Multifunctional Polypyrrole-silver Coated Layered Double Hydroxides Embedded into a Biodegradable Polymer Matrix for Enhanced Antibacterial and Gas Barrier Properties

Haibo HUANG1, Long MAO1,2*, Zhihan LI1, Yuejun LII1,2*, Shuhong FAN1, Yao JIN1, Jianda XIE2

1 Key Laboratory of Advanced Packaging Materials and Technology of Hunan Province, Hunan University of Technology, Zhuzhou 412007, China
2 Fujian Provincial Key Laboratory of Functional Materials and Applications, Xiamen University of Technology, Xiamen 361024, China

*Corresponding author: Long MAO, maolong0412@163.com; Yuejun LIU, yjliu_2005@126.com

Received 21 June 2019; Accepted 10 August 2019

Abstract: In this study, polypyrrole-silver coated layered double hydroxides (LDHs@PPy-Ag) was prepared by chemical polymerization of pyrrole (Py) with silver ions. Silver nanoparticles (AgNPs) could be uniformly reduced onto PPy coatings in situ by redox reaction during simultaneous polymerization process. And LDHs@PPy-Ag/poly(ε-caprolactone) (PCL) nanocomposites were fabricated by solution casting method. It is revealed that spherical AgNPs are loaded on PPy coatings uniformly. Particularly, compared with pure PCL, LDHs@PPy-Ag/PCL nanocomposites with incorporation of only 1 wt% LDHs@PPy-Ag show a 17% increase in tensile strength (36.5 MPa) and a 29% increase in elongation at break (822%). Upon PPy-Ag coatings onto original LDHs, oxygen relative permeability of LDHs@PPy-Ag/PCL nanocomposites decreases to 52% with the same addition. Meanwhile, due to the double antibacterial activity of PPy and AgNPs, the antibacterial rate of LDHs@PPy-Ag reaches 100%. And the corresponding LDHs@PPy-Ag/PCL nanocomposites also show outstanding antibacterial activity. Considering the superiority of their comprehensive performance, antibacterial LDHs@PPy-Ag/PCL nanocomposites can be used further for the application as biodegradable polymeric active packaging materials.

Keywords: antibacterial activity; layered double hydroxides; polypyrrole; silver; gas barrier properties

1 Introduction

Known as a kind of multifunctional anionic layered clay, layered double hydroxides (LDHs) are expressed as the general formula of [(M2+\textsuperscript{m}M3+\textsuperscript{n})(OH)\textsubscript{2}]\textsuperscript{m+}\textsuperscript{n}·mH\textsubscript{2}O, where M\textsuperscript{2+} and M\textsuperscript{3+} occupies the octahedral holes in a brucite [Mg(OH)\textsubscript{2}]-like layer, and A\textsuperscript{n–} is between the hydrated interlayer galleries (Taviot-Guého et al., 2018). The LDHs show great potential in the diverse fields such as plastic additive, catalysis, environmental adsorption, and energy industry (Allou et al., 2017). Meanwhile, the advantages of compositional flexibility, structural scalability, low cost, and facile synthesis have made hybrid LDHs extremely attractive for constructing smart and high-performance multifunctional materials (Veschambres et al., 2016; Taviot-Guého et al., 2018). Furthermore, longer sheets of layered clay homogeneously dispersed in the polymer matrix are distinctly effective in increasing the tortuosity of gas permeating direction and reducing the dependence on the orientation of layered clay (Tan et al., 2016).

