+})$, correlating with the spacing between layers. Their structure is based on brucite-like layers, where a divalent metal cation is located in the center of oxygen octahedral and two-dimensional infinite layers are formed by edge-sharing of octahedral. Moreover, the spacing is changed concomitantly by both the size of the intercalated anions and the degree of hydration [1,3–7].

The lamellar structure and anion exchange properties of LDHs make them attractive for technological applications such as ion-exchangers, adsorbent materials, pharmaceutical stabilizers, and precursors for new catalytic materials [8–11]. LDH, due to its layered structure, is an attractive choice as nanofiller considered for the preparation of multifunctional polymer/layered crystal nanocomposites (NCs). However, its use as a nanofiller is limited by its high-charge density, and the high content of anionic species and water molecules, all resulting in strong interlayer electrostatic interactions between the sheets and pronounced hydrophilic properties. Consequently, it is difficult for a monomer or polymer to penetrate into the LDH layers or the LDH layers to be homogeneously dispersed within hydrophobic polymer matrices. To facilitate the intercalation of polymer in the layers of LDH, or to achieve a good degree of the layer dispersion in polymer matrices, the interlayer space should be modified with suitable organic anions for the purpose of increasing both the interlayer distance and the hydrophobicity of LDH layers [12–16].

Anions are typically intercalated into LDH interlayers by three approaches [1,17]. The first approach is the coprecipitation method, which requires the addition of a solution of M^{2+} and M^{3+} ions into a base solution of the desired anions. The second technique is the

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direct ion exchange method, in which LDHs are stirred in a solution of the chosen anions at a suitable concentration. The last method is the rehydration method in which the calcined LDH is added to a solution of desired anions [18]. The selection of anions for the modification of LDH depends on the next application of LDH. For example, Mg–Al LDHs intercalated with dodecylsulfate and dodecylbenzenesulfonate have been used to adsorb pesticides, such as triadimefon, linuron, atrazine, acephate, and diazinon from aqueous solution [19,20]. Also, LDHs containing interlayer carboxylate anions have attracted considerable attention in recent years due to interesting properties and potential applications, e.g., LDH modified with citrate, malate, and tartrate ions are able to take up hazardous organic materials and heavy metal ions from an aqueous solution [21].

Polyvinyl alcohol (PVA), a polyhydroxy polymer, is a thermoplastic and biocompatible petroleum based polymer. It is also one of the rare polymers with a carbon–carbon single bond backbone that is fully biodegradable [22,23]. Because of the hydroxyl (—OH) groups on alternating carbon atoms, PVA is strongly hydrophilic and soluble in water, helping to promote its degradation through hydrolysis [24]. PVA has been largely studied owing to its good film forming ability, high hydrophilicity, biocompatibility, good chemical resistance and interesting mechanical properties. These properties have led to a wide range of industrial products such as membrane, textile sizing and finishing, adhesive, coatings, paints and as a protective colloid for emulsion polymers [25–28]. Lately, the interest has been focused on its promising biomedical applications such as drug delivery systems, dialysis membrane; wound dressing, scaffolds for tissue engineering, contact lenses, and artificial organs [27,28]. These applications have encouraged researchers to improve thermal, mechanical and barrier properties of NC films, while retaining the optical clarity of PVA. This polymer is the most commercially important water soluble plastic which has been extensively investigated as a matrix for different kinds of nanofillers [26–29]. PVA is sold by the major chemical companies as a clear granular material in a variety of molecular weights. These properties have led to its broad industrial use [30].

More recently, PVA and LDH based NCs have been developed to improve PVA's properties and further explore its applications by solution casting process [31–36]. LDH based NCs have shown the exfoliated nature of the dispersed particles. Inspired by these studies, this work has focused on investigating the properties of PVA and chiral modified LDH (MLDH) bionanocomposites (BNCs) by solution casting method for the first time. The chiral dicarboxylate anion of *N,N′*-(pyromellitoyl)-bis-phenylalanine diacid was prepared in NaOH solution. Different amounts of this novel MLDH were used for the synthesis of PVA/MLDH BNCs. The properties of the hybrids were studied in the film form as a function of the MLDH contents in the polymer matrix. This also examined the relationship between the properties and structures of the organoclay and PVA/nanoclay hybrid films with X-ray diffraction (XRD), Fourier transfer infrared (FTIR) and thermogravimetric analysis (TGA) techniques. The morphology of obtained materials was examined by field emission scanning electron microscopy (FE-SEM) and transmission electron microscopy (TEM).

