



The properties of antimicrobial films derived from poly(lactic acid)/starch/chitosan blended matrix

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ABSTRACT

An antimicrobial material with a slow release property was developed based on poly(lactic acid)/starch/chitosan blends, in which chitosan acted as an antimicrobial agent while PLA and starch together were used as a slow-releasing device. An increase in the starch content drastically improved the hydrophilicity of the blends, which was favorable for the diffusion of the embedded chitosan. Moreover, the release of chitosan was observed to occur in two stages, with a very fast release stage initially and a slow but durable release stage as the latter. These two stages exhibited the effectiveness and long residual action of antimicrobial property of the blends respectively, demonstrating the suitability to be used for foods with high water activity, such as fresh meat. The tensile and thermal properties further verified the promising use of the blend material in packaging.

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1. Introduction

Over the last two decades, there has been a considerably growing interest in developing food packaging materials with an antimicrobial property. This kind of materials are considered as one of the most promising active packaging systems, as they are highly effective in killing or inhibiting spoilage and pathogenic microorganisms that contaminate food, and can limit the possible undesirable flavors that are caused by the direct addition of additives into foods (Appendini & Hotchkiss, 2002; Balasubramanian, Rosenberg, Yam, & Chikindas, 2009). Consequently, they can be used to control the microbiological decay of perishable food products, to maintain the food quality, and to extend the shelf-life of foods. However, although some materials can exhibit an excellent antimicrobial property, their activity cannot last for a long time because their antimicrobial agents are always consumed easily by microorganisms, the environment, and even the food components. Therefore, the development in food antimicrobial packaging expects them to have both effectiveness and long residual action

(Kerry, O'Grady, & Hogan, 2006; Suppakul, Miltz, Sonneveld, & Bigger, 2003).

Many researchers have tried to develop slow-release (also known as time-release) devices for food antimicrobial packaging (Joerger, 2007; Quintavalla & Vicini, 2002). The idea of this design is using the packaging material as a reservoir matrix and a delivery vehicle for efficient migration of the agent(s) from the packaging matrix to the surface of the product at a specific slow rate over a prolonged period. In this case, the concentration(s) of the agent(s) can be maintained where they are needed, and the activity can also be extended.

Various food antimicrobial packaging systems with a slow-release property have been developed, with different polymer matrices used including protein (Oussallah, Caillet, Salmieri, Saucier, & Lacroix, 2004), chitosan (Pranoto, Rakshit, & Salokhe, 2005), zein (Li, Yin, Yang, Tang, & Wei, 2012), poly(vinyl alcohol) (Leimann, Goncalves, Machado, & Bolzan, 2009), low-density polyethylene (LDPE) (Han, Castell-Perez, & Moreira, 2008), cellulose acetate (Gemili, Yemenicioglu, & Altinkaya, 2009), poly(lactic acid) (PLA) (Jin, Liu, Zhang, & Hicks, 2009; Liu et al., 2007), etc. The release mechanisms include swelling induction, thickness induction, and the reservoir system (Mastromatteo, Mastromatteo, Conte, & Del Nobile, 2010).

Among the above polymer matrices, PLA has the most attractive prospect as it is derived from agricultural crops, and is biodegradable, renewable, and environmental-friendly (Yu, Dean, & Li, 2006). Moreover, their mechanical properties, such as tensile modulus

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and impact strength, are similar to those of LDPE and polypropylene. There are lots of publications on PLA-based packaging and drug delivery systems, and the release mechanism of PLA matrix is mostly based on its degradation (Liu et al., 2007). Namely, with the gradual degradation of PLA molecules into water and CO₂, the matrix become loose and the embedded drugs can then be released. However, the application of PLA matrix as the antimicrobial carrier for food packaging is rare. This is because, while most food components are hydrophilic, the hydrophobicity of PLA makes it unfavorable for the migration of hydrophilic antimicrobial agents, and thus a prominent antimicrobial activity cannot be expected (Rhim, Honh, & Ha, 2009). In order to improve the hydrophilicity of PLA matrix, the introduction of hydrophilic components might help to some extent. For instance, some studies showed that the incorporation of pectin as a hydrophilic component into the PLA matrix could contribute to the acceleration of the release rate of nisin (Jin et al., 2009; Liu et al., 2007).

Starch is a hydrophilic, biodegradable, renewable, and cheap material (Liu, Xie, Yu, Chen, & Li, 2009; Liu et al., 2011). It has been used as a controlled release matrix for a long time, especially in drug delivery systems (Chen, Pu, Li, & Yu, 2011; Li, Liu, Chen, & Yu, 2011). The release mechanism of it regards the sensitivity to water and the degradability. However, the application of starch matrix for food antimicrobial packaging remains unpopular because of the poor and instable mechanical properties, as well as the short active period with a fast release of agents.

