Exfoliation and dispersion of LDH modified with *N*-tetrabromophthaloyl-glutamic in poly(vinyl alcohol): Morphological and thermal studies

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Abstract. In this study, modified LDH (M-LDH) was synthesized by the co-precipitation reaction of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and *N*-tetrabromophthaloyl-glutamic (Br-Gl) in short time. M-LDH nano-fillers were embedded into poly(vinyl alcohol) (PVA) matrix via ultrasonic irradiation technique which provided PVA/M-LDH NCs. The morphology and structure of the prepared samples were characterized by Fourier transform infrared spectroscopy, thermogravimetric analysis (TGA), field emission scanning electron microscopy and X-ray diffraction techniques. TGA of the PVA/M-LDH NCs showed that the thermal stability was improved. The enhancement of thermal properties was ascribed to the homogeneous and good dispersion of M-LDH sheets in the PVA matrix by hydrogen bonding between O–H groups of PVA and the M-LDH.

Keywords. Modified layered double hydroxides; nanocomposite; thermal stability; poly(vinyl alcohol).

1. Introduction

Polymer nanocomposites (NCs) are of scientific and industrial interest due to their superior properties arising from the nano-fillers. Various inorganic fillers, fibres and anisotropic particles such as layered silicates,¹ carbon nanotubes^{2–4} and so on, have confirmed to be particularly useful in strengthening polymer matrix. Recently, another kind of inorganic nano-filler, layered double hydroxide (LDH), known as anionic clays, has attracted much attention. The hydroxide layers of LDH have close likeness to the mineral brucite, or $\text{Mg}(\text{OH})_2$, where some divalent cation in the brucite layers are replaced by a trivalent cation, generating positively charged layers. General formula for these compounds is $[\text{M}^{2+}_{1-x}\text{M}^{3+}_x(\text{OH})_2](\text{A}^{m-})_{x/m} \cdot n\text{H}_2\text{O}$, in which both M^{2+} and M^{3+} can be varied, and A^{m-} is usually an exchangeable anion.⁵ LDHs are considered as important layered crystals because of their biocompatibility, biodegradability and their practical applications in catalysis,⁶ flame retardants,⁷ photochemistry,⁸ abilities to intercalate, as antioxidant,⁹ adsorption–desorption of water

pollutant ions,^{10,11} biohybrid beads and in controlled release of medicine.^{12–14} The characteristic that makes LDH appropriate for these applications is the exchangeable nature of the interlayer anions. In the early development of hybrid inorganic–organic composites, modifications with surfactants were developed to convert clay surfaces from hydrophilic to organophilic and to increase the basal spacing of layers.^{15–17}

Glutamic acid (Gl), a non-essential amino acid, has a wide variety of applications, for instance, as antioxidants,¹⁸ gene transfection,¹⁹ detection and identification of cationic and non-ionic surfactants.²⁰

Poly(vinyl alcohol) (PVA) is a polyhydroxy water soluble polymer that has been studied largely due to its many attractive characteristics, such as, biodegradability, biocompatibility and water-solubility. PVA has been used for membranes,²¹ drug delivery systems,²² artificial biomedical devices, bioadhesive anti-bacterial system^{23–26} and hybrid NC coatings.²⁷ These applications have encouraged researchers to improve thermal, mechanical, super-ductility properties of PVA.²⁸ More recently, PVA-based NCs have been developed to improve PVA properties by intercalating various surfactants in LDH nanoparticle.^{29,30}

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This work was focused on investigation of the properties of novel NCs fabricated from PVA and modified LDH (M-LDH). The dicarboxylate anion of (*N*-tetrabromophthaloyl-glutamic) (Br-Gl) diacid was prepared from a reaction of tetrabromophthalic anhydride with Gl. Then Br-Gl diacid was intercalated in LDH to prepare M-LDH. Different amounts of M-LDH were used for the synthesis of PVA/M-LDH NCs under ultrasonic irradiation. The structure and morphology of the M-LDH and PVA/M-LDH NCs were characterized by Fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), thermogravimetric analysis (TGA) and field emission scanning electron microscopy (FE-SEM). Due to the presence of different functional groups in the diacid molecule, it can be dispersed well in the PVA matrix which can also enhance the properties of the hybrid materials.