However, the aggregation of inorganic nanoparticles caused by the minimization of their surface energy, will lead to the loss of surface area and the degradation of the final properties (Liu et al., 2015). As a rule, organic coatings are commonly applied to modify clay to improve the interfacial compatibility between the clay minerals and polymer matrix. Polypyrrole (PPy) is an important member of conductive polymer family. The PPy has high conductivity, facile synthesis, good environmental stability and biocompatibility which can be synthesized by chemical oxidation or electrochemical polymerization of pyrrole (Py) in a mild and friendly environment (Bideau et al., 2016). In general, the chemical oxidative polymerization of the Py requires an oxidant such as ferric chloride, potassium dichromate, or ammonium persulfate. In addition, the PPy is also known to kill bacteria by strong electrostatic adsorption. Many studies have applied the PPy to form effective coatings on various materials by in-situ polymerization to achieve the purpose of surface modification, such as natural fibers (Bideau et al., 2018), carbon nanotubes (Li et al., 2016), graphite oxide (Gu et al., 2010). Based on these studies, we consider using the PPy to form a novel surface coating for the LDHs applied in polymer composites. However, studies on
LDHs coated by the PPy are rarely reported. The PPy coatings on LDHs is an interesting alternative to preserve food quality and improve food safety due to its attractive properties. And the purpose of improving the interfacial compatibility between LDHs and polymer matrix and endowing polymer matrix with antibacterial properties can be both achieved. Furthermore, it is also important to note that silver nanoparticles (AgNPs) are relatively expensive antibacterial agent, which usually used alone in the antibacterial materials at a high cost (da Silva et al., 2017). The demand for similar properties at a lower cost is highly desired. Therefore, we aim to combine the advantages of the PPy and Ag to reduce the high cost of using the AgNPs alone.

On the other hand, the increasing attention to environmental impacts and the availability of fossil materials increased the demand for new packaging materials and technology. Up to now, substantial efforts are ongoing to find alternative packaging that can still prolong the food shelf life and reduce packaging waste. On this issue, the industry is seeking solutions for biodegradable packaging which can solve the waste problem to some extent (Seoane et al., 2018). Aliphatic polyesters are recognized as the most promising materials, mainly from friendly biodegradable polymer. Poly(e-caprolactone) (PCL) is a hydrophobic, semi-crystalline and biodegradable aliphatic polyester, which can be slowly degraded by microorganisms. The excellent physical properties, biocompatibility and commercial availability of the PCL make it an important alternative to traditional non-biodegradable polymers, resulting in a wide range of applications (e.g., packaging, biomedicine and agriculture). However, in practical applications of the PCL, specific packaging requirements like gas barrier and antibacterial properties need to be further satisfied.

Recently, biodegradable nanocomposites based on the LDHs have gained a lot of attention (Shafiei et al., 2016; Mao et al., 2018). However, there is few research on the applications of LDHs/PCL nanocomposites in packaging materials (Bideau et al., 2018). Bugatti investigated the barrier properties of the PCL nanocomposites films at different percentages of ZnAl-LDHs (Bugatti et al., 2010). The results showed that the diffusion parameter decreased obviously with the increasing of ZnAl-LDHs content. According to the fitting of the experimental results, the relative diffusivity of the nanocomposites decreases by ~30%–65% with incorporation of 1 wt% ZnAl-LDHs with different interlayer anions. However, the strength of all the nanocomposites is worse than that of pure PCL. We also proposed a facile, green and mussel-inspired method to prepare surface modified LDHs coated by polyphenolic compounds (e.g., polydopamine (PDA), tannic acid (TA)) (Mao et al., 2017a; Mao et al., 2018). For example, with incorporation of as low as 1 wt% LDHs@PDA in the PCL matrix, a 20% increase in tensile strength, 26% increase in elongation at break and 26% reduction in the oxygen relative permeability were achieved. However, studies on active packaging materials with both good antibacterial, barrier and mechanical properties are rarely reported.

The aim of the current study was to prepare novel multifunctional surface modified LDHs (LDHs@PPy-Ag) via in-situ polymerization of the Py on the LDHs with silver nitrate (as shown in Fig. 1). At the same time, chemical oxidation of the PPy can bind and reduce Ag ions into metallic AgNPs on the LDHs. LDHs@PPy-Ag will show the dual antibacterial effect of PPy and AgNPs. And LDHs@PPy-Ag/PCL nanocomposites were fabricated by the solution casting method. For comparison, ferric chloride, a cheap oxidizer, was also used to trigger the polymerization of Py on the LDHs (LDHs@PPy). And LDHs@PPy/PCL nanocomposites were fabricated by the same method. The study highlight the antibacterial properties of PPy-Ag coatings on the LDHs and demonstrate a potential application in active packaging materials.

