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Biodegradable Poly(propylene carbonate)/Layered Double Hydroxide Composite Films with Enhanced Gas Barrier and Mechanical Properties[*]

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Abstract Relatively well crystallized and high aspect ratio Mg-Al layered double hydroxides (LDHs) were prepared by co-precipitation process in aqueous solution and further rehydrated to an organic modified LDH (OLDH) in the presence of surfactant. The intercalated structure and high aspect ratio of OLDH were verified by X-ray diffraction (XRD) and scanning electron microscopy (SEM). A series of poly(propylene carbonate) (PPC)/OLDH composite films with different contents of OLDH were prepared *via* a melt-blending method. Their cross section morphologies, gas barrier properties and tensile strength were investigated as a function of OLDH contents. SEM results show that OLDH platelets are well dispersed within the composites and oriented parallel to the composite sheet plane. The gas barrier properties and tensile strength are obviously enhanced upon the incorporation of OLDH. Particularly, PPC/2%OLDH film exhibits the best barrier properties among all the composite films. Compared with pure PPC, the oxygen permeability coefficient (OP) and water vapor permeability coefficient (WVP) is reduced by 54% and 17% respectively with 2% OLDH addition. Furthermore, the tensile strength of PPC/2%OLDH is 83% higher than that of pure PPC with only small lose of elongation at break. Therefore, PPC/OLDH composite films show great potential application in packaging materials due to its biodegradable properties, superior oxygen and moisture barrier characteristics.

Keywords: Poly(propylene carbonate); Layered double hydroxide; Gas barrier properties; Biodegradable composite; Packaging.

INTRODUCTION

Barrier materials have attracted considerable attention in the fields of pharmaceuticals packaging and food preservation in order to protect them from detrimental effects of moisture and oxygen[1, 2]. As water vapor and oxygen in the environment can eventually lead to deterioration of food and druggery, the effectiveness of barrier materials in preventing product degradation is directly dependent upon their impermeability to degradative gases. Though inorganic materials such as glass, nano-clays offer excellent barrier properties to gases, they are not suitable for roll to roll processing, flexible and lightweight applications[3]. At the same time, polymers are normally lightweight, flexible, inexpensive and easily processable, but they usually exhibit poor barrier performance[4–6] because of the presence of free volume between molecular chains which can provide convenience for permeation of gases. Therefore, a secondary phase and/or inorganic component added as

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filler/layer to the neat polymer may be a good way to achieve high gas barriers.

Poly(propylene carbonate) (PPC) is a biodegradable aliphatic polycarbonate, which is an amorphous polymer made by alternating copolymerization of carbon dioxide (CO_2) and propylene oxide (PO) using different catalysts[7–9]. The resulting PPC exhibits the structure as illustrated in Fig. 1. For years, our laboratory has successfully synthesized high molecular weight PPC using supported catalyst and its production is known to have been industrialized[10, 11]. PPC is an eco-friendly biodegradable polymer whose synthesis recycles carbon dioxide. PPC has chemical and physical properties such as compatibility with other materials, high translucence, nontoxicity and good processibility[12]. Such properties are advantageous in new materials for packaging applications. PPC has a relatively high density (~1.3 g/cm^3) which means that it has a much closer molecular chains arrangement and much smaller free volume. Therefore, pure PPC has relatively good barrier performance: the oxygen permeability coefficient (OP, 23 °C, 0% RH) and water vapor permeability coefficient (WVP, 23 °C, 85% RH) of pure PPC is ~2.25 cm^3·mm/(m^2·24 h) and ~1.05 g·mm/(m^2·24 h), respectively[13]. However, the barrier and mechanical properties must be improved to expand the application of PPC in packaging field. Aluminum flake[13] and exfoliated graphite[14] with high aspect ratio have been used to enhance the gas barrier and mechanical properties of PPC. But the monotonous color and non-translucence of the composite films caused researchers to develop other satisfying fillers instead. Furthermore, inorganic oxides on polymeric substrates in a layered architecture have been obtained by following complex deposition techniques such as atomic/molecular layer deposition and plasma enhanced chemical vapor deposition[15–17]. They all achieve ultra-high barrier composite films. Nevertheless, all the reported techniques and methods are based on the uneconomical way, which can be considered very difficult to large scale industrial operations.

