

# Highly absorbent polymer/layered double hydroxide composites for the conservation of irrigation water

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**Abstract** From the commercial, industrial, and scientific point of views, clay composites are of particular interest especially in the field of water purification and irrigation. At present, even though a great deal of work on clay materials was carried out, still more remains to be done in order to exploit completely their potential applications. The aim of this study is to prepare a highly absorbent polymer–clay materials to control and manage irrigation water. Here, we report the synthesis of polymer–LDH composites through an incorporation/in-situ polymerization process. In addition, we characterize the prepared composites by different spectroscopic techniques, including, X-ray powder diffraction (XRD), FT-IR spectroscopy, thermogravimetric analysis (TGA), and the scanning electron microscope (SEM). Subsequently, we investigate the effect of the prepared composites on water front distribution and moisture content in sandy soils by using subsurface drip irrigation system. The obtained results have confirmed the composite structure of the prepared materials and have showed an improvement in the polymer water absorptivity, indicating a control process of irrigation water. More information will be discussed in the conference site.

**Keywords:** polymer, LDH

## 1. Introduction

A recent strategy of water management is the use of high molecular weight polymers to soil as a mean to retain the structure of the soil and to decrease the water infiltration<sup>1</sup>. The decrease of water infiltration has several positive effects such as maintaining soil moisture and soil productivity. However the application of synthetic organic polymers as soil conditioners may affect the quality of groundwater, planting process and even soil itself. Thus, there is a need in-the-art of new technology to save the application of organic polymers in soils.

In recent years, absorptive polymer/clay composites have received a great attention because of their relative low production costs and high water absorptivity<sup>2</sup>. Polyacrylate polymers generally exhibit a very high absorptivity in water, however they have the problem of poor resistance to salts, that decreases its soil-application<sup>3</sup>. Layered double hydroxide (LDHs) are a family of natural

and synthetic compounds, consists structurally of brucite-like sheets with hexagonal-shaped crystallite layers<sup>4</sup>. It possesses excellent anion exchanging properties and can be used as matrixes, polymer stabilizers and carriers. In addition, LDH is reported in a number of studies as a soil biocompatible and nontoxic material<sup>5,6</sup>.

Herein we offer an efficient strategy of polymer-soil application by incorporating an anionic high molecular weight polymer (polyacrylic acid, PAA) into a soil-friendly inorganic material; LDH. The formation of organic-inorganic composites of PAA with LDH is expected to improve the soils-application of PAA.

## 2. Experimental Work

### 2.1. Materials

Acrylic acid monomer (distilled under reduced pressure prior to use), ammonium persulphate (analytical grade), magnesium nitrate hexahydrate (purity 99.5%), aluminum nitrate nanohydrate (purity 99.5%) were purchased from Wako Pure Chemical Industries, Ltd. and used as received. All solutions were prepared using deionized water (18.2 MΩ/cm, produced from Milli-Q Gradient ZMQG000kt).

### 2.2. Preparation of NO<sub>3</sub>-LDH

To a round flask containing 30 mL of 1.0 M NaNO<sub>3</sub> solution was added dropwise a 50 mL solution of 8.538 g (0.0333 M) of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and 6.249 g (0.01666 M) of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O ( $Mg^{2+}/Al^{3+} = 2$ ) with constant stirring. During the metal ion addition, the pH of the suspension was kept constant at 8.0 by adding appropriate amounts of 2.0 M KOH solution. The final volume of the preparation medium was augmented to 100 mL by deionized water. The resultant suspension was stirred at 70 C° for 24 h under N<sub>2</sub> flow. At the end of the reaction, the formed Mg-Al LDH material was collected by filtration, washed several times with deionized water, and finally freeze-dried.

### 2.2. Nanohybrid synthesis of AA-LDH by anion-exchange technique.

In a 100 mL round flask was dissolved 2.0 g of AA in 100 mL of deionized water by adjusting the solution pH to 8.0 using 2.0 M NaOH solution. To the AA solution, 1.0 g of NO<sub>3</sub>-LDH was added with constant stirring. The reaction

mixture was stirred at 40 C° for 7 days. After the reaction, the obtained AA-LDH material was collected by filtration (0.45 µm Millipore membrane) and washed several times by 0.1 M NaOH solution and subsequently deionized water. Finally, the collected AA-LDH was freeze-dried.

### 2.3. In-situ polymerizations of AA-LDH nanocomposites

A flask containing 5.0 g AA-LDH and a 0.5wt% of ammonium persulphate initiator in a 100 mL deionized water was degassed under N<sub>2</sub> vacuum by three freeze-thaw cycles. The reaction mixture was stirred and heated to 80 C° in a water bath for 3 h(s). After the polymerization reaction, the PAA-LDH material was collected by filtration, washed several times by 0.1 M NaOH solution and subsequently deionized water. Finally, the collected PAA-LDH was freeze-dried.