![Fig. 1 Schematic illustration of preparation of LDHs@PPy-Ag and LDHs@PPy](http://jbb.xml-journal.net)
2 Materials and Methods

2.1 Materials

The MgAl-LDHs was synthesized by hydrothermal method according to the previous report (Mao et al., 2017b). Poly(ɛ-caprolactone) (PCL) (Capa™ 6800, Shanghai Aladdin Bio-Chem Technology Co., Ltd. (China). Pyrrole (Py), FeCl$_3$·6H$_2$O, and AgNO$_3$ were supplied by Shanghai Aladdin Bio-Chem Technology Co., Ltd. (China). Poly(ɛ-caprolactone) (PCL) (Capa™ 6800, $M_w \geq 80000$) was purchased from Perstorp (Sweden). All other reagents were of analytical pure and used without further purification.

2.2 Synthesis of LDHs@PPy-Ag and LDHs@PPy

The LDHs (0.05 g) was dispersed in deionized water (50 mL) under ultrasonic treatment for 0.5 h. And AgNO$_3$ (0.12 g, 0.7 mmol) was added to LDHs dispersion under magnetic stirring for 5 min. Meanwhile, Py (0.05 mL, 0.7 mmol) was added to deionized water (50 mL) under ultrasonic treatment for 0.5 h until Py was completely dissolved. Then, Py solution was added to LDHs dispersion under magnetic stirring at 70°C for 2 h. The product (LDHs@PPy-Ag) was obtained by centrifugation and finally dried in freeze dryer.

The LDHs (0.05 g) was dispersed in deionized water (50 mL) under ultrasonic treatment for 0.5 h. And FeCl$_3$·6H$_2$O (0.19 g, 0.7 mmol) was added to the LDHs dispersion under magnetic stirring for 5 min. Meanwhile, Py (0.05 mL, 0.7 mmol) was added to deionized water (50 mL) under ultrasonic treatment for 0.5 h until Py was completely dissolved. Then, Py solution was added to LDHs dispersion under magnetic stirring at room temperature for 1 h. The product (LDHs@PPy) was also obtained by centrifugation and finally dried in freeze dryer.

2.3 Fabrication of LDHs@PPy-Ag/PCL, LDHs@PPy/PCL and LDHs/PCL nanocomposites

The mass fraction of LDHs@PPy-Ag, LDHs@PPy and original LDHs in the nanocomposites was set as 1%. The LDHs@PPy-Ag, LDHs@PPy and original LDHs were dispersed in dimethyl formamide under ultrasonic treatment for 30 min, respectively. And PCL (1.4 g) was added to the above dispersions at 40°C under magnetic stirring for 1.5 h, respectively. Then, the above dispersions were heated to 80°C under magnetic stirring for 1.5 h. The above dispersions were treated with ultrasonic treatment for 15 min. Finally, the above dispersions were evaporated to obtain films in the horizontal polytetrafluoroethylene molds at 60°C.