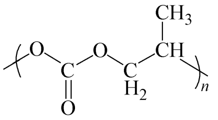

Fig. 1 Structure of poly(propylene carbonate) (PPC) (M_n = 80000)

Layered double hydroxides (LDHs) are a class of hydrotalcite-like or anionic clays whose structure is based on brucite-like layers[18–20], are generally expressed as $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2][A^{n-}_{x/n}mH_2O]$ (M^{2+} and M^{3+} are divalent and trivalent metal cations, such as Mg^{2+}, Al^{3+} respectively, A^{n-} is *n*-valent anion, such as CO_3^{2-}, SO_4^{2-} or NO_3^{-}). The resulting LDHs exhibits the structure as illustrated in Fig. 2. The identities of M^{2+} and M^{3+} may be varied over a wide range, and the interlayer anion (A^{n-}) can be replaced by a number of different anion groups. This flexibility in composition allows functional LDHs with a wide variety of properties to be prepared and is one of their most attractive features[21–24]. LDHs are one type of important layered materials with 2D-organized structure. The barrier properties of polymer can be greatly enhanced if LDHs layers are exfoliated and oriented in the matrix. Because of the strong interlayer electrostatic interactions, small gallery space, and hydrophilic property of LDHs, the interlayer CO_3^{2-} anions must be converted to other bigger anions using anionic surfactants such as sodium dodecyl sulphate (SDS) in order to enable their delamination and exfoliation. Recently, LDHs-based organic-inorganic functional materials have been widely explored in optical devices, photoluminescence, electrochemical sensors and pharmaceutical field[25–30], and the mechanical and barrier properties are enhanced obviously by the incorporation of LDHs fillers into the polymer matrix.

Recently, using exfoliated LDHs nanosheets as building blocks, accessible polymers as matrix, Duan *et al.* reported transparent and flexible multilayer films, which are fabricated by the alternating assembly of cellulose acetate (CA) and LDH nanoplatelets[31]. The films exhibit tremendously enhanced oxygen barrier properties, which are much superior to the previously reported inorganic flake-filled barrier film. Du *et al.* prepared PPC/MgAl-LDH exfoliated nanocomposites by solution intercalation of PPC into the galleries of organic modified MgAl-LDH (OMgAl-LDH)[32]. The thermal properties and tensile strength of PPC are enhanced by the incorporation of OMgAl-LDH. But the solution intercalation process is complicated, high cost and not suitable for industrialization. This gives us impetus to take the challenge of improving barrier properties and tensile strength of PPC/OLDH composite film by a melt-blending method.

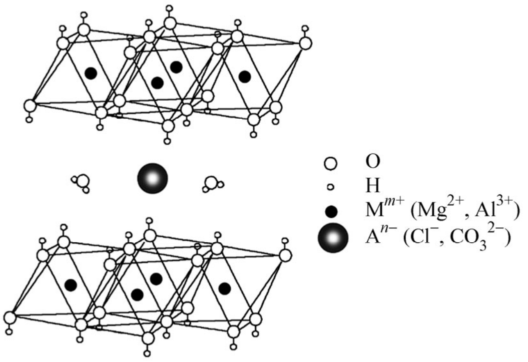

Fig. 2 Structure of layered double hydroxides (LDHs)

To our knowledge, there have been no reports on PPC/OLDH composite films *via* a melt-blending method and their properties for use as packaging materials. In this work, we prepared PPC/OLDH composite films with different OLDH contents *via* a melt blending method, and the effects of OLDH content on the oxygen permeability, water vapor permeability, morphology and mechanical properties of PPC/OLDH composite films were investigated. The incorporation of well crystallized structure and high aspect ratio of OLDH is expected to improve both the barrier and the mechanical properties of PPC.

