



# Large-scale fabrication of linear low density polyethylene/layered double hydroxides composite films with enhanced heat retention, thermal, mechanical, optical and water vapor barrier properties



Jiazhuo Xie<sup>a</sup>, Kun Zhang<sup>a</sup>, Qinghua Zhao<sup>a</sup>, Qingguo Wang<sup>b,\*</sup>, Jing Xu<sup>a,\*\*</sup>

<sup>a</sup> College of Chemistry and Material Science, Shandong Agricultural University, 61 Daizong Street, Tai'an 271018, PR China

<sup>b</sup> College of Food Science and Engineering, Shandong Agricultural University, 61 Daizong Street, Tai'an 271018, PR China

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## ABSTRACT

Novel LDH intercalated with organic aliphatic long-chain anion was large-scale synthesized innovatively by high-energy ball milling in one pot. The linear low density polyethylene (LLDPE)/layered double hydroxides (LDH) composite films with enhanced heat retention, thermal, mechanical, optical and water vapor barrier properties were fabricated by melt blending and blowing process. FT IR, XRD, SEM results show that LDH particles were dispersed uniformly in the LLDPE composite films. Particularly, LLDPE composite film with 1% LDH exhibited the optimal performance among all the composite films with a 60.36% enhancement in the water vapor barrier property and a 45.73 °C increase in the temperature of maximum mass loss rate compared with pure LLDPE film. Furthermore, the improved infrared absorbance (1180–914 cm<sup>-1</sup>) of LLDPE/LDH films revealed the significant enhancement of heat retention. Therefore, this study prompts the application of LLDPE/LDH films as agricultural films with superior heat retention.

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## 1. Introduction

The application of agriculture films had increased dramatically in recent decades, which was attributed to the benefits in increasing soil temperature, reducing weed pressure and certain insect pests, conserving moisture and improving crop yields [1,2]. It was estimated that millions of tons of agricultural films were used worldwide every year [3]. Many polymers such as linear low-density polyethylene (LLDPE), polyvinyl chloride (PVC) and ethylene vinylacetate (EVA), had been extensively used as agricultural films [4–6]. Among them, linear low-density polyethylene (LLDPE), was the most common material for agricultural films, due to the low cost, easy processability, excellent chemical resistance, high durability, well flexibility, high puncture resistance and fine mechanical stretch properties [7,8].

However, the low infrared absorption of LLDPE matrix in the range of 1111–909 cm<sup>-1</sup> which was the main radiant heat loss region emitted from the earth's surface, decreased the heat retention of LLDPE-based agricultural films [9]. This had an adverse effect on the plant growth, especially in the cold night. Therefore,

it was necessary to develop functional films with enhanced heat retention. One of the most effective ways was modification of the LLDPE with the inorganic fillers, e.g. China clay, French chalk, metal oxides (e.g. TiO<sub>2</sub>, ZnO and Sb<sub>2</sub>O<sub>3</sub>) and silica [6]. Nevertheless, entirely different refraction coefficient between these additives and LLDPE matrix and the non-uniform distribution of these additives in LLDPE films, reduced the visible light transmittance of LLDPE composite films. Furthermore, the key absorption regions of these additives were contradictory with overnight infrared radiant heat loss ranges from earth. Therefore, great interest had been attracted to synthesize nano-sized additives with the nearest refraction coefficient and appropriate infrared absorption in recent years.

Layered double hydroxides (LDH), are a class of synthetic layered clays with diverse and replaceable anions in the interlayer space [10–14]. The functional LDH can be obtained by intercalating anions with specific function (e.g. selective infrared absorption) into the interlayer space. Moreover, the refraction coefficient of LDH was similar to that of LLDPE. Hence, LLDPE-based composite films with highly efficient heat retention can be fabricated by adding the LDH with selective infrared absorption. Several works have been made in the past few years. Xu et al. prepared MgAl–CO<sub>3</sub> LDH and MgAl–(CO<sub>3</sub>, SO<sub>4</sub>) LDH as fillers to improve the heat retention of polyethylene films [15,16]. Wang et al. obtained low-density polyethylene composite films with enhanced infrared

\* Corresponding author.