In recent ten years, PLA/starch blends have attracted much interest because the blends are biodegradable and renewable, and can reduce the expensive price of PLA (Yu, Petinakis, Dean, Liu, & Yuan, 2011). Former work have been mainly focused on the compatibility between PLA and starch, and it is found that, without compatibilizer, the hydrophilic starch would separate from the hydrophobic PLA, and exist as aggregations in the PLA matrix. In this case, the mechanical properties of blends were poor, and, in contact with water, starch could be released out easily (Wang, Sun, & Seib, 2001; Xie et al., 2007). In contrast, the addition of a compatibilizer into the blends, such as the methylenediphenyl diisocyanate (MDI) and the maleic anhydride (MA), could improve the miscibility between PLA and starch and thus the mechanical properties of the blends (Jang, Shin, Lee, & Narayan, 2007). Unfortunately, the toxicity of MDI and MA restricted the use of them in materials that were in close contact with food.

To the best of our knowledge, the application of the PLA/starch blend as an antimicrobial matrix has not been reported before. In fact, since starch is a hydrophilic polymer, just as pectin (Yu et al., 2011), the introduction of it into PLA can change the hydrophobicity of PLA, which is favorable for the release of hydrophilic agents. Therefore, it is interesting to understand the release property of antimicrobial films based on the PLA/starch blends.

Chitosan is a nontoxic, biodegradable, biocompatible, and antimicrobial material, and can be used both as a matrix or an additive for packaging (Dutta, Tripathi, Mehrotra, & Dutta, 2009). Some papers have already discussed the properties of PLA/chitosan blends and starch/chitosan blends respectively. Briefly speaking, the starch/chitosan blends displayed a good antimicrobial property, but poor mechanical properties (Xu, Kim, Hanna, & Nag, 2005). Regarding PLA/chitosan blends, since chitosan could not migrate from the PLA matrix to the surface of food, the antimicrobial activity could only take place when the blend was in tight contact with the food (Sébastien, Stéphane, Copinet, & Coma, 2006). The properties of PLA/starch/chitosan blends have not been reported yet.

In this work, the PLA/starch/chitosan blends were fabricated as antimicrobial packaging materials. In the blended films, chitosan was as the antimicrobial agent, PLA was the continuous phase in the matrix, starch acted as the filler to improve the hydrophilicity

of the blends, and glycerol was used as the plasticizer to prepare thermoplastic starch (TPS). Firstly, the hydrophilic behaviors, the microstructures, and the chitosan release behaviors of the blends were determined to predict the antimicrobial property of the blends. After that, the actual antimicrobial activity was evaluated. And based on these results, the effectiveness and long residual action of antimicrobial activity were discussed in detail regarding the application of the blends. At last, the mechanical and thermal properties were also determined.

2. Material and methods

2.1. Materials

The PLA resin (RECODE 101) was purchased from Zhejiang Hisun Biomaterials Co., Ltd. (Zhejiang, China). The number-average molecular weight was 9.89×10^4 Da, the molecular weight distribution index was 1.52, and the crystalline degree was 25.24%. Maize starch was purchased from Huanglong Food Industry Co., Ltd. (Jilin, China). Its moisture content was 13.4%, and the amylose/amylopectin ratio was 26/74. Water soluble chitosan was purchased from Jinan Haidebei Marine Bioengineering Co., Ltd. (Shandong, China). Its deacetylation degree was 85.13, its molecular weight was 7.01×10^4 Da, and its molecular weight distribution index was 8.525. Glycerol was chemically pure and was supplied by Tianjin Damao Chemical Reagent Factory (Tianjin, China).

Two microorganisms were chosen, i.e., *Escherichia coli* (ATCC 25922) and *Staphylococcus aureus* (ATCC 6538). They were both activated before experiments.

2.2. Preparation of PLA/starch/chitosan films

Following previous research work (Liu, Gu, Zeng, & Liu, 2012; Yu et al., 2011), the PLA/starch/chitosan blends were prepared by a Haake twin-screw extruder (Rheomex PTW 24/40p, Ø30, screw diameter $D = 24$ mm, screw length $L = 28D$).

Since PLA molecules were very sensitive to water, TPS plasticized by glycerol was prepared firstly. Maize starch was dried under vacuum at 120 °C for 3 h to remove the moisture. The dried maize starch was blended with glycerol immediately at a ratio of 70/30, and then extruded using the extruder with a rod die. The highest barrel temperature of the extruder was set at 170 °C.