2. Experimental

2.1 Apparatus

The interlayer spacing of all samples were measured by XRD (Bruker, D8 Advance, Germany) with Cu K α radiation ($\lambda = 0.1542$ nm) at 45 kV and 100 mA. The diffraction patterns were collected at 2θ between $5-80^\circ$ at a scanning rate of $0.05^\circ/\text{min}$. Basal spacing was determined from the position of the d(003) reflection. The d-spacing of the samples 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. The reaction was carried out on a MISONIX ultrasonic liquid processor, XL-2000 SERIES. Ultrasound was at a frequency of 2.25×10^4 Hz and power, 100 W. A Jasco-680 FT-IR spectrometer (Japan) was employed KBr pellet technique was applied to monitor the FT-IR spectra of the samples in the range of $4000-400$ cm^{-1} . TGA was performed on an STA503 TA instrument in a nitrogen atmosphere at the heating rate of $20^\circ\text{C}/\text{min}$ from ambient temperature to 800°C . The morphology of M-LDH and NCs was examined by FE-SEM (ZEISS; Σ IGMA-VT).

2.2 Materials

PVA (99% hydrolysis, weight-average molecular weight = 72,000 g/mol), tetrabromophthalic anhydride (4,5,6,7-tetrabromoisobenzofuran-1,3-dione), Gl, and sodium hydroxide (NaOH) were purchased from Merck Chemical Co. Aluminum nitrate $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and magnesium nitrate $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were purchased

from Aldrich Chemical Co. Other solvents and materials were used as obtained without further purification.

2.3 Preparation of Br-Gl diacid

The Br-Gl diacid was synthesized according to the general procedure:³¹ 2 mmol of the tetrabromophthalic anhydride was mixed with 4 mmol of the Gl in 10 mL of acetic acid, and the mixture was stirred at room temperature for 12 h and then refluxed for 24 h. Then the acetic acid was distilled under vacuum and the residue poured into 1% of HCl solution. The solid was filtered, washed with 1% HCl solution and several times with water and then dried in vacuum.

2.4 Preparation of the modified LDH

M-LDH was prepared by an ultrasound-assisted coprecipitation method. A solution of diacid Br-Gl was prepared by dissolving NaOH (0.02 mol) and diacid (0.02 mol) in 20 mL of deionized water. Then aqueous solution of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Mg/Al molar ratio of 2:1) were added dropwise to this solution and the mixture was vigorously stirred at pH = 10 for 20 min at room temperature. The product was sonicated for 1 h and then filtered and washed several times with water, and then dried in vacuum to give the M-LDH nanolayers.

2.5 Preparation of the PVA/M-LDH NC films

PVA/M-LDH NCs were synthesized by a solution casting method. At first, PVA was dissolved in water under stirring at 70°C , and M-LDH was dispersed in water at 60°C to form a suspension. Then PVA was added to the suspensions of M-LDH and stirred at 60°C for 2 h. For uniform dispersing of M-LDH in PVA, this aqueous mixture was sonicated for 1 h and poured into Petri dish in a closed oven at 40°C for approximately 24 h to evaporate water. The M-LDH contents in the PVA NC films were 2, 4 and 8 wt%.

3. Results and Discussion

3.1 Synthesis of M-LDH and PVA/M-LDH NCs

By the condensation reaction of an equimolar amount of tetrabromophthalic anhydride and two equimolar amounts of the Gl in reflux acetic acid corresponding Br-Gl diacid was synthesized, as shown in scheme 1. Then the solution of this compound was added to the solution of aluminum nitrate and magnesium

Scheme 1. Preparation of Br-GI diacid.

nitrate, under ultrasonic irradiation to prepare M-LDH (figure 1).

Novel PVA/M-LDH NCs with 2, 4 and 8 wt% of M-LDH were successfully fabricated by solution casting method. Different amounts of M-LDH were mixed with the PVA and the mixture was dispersed in water, under ultrasonic irradiation to prepare PVA/M-LDH NCs (figure 2). The uniform distribution of M-LDH in the polymer matrix was expected to lead to enhancement of physical, morphological and thermal properties in the resulting NCs.