EXPERIMENTAL

Materials

Industrial grade poly(propylene carbonate) (PPC, M_n = 80000, PDI = 1.9) with the melt flow rate (MFR, 190 °C, 2.16 kg) of 8.6 g/10min, was supplied by Tianguan Enterprise Group (Henan, China). $Al(NO_3)_3 \cdot 9H_2O$, sodium dodecyl sulphate (SDS), sodium dodecylbenzene sulfonate (SDBS) were purchased from Damao Chemical Reagent Factory (Tianjin, China). $Mg(NO_3)_2 \cdot 6H_2O$ and ammonium carbonate were purchased from Guangzhou Chemical Reagent Factory (Guangzhou, China). All chemicals were of analytical purity and used as received. Ultrapure Milli-Q water was used throughout all the experiments. PPC was dried in a vacuum oven at 80 °C for 24 h prior to use.

Synthesis of Mg-Al-CO_3 LDH and Intercalated LDH

Mg-Al LDH used in this study was synthesized on the basis of the previous report with modification[33]. First, $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ were mixed with Mg/Al molar ratio of 3, and then dissolved in deionized water to prepare an aqueous solution. The second aqueous solution of NH_4OH and $(NH_4)_2CO_3$ with molar ratios of 20 was prepared by dissolving in deionized water. The two aqueous solutions were added dropwise alternately to a three-necked, round-bottomed flask with moderate deionized water at 313 K, during which time the pH of the slurry was controlled in a range of 8.9–9.3. After both solutions were completely added, the slurry was stirred for another 90 min and then aged for 10 h at 313 K. After cooling to room temperature, the precipitates were filtered, subsequently washed with deionized water for several times, and dried at 393 K overnight. The white precipitate was the desired Mg-Al LDH.

The Mg-Al LDH was broken into power, subsequently calcined at 773 K under O_2 atmosphere for 6 h. We could obtain a sample of MgO and Al_2O_3, which recorded as LDO. And finally the mixed oxide was dissolved in water, 2% SDS, 2% SDBS aqueous solutions, respectively. And then stirred for 10 h under the protection of nitrogen at 313 K to prepare the intercalated LDH, which signed as LDH-H_2O, LDH-SDS (which also recorded as OLDH), LDH-SDBS respectively.

Preparation of PPC/OLDH Composite Films

The modified OLDH was blended with PPC in a Hakke Rheomix-600 mixer with two roller rotors at 165 °C and a rotary speed of 50 r/min for 7 min. The weight ratios of LDH and PPC were at 0/100, 1/99, 2/98, 3/97 respectively. For each sample, 50 g materials in total were fed into the mixer. The pure PPC was also melted in the same conditions for comparison. PPC/OLDH composites were compressed into sheets at 10 MPa and 165 °C for 5 min. The thickness was controlled at 0.5 mm or 1.0 mm. All the films were stored in a desiccator at room temperature prior to test.

Characterization

X-ray diffraction (XRD)

The test was performed on an Empyrean Diffractometer (Cu Kα radiation (λ = 0.154 nm)) at ambient temperature. Scans were taken from 1.5° to 80° with a step of 0.02° at 3 kW. The LDH, LDO and OLDH samples were tested in fine powder form.

Scanning electron microscopy (SEM)

OLDH fine power was firstly dispersed in acetone at a very low concentration, and then dropped onto a piece of copper, finally dried under an infrared lamp for 10 min. The morphology of the OLDH and fractured surfaces were observed with a scanning electron microscope (SEM, JEOL JSM-6330F). For the fractured surface measurements, PPC/OLDH films were frozen in liquid nitrogen and fragmented to produce a cross-section. All the specimens were coated with a thin layer of gold prior to examination.

Static tensile properties

The static tensile properties were measured at 25 °C and relative humidity (RH) of 50% using a CMT-4104 tensile tester (SANS, Shenzhen, China) according to the standard of ASTM D638. The crosshead speed was set at 50 mm/min. PPC/OLDH sheets were cut into dumbbell shape with dimensions of 25 mm × 4.3 mm × 1.0 mm. Five specimens of each sample were measured and the average results were recorded. Moreover, in order to eliminate the influence of temperature and humidity before they were tested, all the samples were aged for 24 h at 25 °C and 50% RH before testing.