Then the pellets of TPS were mixed with the PLA resin and chitosan (powder in 200 mesh) to prepare blended films by the extruder. The chitosan was introduced during the extrusion process in the melted blend. The highest temperature on extruder barrier was set to be 160 °C, in order to prevent the decomposition of chitosan. The thickness of films was about 0.15–0.18 mm. The components and abbreviations of samples were listed in Table 1.

Table 1
Abbreviation and components of samples.

Samples	TPS (%)	PLA (%)	Chitosan (%)
S-0	0	100	0
S-30	30	70	0
S-40	40	60	0
S-50	50	50	0
S-0/5	0	95.0	5.0
S-0/10	0	90.0	10.0
S-30/5	28.5	66.5	5.0
S-40/5	38.0	57.0	5.0
S-50/5	47.5	47.5	5.0
S-40/10	36.0	54.0	10.0

2.3. Determination of the hydrophilic property

Dynamic contact angles (DCA), which were determined by a contact angle meter (OCA 40, Data physics Co. Ltd., German), were used to evaluate the hydrophilicity of PLA/starch blended films. The sample was placed on the platform of the facility; 3 μ L of water was dropped on its surface; and a camera was used to record the spreading of water. The DCAs were determined automatically by the OAC imaging analysis software under a frequency of 2 Hz. The evaluation time was 100 s.

2.4. Microstructure characterization

A scanning electron microscope (SEM) (S3400N, Hitachi, Japan) was used to examine the morphologies of the normal surface and the freeze-fracture section of the sample S-40/5. The freeze-fracture section was obtained by immersing the sample in liquid nitrogen for 3 min followed by manually fracturing it. In order to reflect the release of chitosan, the whole film was immersed in water for 24 h under room temperature, and then was fractured similarly. All the samples were mounted and carbon-coated and a voltage of 15 kV was used for the SEM imaging.

2.5. Determination of the release property

The potential application of the PLA/starch/chitosan blends as antimicrobial films is for foods with high water activity, such as fresh meat. Consequently, an agar culture medium was used to simulate that application environment. Specifically, the agar culture medium was prepared in 1.5% solution.

An integrated and homogeneous blend was placed on the surface of agar culture medium tightly, and then stored in an environment of 90% relative humidity at room temperature. After specific periods of time (0 h, 2 h, 12 h, 24 h, and 72 h), small pieces were cut off from the whole film to detect the total concentration of chitosan (C_T) and the residual concentration of chitosan (C_R). Specifically, since only chitosan contained nitrogen element in the film, the concentration of nitrogen element was measured by a Kjeldahl apparatus (8200, Foss, Sweden) to reflect the concentration of chitosan. The release ratio of chitosan was calculated as: release ratio = $(C_T - C_R)/C_T \times 100\%$. All results were the averages of triplicate parallel experiments.

2.6. Evaluation of the antimicrobial property

The antimicrobial properties of blends were evaluated by the agar diffusion method and the accelerated-release method respectively.

For the agar diffusion method, the blends were cut into 15.0 ± 0.1 mm diameter disks using a circular knife. Film disks were then placed on agar plates that had previously been seeded with 0.1 mL of a bacterial suspension containing 10^6 CFU/mL of the target microorganism. The control sample was placed in the center of agar media to contrast the antimicrobial properties of blends. The plates were incubated at 37 °C for 24 h. Afterwards, the zones of inhibition of the film disks on the plates were observed.

Regarding the accelerated-release method, the growth curves of microorganisms that were restrained by the blends after an accelerated release were used to evaluate the long residual action of antimicrobial property. Specifically, the bacterial suspensions were formed by the activated microorganisms. The films were sterilized by an ultraviolet lamp for 30 min, and then immersed into bacteria-free water for 24 h. After that, the films and the bacterial suspensions (1 mL) were added into culture solutions (lysogeny broth) immediately. The solutions were placed in an environment of 37 °C temperature and 90% relative humidity. The optical density

(OD) values of solutions, which were measured by a spectrophotometer under the light of a wavelength of 620 nm, were recorded after 3, 6, 9, and 12 h. The growth curves of microorganisms were stippled and linked up by these OD values. The growth curves of the controlled samples were based on bacterial culture solutions without any film sample.

As the possible release of starch and chitosan from the blends would disturb the results, the sample OD values (OD_s) and the empty OD values (OD_e) were determined. The former ones were the OD values of bacterial suspension with the antimicrobial films, and the latter ones were the values with the empty blends (PLA/starch blends). The final OD values (OD_f) were the results by subtraction of OD_e from OD_s .

2.7. Evaluation of the tensile properties

The tensile properties of blended films were evaluated in accordance with the ASTM D5938 Standard on an Instron tensile testing apparatus (5566). The tensile strength and the elongation were measured at a crosshead speed of 10 mm/min.