\*\* Corresponding author.

E-mail addresses: [wqgyyy@126.com](mailto:wqgyyy@126.com) (Q. Wang), [jiaxu@sdau.edu.cn](mailto:jiaxu@sdau.edu.cn) (J. Xu).

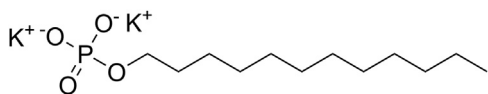


Fig. 1. Chemical structural formula of PDP.

absorption containing LDH particles intercalated with organic anion containing P–O bonds with infrared absorption region in  $1180\text{--}914\text{ cm}^{-1}$ , corresponding to the main radiant heat loss region emitted from the earth's surface [6,17,18]. However, the disadvantages of the LDH mentioned above, such as complicated preparation process, low quantity and unsuitable infrared absorption range caused a major limitation for the industrial application as agricultural films [19–22].

High-energy ball milling, also called mechanochemical method, can obtain a larger number of LDH products with expected properties in a reaction process by grinding inorganic salts and organic reactants in one pot [23–25]. Potassium dodecyl phosphate (PDP,  $\text{C}_{12}\text{H}_{25}\text{PO}_4\text{K}_2$ ) is an aliphatic long-chain reactant. The chemical structural formula is shown in Fig. 1. The P–O bonds endow the PDP strong infrared absorption and the long aliphatic chains are compatible with the LLDPE matrix during the fabrication process [26,27]. Based on these advantages, LDH with suitable infrared absorption range can be large-scale synthesized, which makes it possible to develop LLDPE/LDH films as agricultural films with superior heat retention for commercial application.

In this work, we synthesized the LDH with selective infrared absorption using high-energy ball milling and LLDPE/LDH films with superior heat retention using melt blending and blowing process. The effects of LDH content on the structure and properties (thermal, mechanical, water vapor barrier, optical properties and heat retention) of LLDPE/LDH films were investigated.

## 2. Materials and methods

### 2.1. Materials

Linear low density polyethylene (LLDPE) (trade name: DGM1820) with melt flow rate (MFR)  $2.65\text{ g}\cdot(10\text{ min})^{-1}$  ( $190\text{ }^\circ\text{C}$ , 5.00 kg), was supplied by Sinopec Group (Tianjin, China). Al ( $\text{NO}_3$ )<sub>3</sub>·9H<sub>2</sub>O (99%), Zn( $\text{NO}_3$ )<sub>2</sub>·6H<sub>2</sub>O (99%) and NaOH (99%) were obtained by Aladdin Reagent Co., Ltd. (Shanghai, China). Potassium dodecyl phosphate (PDP) (97%) was purchased from Lihou Chemical Co., Ltd. (Guangzhou, China). All reagents were analytically pure and used without treatment.

### 2.2. Synthesis of ZnAl-PDP LDH

The ZnAl-PDP LDH was large-scale synthesized by high-energy ball milling using a QM-3SP2 planetary ball mill [28]. A mixture of 19.2 g (0.48 mol) NaOH, 51.3 g (0.15 mol) PDP, 22.5 g (0.06 mol) Al ( $\text{NO}_3$ )<sub>3</sub>·9H<sub>2</sub>O and 53.5 g (0.18 mol) Zn( $\text{NO}_3$ )<sub>2</sub>·6H<sub>2</sub>O was milled for 30 min. The autorotation rate was 400 rpm while the revolution speed was constant at 200 rpm. Four agate pots (Inner volume: 500 cm<sup>3</sup>) and a number of agate balls (Diameter: 20 mm, Quantity: 8; Diameter: 10 mm, Quantity: 400; Diameter: 6 mm, Quantity: 2000) were used at a mill process. The total volume of agate-balls and raw material was three quarters of the agate pot. The slurry product was washed 3 times and dried at  $70\text{ }^\circ\text{C}$  for 48 h. The obtained white ZnAl-PDP LDH powders (180 g) were ground and filtrated using the 800 mesh (0.015 mm) sieve. The ZnAl-PDP LDH product was abbreviated to LDH in the text below.