Oxygen transmission rate (OTR)

The oxygen transmission rate (OTR) measurements were performed at a constant temperature of 23 °C under dry conditions according to ASTM D3985-05. The OTR of PPC/OLDH films were measured using an Y202D oxygen permeation analyzer (GBPI Packing Test Instruments Co. Ltd, Guangzhou, China). It adopts coulometry theory and equal-pressure method. It has two chambers separated by the test sample. The upper one is filled with oxygen (test gas) and the lower is filled with nitrogen (carrier gas). The oxygen which permeates through test sample is picked up by nitrogen, and then carried to the sensor. The amount of oxygen measured by the sensor determines the transmission rate (OTR). Because of the OTR value is relative to both thickness and oxygen partial pressure difference between rich and poor oxygen atmospheres, results were normalized using the following Eq. (1):

$$\mathrm{OP} = \frac{\mathrm{OTR} \times e}{\Delta p} \tag{1}$$

where OP is the oxygen permeability coefficient ($\mathrm{cm^3 \cdot mm/(m^2 \cdot 24\ h \cdot 0.1\ MPa)}$), OTR is the oxygen transmission rate ($\mathrm{cm^3/(m^2 \cdot 24\ h)}$), e is the film thickness (mm), and Δp is the oxygen partial pressure difference. In this work, the oxygen Δp is 0.1 MPa. Moreover, all samples were cut into a circular shape of 50 $\mathrm{cm^2}$ film and two films of each sample were tested and the results were averaged.

Water vapor transmission rate (WVTR)

The water vapor transmission rate (WVTR) measurements were performed at a constant temperature of 23 °C under 85% RH conditions. The WVTR of PPC/OLDH films were measured with “Infrared detection sensor methods”, (ISO 15106-2) using a WVTR analyzer (PERMATRAN-W Model 3/61, Mocon. Inc, USA). In the testing process, the test gas (water vapor) is present in the upper half of the test cell while nitrogen (carrier gas) is routed through the lower half of the test cell. The cell halves are separated by a sample of the material to be tested. Water vapor which permeates the material is picked up by the nitrogen (carrier gas). And then, the nitrogen exits the cell and passes through the sensor. Mocon WVTR software is used to determine the water vapor transmission rate (WVTR). The system provides a fixed number of test cycles process and WVTR is determined when the sample has reached equilibrium. Then the water vapor permeation coefficient (WVP) is calculated according to the following Eq. (2):

$$\mathrm{WVP} = \mathrm{WVTR} \times e \tag{2}$$

where WVP is the water vapor permeability coefficient (g·mm/(m^2·24 h)), WVTR is the water vapor transmission rate (g/(m^2·24 h)), e is the film thickness (mm). The measurements were performed in triplicate for each sample.

RESULTS AND DISCUSSION

Structure of LDH, LDO, OLDH

The X-ray diffraction (XRD) patterns of the synthesized magnesium-aluminum samples were presented in Fig. 3. As shown in Fig. 3(a) (pattern 1), the diffraction peaks at around 11.6°, 22.5°, 34.3°, 62.3° are corresponding to characteristics of LDH[33]. No other crystalline phase was detected, indicating the high and regular crystallinity of LDH. According to the XRD patterns of pristine LDH, the (003) basal plane of LDH observed at about 11.6° corresponds to an interlayer spacing of 0.78 nm (calculated from the Bragg equation). We can see that calcination in O_2 at 773 K for 6 h of powered LDH containing carbonate anions affords an almost amorphous mixed metal oxide phase (Fig. 3a (pattern 2)) which can be rehydrated to reconstruct an LDH phase (Fig. 3a (patterns 3–5)) containing interlayer hydroxide ions after exchanging with relevant aqueous solutions.