2.4 Characterization

Fourier transform infrared spectroscopy (FT-IR) spectra were recorded by a spectrophotometer (ALPHA, Bruker). The samples were mixed and ground with KBr and then pressed to pellets. The X-ray diffraction (XRD) patterns were recorded by a powder diffractometer (X’pert, Panalytical), using Cu Kα target at a scanning rate of 5°/min. UV-visible absorption spectra were obtained from a spectrophotometer (SPECORD 210 PLUS, Analytikjena) at room temperature. The surface micromorphology of the samples were observed by SEM (sigma500, Zeiss) and TEM (Talos, FEI), respectively. The chemical elemental analysis of the samples was characterized by energy-dispersive X-ray spectrometry (EDS) (X-Max®, Oxford). Differential scanning calorimetry (DSC) (DSC214, Netzsch) was employed for thermal analysis. The samples were measured in the temperature range from –30°C to 150°C with heating and cooling rates of 10°C/min using nitrogen as protection gas. The following expression was used to calculate crystallinity of PCL ($\chi$), $\chi = [\Delta H_m/(\Delta H_0 \times \phi)] \times 100\%$, where $\Delta H_m$ was the measured enthalpy of melting, $\Delta H_0$ was melting enthalpy of 100% crystalline PCL (136 J/g) (Ludueña et al., 2007) and $\phi$ was the mass fraction of PCL.

3 Results and Discussion

3.1 Chemical structure of LDHs@PPy and LDHs@PPy-Ag

In Fig.2, FT-IR spectra of the original LDHs, LDHs@PPy and LDHs@PPy-Ag show almost identical characteristics of typical LDHs (Liu et al., 2014) Compared with original LDHs, LDHs@PPy-Ag and LDHs@PPy show additional peaks at 1464 cm$^{-1}$ and 1128 cm$^{-1}$, which attributed to the
conjugated C—N stretching vibration in py ring (Li et al., 2013). And the peaks at 1284 cm$^{-1}$ and 1071 cm$^{-1}$ are related to the stretching and deformation vibration of C—H (da Silva et al., 2017). In addition, in the FT-IR spectrum of original LDHs, the bands recorded below 700 cm$^{-1}$ are attributed to the vibration of metal-oxygen bonds (Liu et al., 2014). It is preliminary evidence that PPy is synthesized on the LDHs surface.

![Fig. 2 The FT-IR spectra of LDHs, LDHs@PPy and LDHs@PPy-Ag](image)

The successful synthesis of LDHs@PPy-Ag is further confirmed by XRD and UV-vis as shown in Fig. 3. As shown in Fig. 3a, the diffraction reflections of original LDHs are sharp and symmetrical, and the baseline is stable, indicating well-formed crystal layered structures. And the characteristic diffraction peaks at (003), (006) and (110) of typical LDHs (JCPDS file No. 38-0487) are easily identified in all the patterns (Liu et al., 2014). In addition to characteristic diffraction peaks of typical LDHs, (111) and (200) diffraction peaks of Ag are observed in the XRD pattern of LDHs@PPy-Ag (Wang et al., 2013). In Fig. 3b, original LDHs and LDHs@PPy both displays no visible absorption peak between 300 nm and 800 nm. After loading AgNPs onto the surface of LDHs@PPy-Ag, there is a clear peak at 430 nm (Xu et al., 2011). This is due to characteristic of AgNPs induced by surface plasmon absorption (Zhang et al., 2013), which further indicates the successful synthesis of LDHs@PPy-Ag.

### 3.2 Microtopography of LDHs@PPy and LDHs@PPy-Ag

Micromorphologies of LDHs@PPy are investigated by TEM under different magnifications, as shown in Fig. 4. Obviously, a soft coating (~15 nm) is observed on the layered particles. Furthermore, the average diameter of LDHs@PPy is ~1500 nm evidenced from TEM image. In order to obtain direct evidence of PPy coatings on the LDHs, chemical composition was also investigated by

![Fig. 4 The TEM images of LDHs@PPy at low magnification (a) and high magnification (b), EDX scans of LDHs@PPy (c)](image)
EDS (Fig. 4c). The large peaks for carbon, oxygen, magnesium, and aluminum in the EDS spectrum indicate the basic components of the LDHs. It is worth noting that the small peaks for nitrogen and iron indicate further the existence of PPy (Kim et al., 2015b).