### 2.4. Characterization and measurements

X-ray powder diffraction patterns were recorded on a Rigaku X-ray diffractometer using CuK $\alpha$  radiation at  $\lambda=1.5405 \text{ \AA}$ . The measurement was performed in the 2 $\theta$  range 1.5-70°. Infrared spectra (KBr disk method) were recorded on a Bio-Rad FTS 3000MX FT-IR spectrophotometer. The scanning electron micrographs (SEM) were captured by a Hitachi FE-SEMS-4700 microscope.

Soil samples with a mass of 100 g were placed in battery dishes. PAA and PAA-LDH emulsions with 0.2 wt % were sprayed on the surface of the soil. The sprayed soils were remained two days to dry at room temperature. The static water-measure technique was used to determine the water-

stability of the soil aggregates. Admixed aggregates of similar diameter (visually approximated) were then selected and replaced on a filter paper in new battery dishes. The soil aggregates were immersed in water. The time of immersion until collapse was recorded. The collapse is considered when interior water began to effuse. The average values of triplicate measurements were obtained. The water-stability test was repeated by using 0.4 and 0.6 wt% of PAA and PAA-LDH.

## Results and discussion

The scanning electron microscopy was used to investigate the nanocomposite structure of the prepared materials. Figure 1 displays the SEM images of the synthesized NO<sub>3</sub>-LDH material, AA-LDH and PAA-LDH composites. The inset of image a, shows uniform and regular hexagonal platelets characteristic for LDH particles. The regularity of the LDH particles confirmed the good crystallinity recorded by X-ray measurement. In the case of AA-LDH (images b), aggregates composed of small nanoparticles were observed. On the other side, PAA-LDH (images c), showed a considerable difference.

The surface of the aggregates exhibited a porous morphological structure. Hence, the PAA-LDH material can swell through the diffusion of the water molecules into the pores of the nanocomposites structure. In conclusion, the recorded SEM images confirmed the nanocomposite structure of PAA-LDH and captured the morphological ability of PAA-LDH to absorb and keep water molecules during soil-water application.

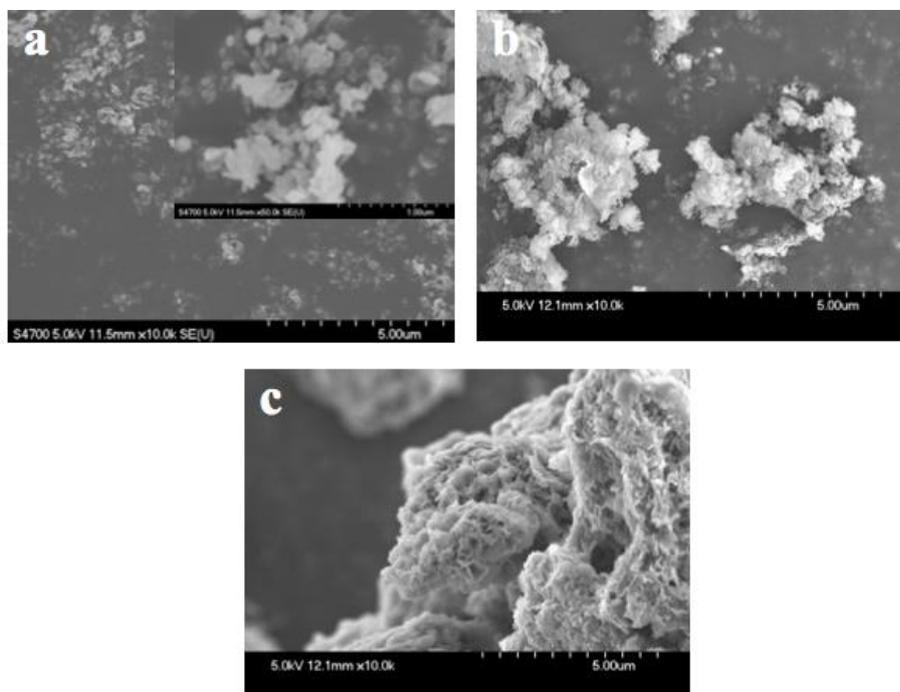
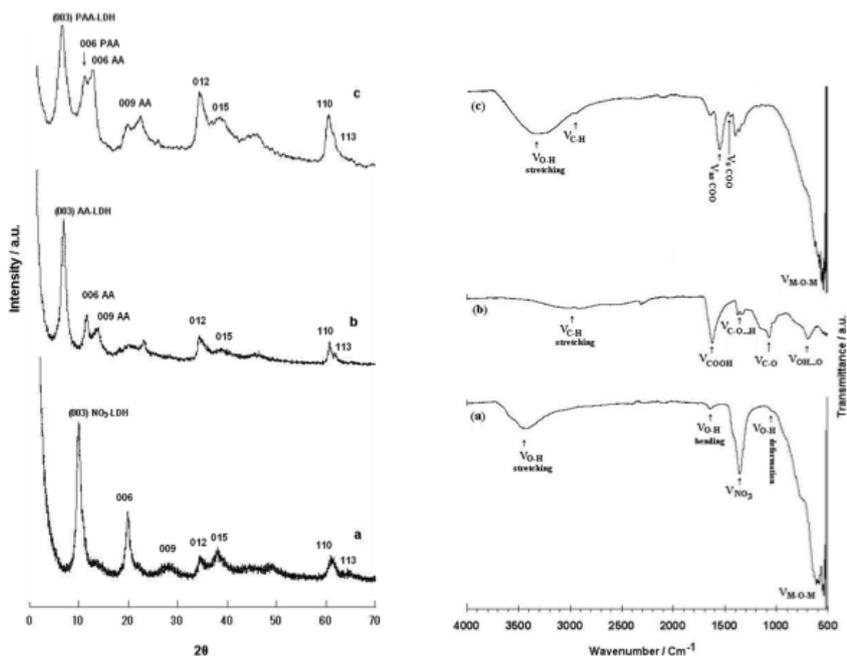