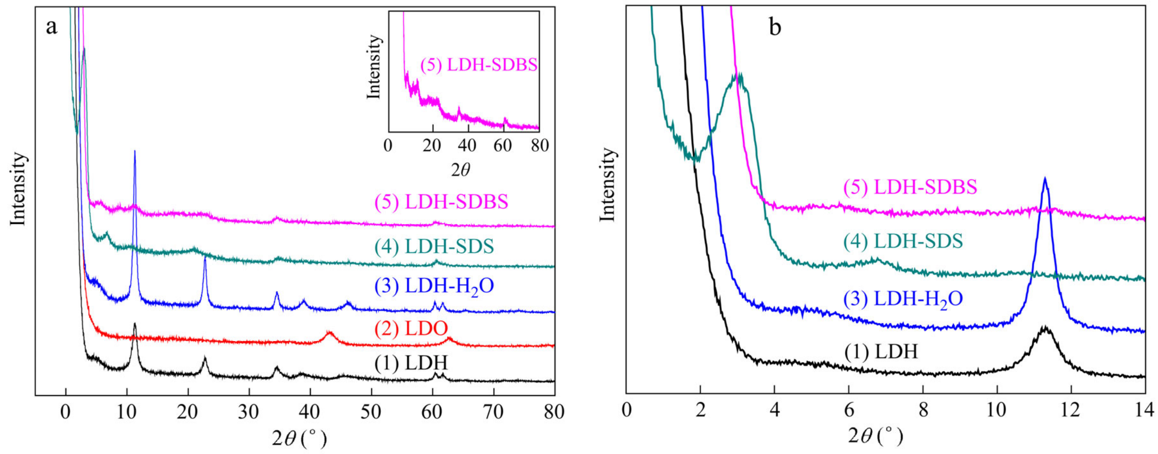

Fig. 3 XRD patterns of the synthesized magnesium-aluminum samples ((a) at a large angle range; (b) at a small angle range): (1) after being dried at 393 K for 10 h; (2) after calcination in O_2 at 773 K for 6 h; after being rehydrated in (3) water, (4) SDS aqueous solution and (5) SDBS aqueous solution

As shown in Fig. 3(a) (pattern 3), compared with LDH, the diffraction peaks of LDH-H_2O do not migrate at all. This means that water molecule has no effect on intercalation of LDH, which is mainly because water molecule is too small. At the same time, the flat baseline and shaped peaks indicate that LDH-H_2O has a highly crystalline structure after rehydration. However, the messy baseline and peaks in Fig. 3(a) (pattern 5) show a relatively poor crystallinity in LDH-SDBS. The diffraction peak of (003) basal plane moves from 11.6° to 6.1° corresponds to a larger *d*-spacing. All this phenomena reveal a partly intercalated structure in LDH-SDBS which mainly because SDBS is too big and it is difficult to enter into the layers of LDH.

Because of the appropriate size of SDS, LDH-SDS has a high crystallinity and very good intercalated structure (Fig. 3a (pattern 4)). As shown in Fig. 4, owing to the different charge of dodecyl sulfate anions as that of the nanoplatelets in LDH, the Coulomb attraction is dominated for the adsorption of SDS by LDH. At the same time, the SDS molecules would be uniformly tilted at a certain angle to the surface of nanosheets as the amount of their adsorption is enough for packing (Fig. 5)[34]. Most importantly, the increased interlayer spacing (nearly four times larger than the initial LDH) and organic segment (SDS) in OLDH are expected to exhibit better compatibility and barrier properties in PPC/OLDH (Figs. 3b and 5).