The TEM and SEM are applied to further observe the micromorphology of LDHs@PPy-Ag directly, as shown in Fig. 5 and Fig. 6, respectively. After the reduction process during the chemical oxidative polymerization of Py, AgNPs are uniformly adsorbed on the LDHs@PPy-Ag, as shown in Fig. 5a and Fig. 5b. The thickness of the PPy coatings is ~6 nm. And the average diameters of AgNPs on the LDHs@PPy-Ag can also be estimated at ~20 nm. In Fig. 5c, LDHs@PPy-Ag possesses Ag (111) crystal planes with a lattice spacing of 0.24 nm (Zhao et al., 2015).

In Fig. 6a and Fig. 6b, upon PPy-Ag coatings onto LDHs, AgNPs are uniformly distributed on the LDHs@PPy-Ag. Meanwhile, LDHs@PPy-Ag is evenly dispersed in the field of observation. In Fig. 6c and Fig. 6d, the uniform distribution of elements reflects the uniform distribution of Ag and PPy. It is revealed that original LDHs is well coated by PPy-Ag.

3.3 Antibacterial properties of LDHs@PPy, LDHs@PPy-Ag and nanocomposites prepared

In order to quantitatively evaluate the antibacterial properties of original LDHs, LDHs@PPy and LDHs@PPy-Ag, bacterial colony counter was used to count the number of colonies in the petri dishes with different nanoparticles. And the antibacterial activity was also evaluated by the
antibacterial rate. In Fig. 7a, original LDHs still shows a certain degree of antibacterial activity, and the antibacterial rate reaches 35.19%. Upon coating of PPy onto LDHs, the antibacterial activity of LDHs@PPy is significantly improved, and the antibacterial rate is up to 99.97%. Due to the dual antibacterial effects of PPy and AgNPs, the antibacterial rate of LDHs@PPy-Ag reaches about 100%. It is generally believed that Ag ions released from unstable AgNPs are responsible for its excellent antibacterial activity. A large surface area of AgNPs contributes to the release of more Ag ions, as a result of more exposure to bacteria. Therefore, LDHs@PPy-Ag exhibits the best antibacterial properties. In general, the antibacterial properties of nanoparticles are closely related to that of the nanocomposites prepared by them. In Fig. 7b, not surprisingly, the presence of original LDHs does not improve the antibacterial properties of PCL matrix. And the antibacterial rate of LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites both exceeds 99.99%. Especially for LDHs@PPy-Ag/PCL nanocomposites, its concentration of Escherichia coli is only 800 CFU/cm². Therefore, LDHs@PPy-Ag/PCL nanocomposites show the best antibacterial properties.

![Fig. 7 Antibacterial properties of (a) LDHs@PPy and LDHs@PPy-Ag, (b) LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites](image)

### 3.4 Thermal properties of LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites

Figure 8 shows DSC cooling and second heating curves of LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites. And the related results of thermal analysis are shown in Table 1. As shown in Fig. 8a and Table 1, there is a crystallization exothermic peak ($T_c$) at 29.9°C in the DSC cooling curve of PCL, which is attributed to the $\alpha$-polymorph (Pucciarrello et al., 2007). With the addition of original LDHs, $T_c$ and $\chi$ of LDHs/PCL nanocomposites occur at higher value. An increase in $T_c$ and $\chi$ is due to the fact that original LDHs can act as the heterogeneous nucleating agent to promote the crystallization process of PCL (Peng et al., 2010). Compared with original LDHs, LDHs@PPy and LDHs@PPy-Ag show more significant heterogeneous nucleation because of higher $T_c$ and $\chi$. In Fig. 8b, the melting temperature ($T_m$) of pure PCL is 56.7°C while $T_m$ of these nanocomposites shows no obvious change.