3.2 FT-IR study

PVA, LDH, M-LDH and PVA/M-LDH NCs containing 2, 4 and 8 wt% of M-LDH sheets were characterized by FT-IR spectroscopy. For LDH- CO_3^{2-} , the broad peak centred at about 3400 cm^{-1} arises from O-H stretching vibration of the metal hydroxide layer and interlayer water molecules. The strong peaks at 1373 and 1045 cm^{-1} were attributed to the stretching vibration of CO_3^{2-} . In the FT-IR spectrum of the Br-GI, bands at $1770\text{--}1717\text{ cm}^{-1}$ were attributed to C=O stretching vibration. Bands in $1300\text{--}1000\text{ cm}^{-1}$ range are assigned to the C-O stretching and in $1600\text{--}1475\text{ cm}^{-1}$ range, assigned to C=C stretching vibration of Br-GI (figure 3b). Band broadening resulted due to intercalation and electrostatic interaction between chiral diacid molecules (figure 3c). In the case of PVA, a broad absorption peak centred at around 3350 cm^{-1} is ascribed to O-H stretching vibration of hydrogen bond of hydroxyl groups. The absorption peak around 2938 cm^{-1} is related to stretching vibrations of -CH

Figure 1. Preparation of the M-LDH.

Figure 2. Preparation of the PVA/M-LDH NCs.

Figure 3. (a) FT-IR spectra of LDH; (b) Br-Gl; (c) M-LDH; (d) PVA; and (e–g) different PVA/M-LDH NCs of M-LDH.

and CH_2 groups. Strong absorption peak observed at 1708 cm^{-1} is characteristic of the carbonyl group of the acetate in the partially hydrolyzed PVA. The peaks at 1428 and 1330 cm^{-1} are characteristic of the O–H and C–H deformation vibration, respectively. The absorption peak at $1000\text{--}1100\text{ cm}^{-1}$ could be assigned to the C–O stretching and O–H bending vibrations arising from the PVA chain (figure 3d). It could be easily seen that for PVA/M-LDH NCs 2, 4 and 8 wt%, the NCs have characteristic band of neat PVA with a little shift to the left (figure 3e–g).

3.3 X-ray diffraction

One of the complementary techniques to characterize the extent of intercalation and delamination of the nano-filler having layered structure is XRD. The XRD spectra of pristine LDH, M-LDH, PVA and PVA/M-LDH NCs with 4 and 8 wt% of MLDH are shown in figure 4. Before organic treatment, the basal spacing of

Figure 4. XRD patterns of LDH, M-LDH, PVA, PVA/M-LDHNCs with 4 and 8 wt% of M-LDH.

the pure LDH was 0.75 nm , which corresponds to the (003) diffraction peak with $2\theta = 11.84^\circ$. The XRD pattern of pristine LDH showed that this compound is highly crystalline in nature. After treatment with chiral dicarboxylic acid Br-Gl, the XRD pattern of M-LDH showed absence of (003) diffraction peak as a result of the exfoliation. As shown in figure 4, PVA has a low degree of semi-crystalline structure due to numerous hydrogen bonds of the hydroxyl groups. The XRD patterns of PVA/MLDH NCs showed similar XRD patterns to the PVA when the M-LDH composition was 4% and 8 wt%.

3.4 Thermal degradation characteristic

Comparison of TGA of the M-LDH with LDH gives an indication of how the interlayer surfactant anions manipulate the decomposition of the host material. As shown in figure 5, TGA of LDH and M-LDH suggests a two-stage decomposition process: the first weight loss stage is related to the loss of absorbed water molecules and the second weight loss stage between 370 and 500°C could be assigned to the removal of interlayer carbonate and dehydroxylation of the metal hydroxide layer.³²

As shown in figure 6, a three step degradation can be observed for PVA. The first step of weight loss is related to the loss of absorbed water. The second weight loss is associated with the degradation of the PVA by dehydration reaction of the polymer chain. The third step of weight loss is related to the cleavage backbone of PVA polymer. In case of PVA/M-LDH NCs, an increase in thermal stability between $250\text{--}470^\circ\text{C}$ for

Figure 5. TGA curves of pure LDH and M-LDH.