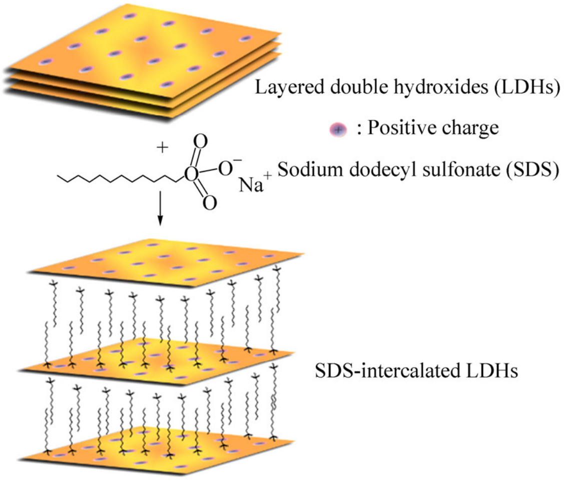

Fig. 4 Schematic of intercalation of SDS in LDH

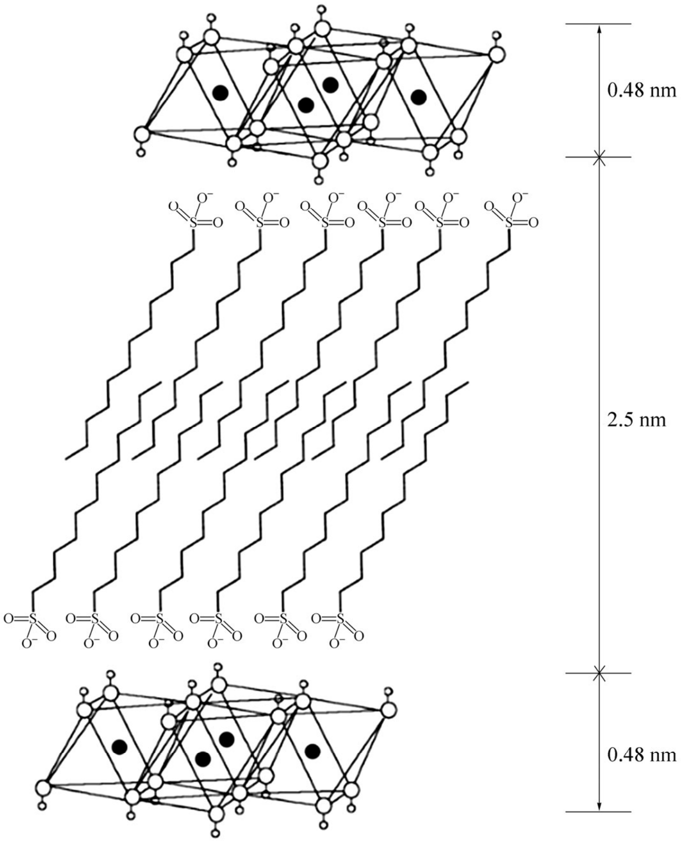

Fig. 5 Crystallographic structure of LDH-SDS

Morphology of PPC/OLDH Composite Films

As shown in Fig. 6(a), OLDH particles exhibit platelet structure with average size about 8.83 μm. Because of its nanoscale thickness, OLDH platelets have been prepared with high aspect ratio. From morphologies of the cross section of the PPC/OLDH composites, we can see that OLDH are well dispersed within the composites and oriented parallel to the composite sheet plane. The obscure interface between OLDH and PPC indicates the good interfacial adhesion between OLDH and PPC matrix (Fig. 6c). However, for PPC/3%OLDH composite, some cracks can be observed at the interface of OLDH and PPC (Fig. 6d). This phenomenon shows that the agglomeration of OLDH sheets may occur within PPC matrix. The existence of the cracks might bring negative effect on the tensile strength and gas barrier performance of the composite films.

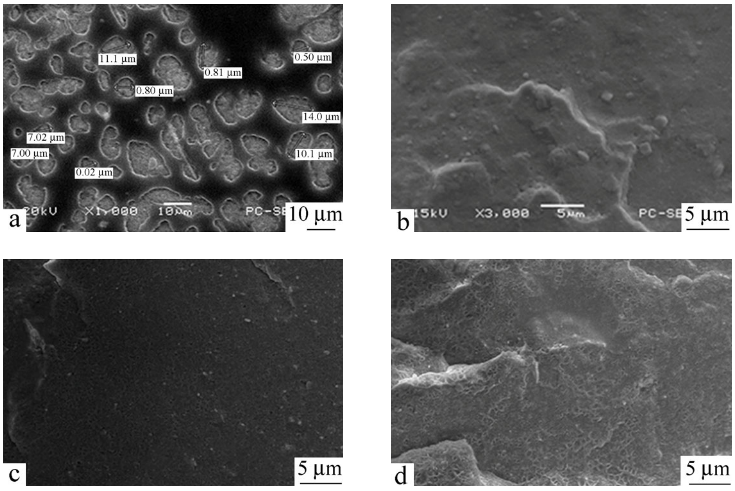

Fig. 6 SEM images of OLDH and PPC/OLDH composite films: (a) OLDH, (b) Pure PPC, (c) PPC/2%OLDH and (d) PPC/3%OLDH