![Fig. 8 The DSC (a) cooling and (b) second heating curves of LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites](image)
Table 1 The related results of LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites according to thermal analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$T_m$ (°C)</th>
<th>$T_c$ (°C)</th>
<th>$\chi$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>44.75</td>
<td>56.7</td>
<td>29.9</td>
<td>33.2</td>
</tr>
<tr>
<td>LDHs/PCL</td>
<td>49.70</td>
<td>56.7</td>
<td>31.6</td>
<td>36.9</td>
</tr>
<tr>
<td>LDHs@PPy/PCL</td>
<td>52.01</td>
<td>56.7</td>
<td>32.5</td>
<td>38.6</td>
</tr>
<tr>
<td>LDHs@PPy-Ag/PCL</td>
<td>51.85</td>
<td>56.2</td>
<td>32.4</td>
<td>38.5</td>
</tr>
</tbody>
</table>

(56.2°C–56.7°C). It shows that original LDHs, LDHs@PPy and LDHs@PPy-Ag do not affect $T_m$ of PCL matrix obviously.

The XRD analysis of LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites further verified the results of DSC analysis, as shown in Fig. 9a. For all the nanocomposites, XRD patterns exhibit reflections at 2θ=21.16°, 21.79° and 23.41°, corresponding to (110), (111) and (200) planes of the orthorhombic crystal form for PCL, respectively. Compared with pure PCL, all the nanocomposites show higher diffraction peak intensity of PCL chains. It reveals that original LDHs, LDHs@PPy and LDHs@PPy-Ag all facilitate the crystallization of PCL chains as a result of an increase in crystallinity. This is consistent with the results of DSC analysis. In addition, in all the nanocomposites, (003) crystal plane of typical LDHs shows similar diffraction intensity and diffraction angle (~11.74°). This is consistent with the XRD analysis of LDHs@PPy and LDHs@PPy-Ag.

Fig. 9 The XRD patterns (a) and TGA curves (b) of LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites

The TGA curves of LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites are shown in Fig. 9b. According to previous studies (Pucciariello et al., 2007; Costantino et al., 2009), the thermal stability of LDHs/polymer nanocomposites decreases gradually with the increase of LDHs. Sure enough, the thermal stability of all the nanocomposites is not as good as that of pure PCL. However, compared with LDHs/PCL nanocomposites, LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites exhibit better thermal stability. Owing to the high thermal stability of PPy relatively, core-shell structured LDHs@PPy and LDHs@PPy-Ag contribute to delay of thermal degradation (Mao et al., 2017b). Therefore, LDHs@PPy and LDHs@PPy-Ag improve the thermal stability of their nanocomposites in comparison to LDHs/PCL nanocomposites.

3.5 Mechanical properties of LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites

The mechanical parameters derived from the stress-strain curves are shown in Table 2. Compared with pure PCL, deformation at the yield point, stress at breaking, and deformation at breaking of all the nanocomposites are improved to some extent. Particularly, compared with pure PCL, LDHs@PPy/PCL nanocomposites show a 32% increase in tensile strength (41.3 MPa) and a 31% increase in elongation at break (830%). And compared with LDHs@PPy/PCL nanocomposites, the mechanical properties of LDHs@PPy-Ag/PCL nanocomposites are slightly reduced, but still significantly improved. At this low filler content, the improvement of mechanical properties is a typical feature of nanocomposites (Pucciariello et al., 2012).

Table 2 Mechanical parameters of LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites according to stress-strain curves

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma_y$ (MPa)</th>
<th>$\varepsilon_y$ (%)</th>
<th>$\sigma_b$ (MPa)</th>
<th>$\varepsilon_b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PCL</td>
<td>23.9±0.9</td>
<td>19.1±1.2</td>
<td>31.3±1.4</td>
<td>635±51</td>
</tr>
<tr>
<td>LDHs/PCL</td>
<td>24.7±1.1</td>
<td>19.4±1.8</td>
<td>32.4±1.6</td>
<td>714±36</td>
</tr>
<tr>
<td>LDHs@PPy/PCL</td>
<td>21.5±0.8</td>
<td>20.6±2.1</td>
<td>41.3±1.3</td>
<td>830±42</td>
</tr>
<tr>
<td>LDHs@PPy-Ag/PCL</td>
<td>22.8±0.7</td>
<td>23.9±1.9</td>
<td>36.5±1.1</td>
<td>822±53</td>
</tr>
</tbody>
</table>

Notes: $\sigma_y$, stress at the yield point; $\varepsilon_y$, deformation at the yield point; $\sigma_b$, stress at breaking; $\varepsilon_b$, deformation at breaking.