2. Experimental

2.1. Materials

PVA (99% hydrolysis, weight-average molecular weight = 72,000 g/mol), L-phenylalanine amino acid ($C_6H_{13}NO_2$, 131.18 g/mol, ≥99%), Pyromellitic dianhydride and sodium hydroxide (NaOH) were purchased from Merck Chemical Co. Hydrotalcite; ($Mg_6Al_2(CO_3)(OH)_{16}\cdot 4(H_2O)$) was purchased from Sigma–Aldrich Co.

2.2. Characterization techniques

The reaction was carried out on a MISONIX ultrasonic liquid processors, XL-2000 SERIES. Ultrasound was a wave of frequency 2.25×10^4 Hz and power of 100 W.

FT-IR spectra were recorded on Jasco-680 (Japan) spectrophotometer with 2 cm^{-1} resolution. The KBr pellet technique was applied to monitor changes in the FT-IR spectra of the samples in the range of 4000–400 cm^{-1}. The vibrational transition frequencies have been reported in wavenumbers (cm^{-1}).

The interlayer spacing of the organoclays was measured by an XRD (Bruker, D8 Advance, Germany) with Cu $K\alpha$ radiation ($\lambda = 0.1542$ nm) at 45 kV and 100 mA. The diffraction patterns were collected between 2θ of 1.2° and 80° at a scanning rate of 0.05/min. Basal spacing was determined from the position of the $d(0\,0\,1)$ reflection. The scanning speed was 0.02/s. The d-spacing of the organic montmorillonite was analyzed using Bragg's equation ($n\lambda = 2d \sin\theta$). Where n is an integer, λ is the wavelength, θ is the glancing angle of incidence, and d is the interplanar spacing of the crystal.

TGA was performed on an STA503 WinTA instrument in a nitrogen atmosphere by the heating rate of 10 °C/min from ambient temperature to 800 °C at the nitrogen atmosphere.

The morphology of the MLDH and BNCs was examined by FE-SEM (HITACHI; S-4160). The powdered sample was dispersed in H_2O, and then the sediment was dried at room temperature before gold coating.

The dispersion of the nanoclay within the medium was controlled by TEM. The TEM images were obtained from a Philips CM120 using an accelerator voltage of 100 kV. The inorganic components appeared black/gray on the micrographs.

2.3. Synthesis of chiral LDH

The preparation was performed in a nitrogen atmosphere to exclude carbon dioxide, whose presence could lead to the formation of a carbonate LDH. *N,N′*-(pyromellitoyl)-bis-L-phenylalanine diacid pillared LDH was prepared by adding superfluous diacid (2.5 g) to a suspension of the LDH in 100 ml of distilled water. The suspension was slowly dissolved with effervescence and a clear solution was obtained. This solution was added dropwise to an alkaline solution (NaOH, 2.0 g) in 100 ml of distilled water and the pH was maintained above 9. The resulting white precipitate was aged for 24 h at 65 °C, and then filtered until all of the supernatant liquid was removed. The sample was washed several times with large amounts of distilled water, and then dried at 70 °C in a vacuum oven to give the modified chiral LDH.

2.4. Synthesis of PVA/MLDH BNCs

PVA/MLDH BNCs were synthesized by a solution-intercalation method using ultrasound energy: At first, distilled water was mixed with MLDH to form clay/water suspension of ≤2.5% concentration. The suspension was stirred for 3 h at 40 °C and sonicated for 1 h. Then, low-viscosity, fully hydrolyzed PVA was added to the stirred suspensions to make the total solid (silicate plus polymer) concentration $w = 5\%$. The mixture was then heated to 90 °C for 6 h to dissolve PVA. The mixed solution was condensed and the total solid concentration was controlled at $w = 10\%$. After being sonicated for 1 h, the final films were made via casting on a Petri dish in a closed oven at 40 °C for 24 h; the thickness of the films was controlled from 0.15 to 0.3 mm.