Tensile Strength of PPC/OLDH Composite Films

The tensile strength (TS) and elongation of PPC/OLDH composite films were examined using a temperature-controlled tensile tester. As shown in Fig. 7(a) and Table 1, we can see that the TS of PPC/OLDH films are improved greatly comparing with pure PPC. Furthermore, the tensile strength increased by 83% upon the incorporation of 2% OLDH, but the elongation at break of the PPC/OLDH composite decreases slightly with the incorporation of OLDH. In short, the addition of OLDH leads to the improvement in tensile properties of the composite films.

Table 1. Tensile strength of the PPC/OLDH composite films

Sample	Tensile strength (MPa)	Elongation at break (%)
PPC	9.38 ± 0.4	939 ± 5
PPC/1%OLDH	16.5 ± 0.5	678 ± 5
PPC/2%OLDH	17.2 ± 0.2	719 ± 5
PPC/3%OLDH	14.8 ± 0.4	745 ± 5

As well known, the mechanical performance of polymer/filler blend system is dependent on the particle size, the content of the filler, and the interfacial adhesion between the fillers and the polymer matrix, as well as the dispersion of the fillers within the matrix[35]. PPC can be described as a thermoplastic polymer which is ductile and flexible at temperatures higher than 20 °C[36], while the oriented OLDH particle in PPC matrix is rigid filler. Therefore, the TS of PPC is improved greatly with the addition of OLDH. At the same time, as the high aspect ratio of the OLDH and the good adhesion between PPC and OLDH, there is no significant change in elongation when the OLDH is added.

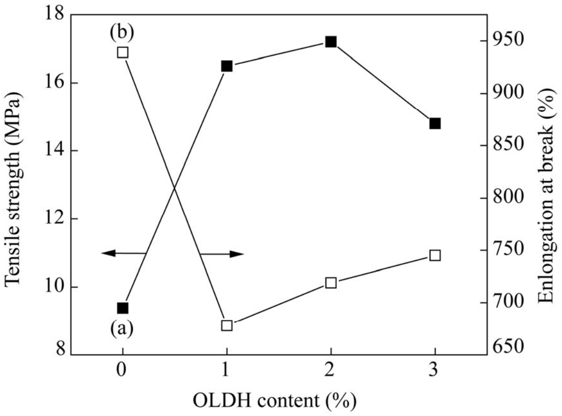

Fig. 7 Tensile properties for neat PPC and PPC/OLDH (different OLDH) blends: (a) tensile strength and (b) elongation at break

Barrier Properties of PPC/OLDH Composite Films

As well known, layered inorganic particles offer high barrier properties to gases. Adding a secondary phase and/or inorganic component as filler/layer to the neat polymer can be a good way to achieve high gas barriers. It is believed that the addition of layered inorganic particles in the polymeric matrix would improve its barrier performance by inducing a long diffusion length as gases diffuse through the material, decelerating the process of penetration[37].

In this work, the OTR and WVTR of PPC/OLDH composite films were investigated to evaluate the enhancement effect of OLDH filling on the oxygen and water vapor barrier performance of PPC. The oxygen permeability coefficient (OP) and water vapor permeability coefficient (WVP) are calculated from the measured OTR and WVTR values. As shown in Table 2, we can obviously see that both OP and WVP of the PPC/OLDH composite films decrease with the increase of the content of OLDH. Furthermore, compared with the pure PPC, the OP and WVP values are reduced by 54% and 20% respectively just upon 2% OLDH incorporation. This phenomenon can be attributed to the high aspect ratio of OLDH platelets within PPC matrix, which induce a long diffusion length of the oxygen and water vapor molecules (Fig. 8). At the same time, there is no significant change in water vapor permeability coefficient when the OLDH is added, this can be mainly attributed to the hydrophilic hydroxyl groups of OLDH, which facilitate the diffusion of water vapor. However, the OP and WVP increase with OLDH loading level up to 3%, this could be due to the aggregation of OLDH and some cracks emerge at the interface between OLDH particles and PPC matrix. In addition, in our previous work, we try to prepare thinner PPC/2%OLDH composite films (~20 μm) *via* a solution casting method. The experiment results show that the OP and WVP values are reduced by 62% and 26% respectively. This indicates that PPC/OLDH films have good gas barrier performance even in thinner thickness, which are suitable for practical application.