To further understand the relationship between material structure and mechanical properties, SEM images of
fracture surfaces for all the nanocomposites are shown in Fig. 10. According to our previous research (Mao et al., 2017b), overall fracture surface of pure PCL is rough. And a large number of bulges and voids can be observed in the region of fracture, which indicates plastic deformation. Similarly, results of Fig. 10a–10c also show rough and well stretched surface (numerous curled broken fibrils) after fracture, indicating the existence of original LDHs, LDHs@PPy and LDHs@PPy-Ag enhances the flexibility of PCL matrix (Du et al., 2010; Liau et al., 2014; Bai et al., 2016). Apparently, there are some interface defects between original LDHs and PCL matrix (Fig. 10d), and this indicates that the interfacial compatibility is relatively poor. However, as shown in Fig. 10e and Fig. 10f, LDHs@PPy and LDHs@PPy-Ag are both tightly combined with PCL matrix without visible interface gap. This indicates that the interfacial compatibility has been improved markedly, which can conclude that LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites have better mechanical properties than LDHs/PCL nanocomposites (Mao et al., 2017b; Mao et al., 2018). In addition, the better interfacial bonding, the fewer the interfacial defects, which is also closely related to the gas barrier properties of materials.

![Fig. 10](image)

The SEM images of fracture surface for LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites at different magnifications

### 3.6 Gas barrier properties and mechanism of LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites

Gas barrier properties of LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites are shown in Fig. 11. When the original LDHs content reaches 1 wt%, $R_p$ (relative permeability=$P/P_0$) decreases obviously to 67%. Upon PPy coatings onto LDHs, $R_p$ of LDHs@PPy/PCL nanocomposites further decreases to 44% with the same addition. The results show that LDHs@PPy can significantly improve the oxygen barrier properties of PCL matrix. Only when clay is better dispersed in the PCL matrix and the interface compatibility between modified clay and PCL matrix is better, can it help to reduce interface defects and prolong the tortuous path of gas diffusion (Huang et al., 2014). The presence of AgNPs may reduce the interfacial compatibility between LDHs@PPy-Ag and PCL matrix, resulting in the decrease of the barrier properties for the final nanocomposites (Mao et al., 2019). However, the oxygen barrier properties of LDHs@PPy-Ag/PCL nanocomposites ($R_p$=52%) are still better than those of LDHs/PCL nanocomposites. Therefore, PPy and PPy-Ag coatings play important roles in reducing gas permeability in LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites.

![Fig. 11](image)

Gas barrier properties of LDHs@PPy/PCL and LDHs@PPy-Ag/PCL nanocomposites
According to considerable studies in references (Bharadwaj, 2001; Xu et al., 2006; Choudalakis et al., 2009; Zare-Shahabadi et al., 2011; Avérous et al., 2012; Wu et al., 2013; Genovese et al., 2014; Layek et al., 2015), the barrier mechanism of clay in the nanocomposites is mainly attributed to the bulk effect and barrier effect. As a rule, clay/polymer nanocomposites consist of an impermeable phase (layered clay) and a permeable phase (polymer matrix) that dispersed in polymer matrix. Three main factors of layered clay can affect the gas barrier properties of clay/polymer nanocomposites: volume fraction, micromorphology and orientation (Bugatti et al., 2010). Based on Nielsen’s detour theory, classical relative permeability equation can be expressed as follow,

\[
R_p = \left(1 - \phi_s\right) + \frac{L}{2W} \phi_s
\]