Figure 1.. SEM images of NO<sub>3</sub>-LDH (a), AA-LDH (b), and PAA-LDH (c) hybrids



**Figure 2.** X-ray diffraction patterns of NO<sub>3</sub>-LDH (a) AA-LDH (b), PAA-LDH (c)

**Figure 3.** Infrared spectra of, NO<sub>3</sub>-LDH (a), PAA (b), and PAA-LDH (c)

Figure 2 shows the XRD patterns of LDH, AA-LDH and PAA-LDH nanocomposites. Pattern A indicates the formation of the NO<sub>3</sub> form of LDH with sharp and symmetric (001) reflections. Using Bragg's law ( $n\lambda = 2d \sin \theta$ ), the basal d-spacing was calculated to be 8.9 Å. The anion exchange process of AA anions resulted in a shift to a lower angle with an increase in the basal d-spacing. The calculated gallery height was found to be 12.6 Å (pattern B). The AA-LDH nanocomposites

interlayer distance was calculated by subtracting the inorganic layer thickness (4.8 Å) from the d<sub>003</sub>-spacing.

The determined value (7.8 Å) was slightly larger than AA molecular length (6.0 Å). However, LDH attaches its interlayer anions through an electrostatic interaction. Thus, we speculated that AA molecules were stacked into LDH as a monolayer through the attachment of AA carboxyl groups with the LDH positive layers. In the case of PAA-LDH (pattern c), the

basal spacing reflections are broadened, indicating a turbostratic disorder of the LDH

layers. This result was an indication of the stacking polymerization process of AA-LDH.

Figure 3a exhibited the characteristic bands of NO<sub>3</sub>-LDH, in particular the lattice vibration modes ( $\nu_{M-O-M}$ ,  $\nu_{M-O}$ ) at 540, 630, and 775 cm<sup>-1</sup> and the asymmetric stretching band of the interlayer nitrate

( $\nu_{NO_3}$ ) at 1365 cm<sup>-1</sup> as well as the vibration modes of the hydroxyl groups of LDH layers ( $\nu_{O-H}$ ); bending at 1050 cm<sup>-1</sup>, deformation at 1660 cm<sup>-1</sup> and stretching at 3450 cm<sup>-1</sup>. Figure 3b showed the characteristic features of PAA. The stretching vibration modes of alkyl groups ( $\nu_{C-H}$ ) were detected at 3030 cm<sup>-1</sup>. The stretching vibration band of COOH group was assigned at 1709 cm<sup>-1</sup>. The combinations of the in-plane deformation modes of C-

O...H and the stretching vibration modes of C-O were recorded at 1400-1350 cm<sup>-1</sup> and 1150-1100 cm<sup>-1</sup>, respectively. The broad band at 800 cm<sup>-1</sup> is associated to an out-of-plane OH...O deformation, indicating a strong intermolecular hydrogen bonding. As a result of intercalation of PAA with LDH (spectrum c), new bands are emerged such as asymmetric and symmetric modes of COO<sup>-</sup> at 1560 and 1460 cm<sup>-1</sup>, respectively, besides the characteristic bands of PAA and LDH.

The lack of the inorganic anion (NO<sub>3</sub>) in the interlayer gallery indicated the formation of monophasic nanocomposites of PAA-LDH.

The FT-IR data emphasized the grafting between PAA and LDH through electrostatic interaction. Such kind of interaction enables LDH nanoparticles to act as network points in the composite structure after the polymerization process of AA units. In addition, this crosslinking behaviour improves the hydrophilic capacity of PAA through the increase of the polymeric PAA chain length. Moreover, it decreases the dissolution behaviour of the free applicable PAA into soils, where PAA is highly soluble in water.

By using a 0.2 wt % of soil stabilizer, PAA-soil aggregates were collapsed after 15 min, while PAA-LDH soil aggregates were collapsed after 96 min. With the increase of soil stabilizer-concentration to 0.4 wt % and 0.6 wt %, the collapsing time of the aggregates was increased. The PAA-treated soil-aggregates showed an explosive collapse to the initial integrity of soil, while the PAA-LDH modified-aggregates showed a gradual collapse. The collapse of PAA-LDH soil-aggregates is characterized by an initial collapse on the edges of the aggregates followed by a slow collapse rate into secondary aggregates of smaller size, and finally the secondary aggregates were collapsed. In conclusion, PAA-LDH modification

stabilized the soil aggregates and improved the water-stability.

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