Figure 6. TGA curves of PVA and PVA/M-LDH NCs with 2, 4 and 8 wt % of M-LDH.

the NCs was observed. The increase in thermal stability was pointed out by an increase of about 70°C in the onset of the thermal decomposition temperature. This was similar to result obtained for other LDH-based NCs.³³ The NC films showed more resistance toward thermal degradation. The residue at 800°C (char yield) for NCs with 2, 4 and 8 wt% of M-LDH were 5%, 10% and 20%, respectively. Char yield for NCs 4 and 8 wt% of M-LDH was significantly increased (figure 6). The improvement of thermal properties maybe attributed to the homogeneous and well-dispersed M-LDH sheets in the PVA matrix and strong hydrogen bonding between O–H groups of PVA and the layers of M-LDH sheets.³⁴ The char yield of hybrid PVA/M-LDH NCs is obviously elevated in comparison to PVA, displaying that the thermal stability of the hybrid NCs is enhanced by the incorporation of M-LDH nanolayers.

3.5 FE-SEM and TEM studies

To study the changes in the morphology of LDH, M-LDH, PVA and PVA/M-LDH NCs, FE-SEM imaging of the samples was carried out. The morphological images

Figure 7. (a, b) FE-SEM images of LDH and; (c, d) M-LDH.

of LDH and M-LDH were investigated by FE-SEM as shown in figure 7. The unmodified LDH showed rough plate-like shapes loaded on top of each other (figures 7a, b). In the case of M-LDH, FE-SEM results demonstrated that the M-LDH layers lost their ordered stacking structure and were exfoliated (figure 7c, d). To further confirm the nanostructure of M-LDH and verify the conclusions from XRD and FE-SEM, TEM was carried out. Figure 8 shows the TEM of M-LDH. As shown in TEM photograph of M-LDH (figure 8a, b), dark colour indicated better ordered intercalated structure, and light gray showed uniform ultrathin sheets that was exfoliated.³⁵

The FE-SEM micrographs of PVA and PVA/M-LDH NCs with different M-LDH content are shown in figure 9. According to the results, the morphology of neat PVA was completely changed (figure 9a, b). The micrographs of the PVA hybrids with 2 wt% (figure 9c, d), 4 wt% (figure 9e, f) and 8 wt% M-LDH (figure 9g, h) showed that M-LDH nanosheets were well-dispersed in the polymer matrix, because M-LDH nano-filler had outstanding adhesion and strong interfacial bonding with PVA. It is observed that M-LDH nanosheets were homogeneously dispersed in the polymer matrix.

Figure 8. (a, b) TEM images of M-LDH.

Figure 9. (a, b) FE-SEM images of PVA; (c, d);PVA/M-LDH NCs 2 wt%; (e, f) PVA/M-LDH NCs 4 wt%; and (g, h) PVA/M-LDH NCs 8 wt%.

4. Conclusions

In an efficient, simple and low cost strategy involving the use of ultrasonic irradiation technique, nanostructure M-LDH intercalated with Br-GI was prepared to improve the thermal stability of PVA matrix. Then, NCs of PVA were prepared by a solution-intercalation method using the ultrasound energy, with different compositions (2, 4 and 8 wt%) of M-LDH. Dispersion of M-LDH was studied in FE-SEM micrographs. According to FE-SEM results, the morphology of the neat PVA was totally changed and the inorganic nanoparticles were dispersed homogeneously in the PVA matrix. TGA indicated that thermal stability of the NCs was improved. Due to the homogeneous dispersion of M-LDH nanosheets in the PVA matrix and strong hydrogen bonding between O–H groups of PVA and the layers of M-LDH, an increase in thermal stability by about 70°C in the onset of the thermal decomposition was observed. Existence of amino acids in novel organo-modified nanoclay and PVA makes synthesized NCs suitable for industrial application such as fibres, textiles, packaging and so on.

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