(1)

where \(\phi_s\) represents the volume fraction of clay. Assuming clay is considered to be a disk with diameter (\(L\)) and thickness (\(W\)). The aspect ratio (\(L/W\)) of original LDHs, LDHs@PPy and LDHs@PPy-Ag is ~37.5, ~21.4 and ~28.8, respectively. For example, the average diameter of LDHs@PPy is ~1500 nm evidenced from TEM images. Estimated from our previous research, the lateral thickness of original LDHs and PPy coatings are ~40 nm and ~15 nm, respectively. Therefore, the lateral thickness of LDHs@PPy is ~70 nm. The aspect ratio of LDHs@PPy is thus ~21.4. The aspect ratio of LDHs@PPy-Ag is also estimated in this way.

According to the above equation, the predicted and experimental values of relative permeability are shown in Fig. 12. The results show that \(R_p\) of the predicted values is significantly higher than that of the experimental values. And the deviation (23.9%–49.7%) between predicted and experimental values is large in the whole region. The true cause lays in the fact that the above equation is based on a complete geometric analytical procedure. Two important factors should be considered: a final change of polymer matrix behavior due to the incorporation of clays and the interaction interface (Gain et al., 2005). It should be pointed out that the better interface compatibility between clay and PCL matrix, the greater deviation of \(R_p\). Especially in our clay/polymer nanocomposites, surface modification of LDHs (LDHs@PPy and LDHs@PPy-Ag) can lead to very different surface-to-bulk ratios eventually. Meanwhile, it can also cause interactions of different types toward the polymer chains, resulting in more strong interface (Avérous et al., 2012; Wu et al., 2013; Genovese et al., 2014).

4 Conclusions

In this study, in order to avoid the use of Ag alone and reduce costs, we reported the preparation of LDHs@PPy-Ag by chemical polymerization of pyrrole with silver nitrate. And LDHs@PPy-Ag LDHs/PCL nanocomposites were prepared via solution casting method to obtain homogeneous films. For comparison, the common ferric ions were also used to trigger the polymerization of Py on the LDHs (LDHs@PPy). And LDHs@PPy/PCL nanocomposites were prepared in the same way. It is revealed that obtained AgNPs are distributed on PPy coatings uniformly. And the average diameters of AgNPs can also be estimated at ~20 nm. The thickness of PPy coatings in the LDHs@PPy and LDHs@PPy-Ag is ~15 nm and ~6 nm, respectively. With this nanoscale coatings on the LDHs, the mechanical and gas barrier properties of the final nanocomposites are improved significantly. The improvement is attributed to strong interface interaction and heterogeneous nucleation. To a certain extent, the incorporation of AgNPs on PPy coatings reduces the interface compatibility between LDHs@PPy-Ag and PCL matrix. However, gas barrier and mechanical properties of LDHs@PPy-Ag/PCL nanocomposites are still better than those of LDHs/PCL nanocomposites evidently. Meanwhile, due to the double antibacterial activity of PPy and AgNPs, the antibacterial rate of LDHs@PPy-Ag reaches 100%. And LDHs@PPy-Ag/PCL nanocomposites show the best excellent antibacterial activity. Thanks to the superiority of its comprehensive performance, antibacterial LDHs@PPy-Ag/PCL nanocomposites can be promising materials to be applied in packaging industry widely.

Acknowledgments

This study was supported by National Natural Science Foundation of China (No. 11872179), Science and Technology Planning Project of Fujian Province (No. 2018H6024), Natural Science Foundation of Hunan Province (No. 2019JJ50132), High-Level Talents Support Plan of Xiamen University of Technology (No. YKJ19008R), Open Fund for Innovation Platform of

http://jbb.xml-journal.net
University in Hunan Province, China (No. 18K079). Open Fund of Fujian Provincial Key Laboratory of Functional Materials and Applications (Xiamen University of Technology), China (No. fma2018004, No. fma2017110).

References