### 2.3. Fabrication of LLDPE/LDH films

The LLDPE/LDH composite films were fabricated via melt blending and blowing process. Firstly, LLDPE and LDH powder were mixed by a SHR-10A high speed mixer for 10 min with a rotary speed of 60 rpm. The obtained mixture was fed to a SHJ135 co-rotating twin screw extruder at a rate of  $600\text{ g min}^{-1}$ . The temperature conditions was 165/202/186/186/186/180/202  $^\circ\text{C}$  from the barrel section just after the feed throat to the die. Then, the LLDPE/LDH composites were extruded into films through a SGXM-1800 single-screw blown film unit at a temperature difference from feed to die zone between  $130\text{ }^\circ\text{C}$  and  $155\text{ }^\circ\text{C}$ . The fabrication process of LLDPE/LDH composite films was shown in Fig. 2. The film thickness was controlled at  $70 \pm 1\ \mu\text{m}$ . The mass ratios of LLDPE and LDH were 100/0, 99.5/0.5, 99/1, 98/2 and 96/4 respectively, abbreviated as LDH-0, LDH-0.5, LDH-1, LDH-2 and LDH-4 in the text below. For each sample, the total mass was constant (4000 g). All the films were stored in a desiccator at room temperature prior to test.

### 2.4. Characterization of LDH and LLDPE/LDH films

Fourier transform infrared (FT IR) spectra were obtained on a Thermo Nicolet 380 spectrometer in the range  $4000\text{--}400\text{ cm}^{-1}$  using KBr disk method. The resolution was  $4\text{ cm}^{-1}$  by co-adding 32 consecutive scans. The X-ray diffraction (XRD) patterns were recorded on a BRUKER D8 Advance diffractometer (Cu K $\alpha$  radiation ( $\lambda = 1.54056\text{ \AA}$ )) at 40 mA and 40 kV. Scans were taken from  $1^\circ$  to  $50^\circ$  with a scan speed of  $4^\circ\text{ min}^{-1}$  and a step of  $0.02^\circ$ . A JEOL JSM-6380LV scanning electron microscope (SEM) was used to observe the morphology of the sample films fracture surface. The sample films were first frozen in liquid nitrogen, then broken them off. The fracture surfaces were coated with gold before observation.

### 2.5. Thermal analysis

The melting and crystallization behavior were investigated using a Netzsch DSC 200PC differential scanning calorimeter (DSC) under nitrogen atmosphere ( $50\text{ mL min}^{-1}$ ) with 8–10 mg samples with heating and cooling rate of  $10\text{ }^\circ\text{C min}^{-1}$ . Firstly, the samples were heated to  $200\text{ }^\circ\text{C}$ , held at  $200\text{ }^\circ\text{C}$  for 3 min for erasing the thermal history, then cooled to  $0\text{ }^\circ\text{C}$  and heated to  $200\text{ }^\circ\text{C}$  once again. The values were reported during the cooling scan and the second heating process. Thermogravimetric analysis (TGA) traces were carried out on Shimadzu DTG-60A thermal analysis instrument in the range  $30\text{--}600\text{ }^\circ\text{C}$  with a heating rate of  $10\text{ }^\circ\text{C min}^{-1}$  in air ( $100\text{ mL min}^{-1}$ ).

### 2.6. Mechanical properties

Tensile and tear test were measured using a SUNS UTM2502 electronic universal testing machine according to GB/T 1040.3-2006 and QB/T 1130-91, respectively. Five specimens of each sample film were measured and the average results were recorded.

### 2.7. Water vapor barrier properties

The water vapor transmission (WVT) was performed using a PERME W3/030 automatic water vapor transmission tester at a constant temperature of  $23\text{ }^\circ\text{C}$  under 57% RH conditions with GB 1037-88. Three specimens of each sample film were measured with circles (diameter 0.074 m) and the average value was recorded.

The WVT was calculated according to the following Eq. (1):

$$\text{WVT}(\text{g/m}^2\cdot 24\text{h}) = (24\cdot\Delta m)/(A\cdot t) \quad (1)$$

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