Table 2. OTR, OP, WVTR and WVP of the PPC/OLDH composite films

Sample	Thickness (μm)	OTR ($cm^3/(m^2 \cdot 24\ h)$)	OP ($cm^3 \cdot mm/(m^2 \cdot 24\ h)$)	WVTR ($g/(m^2 \cdot 24\ h)$)	WVP ($g \cdot mm/(m^2 \cdot 24\ h)$)
PPC	485 ± 5	4.60 ± 0.001	2.25 ± 0.004	2.66 ± 0.05	1.25 ± 0.02
PPC/1%OLDH	518 ± 5	3.09 ± 0.001	1.60 ± 0.005	2.20 ± 0.05	1.14 ± 0.03
PPC/2%OLDH	505 ± 5	2.06 ± 0.001	1.04 ± 0.006	2.04 ± 0.05	1.03 ± 0.03
PPC/3%OLDH	511 ± 5	3.62 ± 0.001	1.85 ± 0.006	2.27 ± 0.05	1.16 ± 0.03

Table 3 shows the gas barrier performance of some polymer films used in flexible packaging applications[38, 39]. The oxygen and water vapor permeability coefficients of PPC/2%OLDH composite film are lower than those of PE, PP, PA6, even slight lower than those of the composite film of PPC with aluminum flake (PPC/3%AlF). This indicates that PPC/OLDH composites have competitive potential as packaging materials. Besides, the gas barrier performance of PPC/OLDH is better than that of PE, PP together with its totally biodegradable nature.

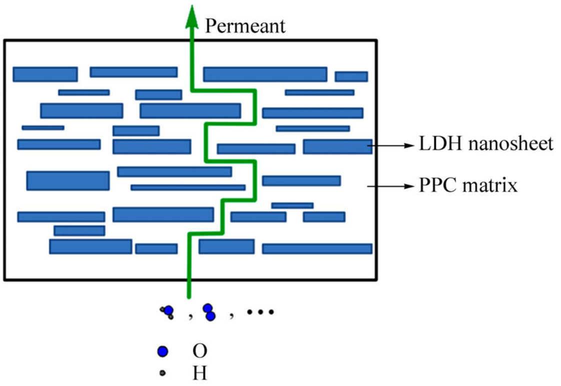

Fig. 8 Model for tortuous path of gas through PPC/OLDH composite

Table 3. Gas barrier performance of some polymer films used in flexible packaging applications

Sample	OP (cm^3·mm/(m^2·24 h))	WVP (g·mm/(m^2·24 h))
PPC	2.25	1.05
PPC/2%OLDH	1.04	1.03
PPC/3%AlF[13]	1.10	0.92
PE[39]	50–200	0.5–2
PA[39]	1.41	0.5–10

CONCLUSIONS

Well crystallized and high aspect ratio LDH can be readily synthesized by means of classical co-precipitation in aqueous solutions and the organic modified OLDH was prepared by anion exchange with SDS. SEM results show that OLDH platelets are well dispersed within the composites and oriented parallel to the composites sheet plane. In terms of oxygen and water vapor barrier performance of PPC/OLDH composite films, because of a long diffusion length as gases diffuse through the material induced by impermeable OLDH within PPC matrix, the oxygen and moisture permeation barrier properties put forward a significant improvement. Compared with the pure PPC, the OP and WVP values are reduced by 54% and 20% respectively just upon 2% OLDH incorporation. Meanwhile, the addition of OLDH particle fillers into PPC matrix can greatly enhance the tensile properties of PPC, especially the TS increased by 83% upon the incorporation of 2% OLDH. Therefore, the biodegradable PPC/OLDH composite films show great potential application in packaging materials.

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