2.8. Evaluation of the thermal property

A Perkin-Elmer DSC Diamond-I with an internal coolant (Inter-cooler 1P) and nitrogen purge gas was used to evaluate the thermal properties of blends. The instrument was calibrated for the temperature and heat flow using indium and zinc as the standards. A baseline for an empty pan was established at the corresponding heating rate. Samples were cut into tiny pieces of about 2 mg, and sealed in an aluminum pan (PE No. 0219-0041). The temperature program was set as: firstly, samples were heated from 0 °C to 200 °C under 20 °C/min, hold for 1 min and then cooled to 0 °C, in order to clear up their thermal history; after that, samples were heated to 200 °C under 20 °C/min again, to evaluate the thermal property. All results were the averages of triplicate parallel experiments.

3. Results and discussions

3.1. Hydrophilic behavior

Since the PLA/starch blends were neither soluble nor swollen in water, their water contact angles influenced the soaking rate of water into the blends, which was the initial factor for the diffusion of components embedded in the blends. In other words, the more hydrophilic the blend is, the more easily do the embedded components diffuse out (Helmroth, Dekker, & Hankemeier, 2002).

The DCAs of PLA/starch blends were shown in Fig. 1. The lines were the fitting curves based on the scattered points to show the change trends more clearly. Firstly, it could be seen that, while the DCA of the sample S-0 (pure PLA film) was very stable and linear, the results of blended films (S-30, S-40, and S-50) dispersed distinctly. The reason for this is that the surface of the PLA film was much smoother than those of the blends (seen in Fig. 2a), and the rough surface could cause the variation in the DCAs results.

The initial DCA of the PLA film (S-0) was about 80°, which was decreased slightly with the increasing time. This indicates that the water drop could be kept on the surface of film and its soaking rate was slow. The DCAs of the blends (S-30, S-40, and S-50) were much lower than those of the PLA film, meaning the improved hydrophilicity. And their DCAs declined much more sharply than that of the PLA film, suggesting the fast soaking rate of water. Moreover, the DCAs of blends dropped much more abruptly with an increase in the starch content (S-50 > S-40 > S-30), which means that the soaking rate of water became faster with a higher starch content.

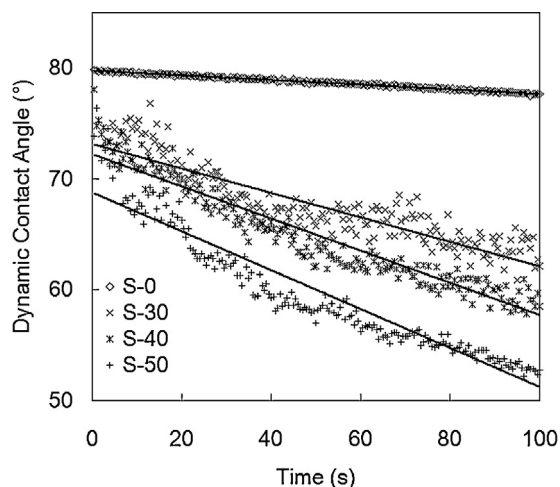


Fig. 1. The dynamic contact angles of PLA/starch blend materials.

The results of DCAs show that, with the introduction of starch, the hydrophilic property of blends was improved distinctly and water could immerse into the blends. Since the migration of the embedded chitosan is caused by the hydrophilicity and the immersion of water, theoretically, the release of chitosan and the

antimicrobial ability of blends can be improved by the introduction of starch.

3.2. Microstructures

The morphologies of the surface and the freeze-fracture section of the sample S-40/5 before and after the release could be seen in Fig. 2.

In Fig. 2a, the surface of the blend was rough, which could be the reason for the fluctuation of the DCA in Fig. 1. In Fig. 2b, as expected, the inner structure of the blend was not integrated and homogeneous, and some aggregations could be observed, especially in the center of the blend. These aggregations were the blend of chitosan and starch, as both starch and chitosan were hydrophilic and thus be miscible with each other. Fig. 2c shows the film freeze-fractured surface after immersion in water for 24 h, so the holes represented the removed starch/chitosan aggregations from the surface. It could be seen that the holes mainly appeared in the center of the film, and fewer holes existed closer to the surface.

Fig. 2 shows that, without compatibilizer, starch and PLA were just blended physically. The hydrophobic PLA occupied the surface of blends and the hydrophilic starch/chitosan aggregations were mainly embedded in the center of PLA matrix. Moreover, when the blend contacted water, the immersion of water made the aggregations of starch/chitosan near the surface leach out, leaving channels to the inner of the blend, so the embedded aggregations could be

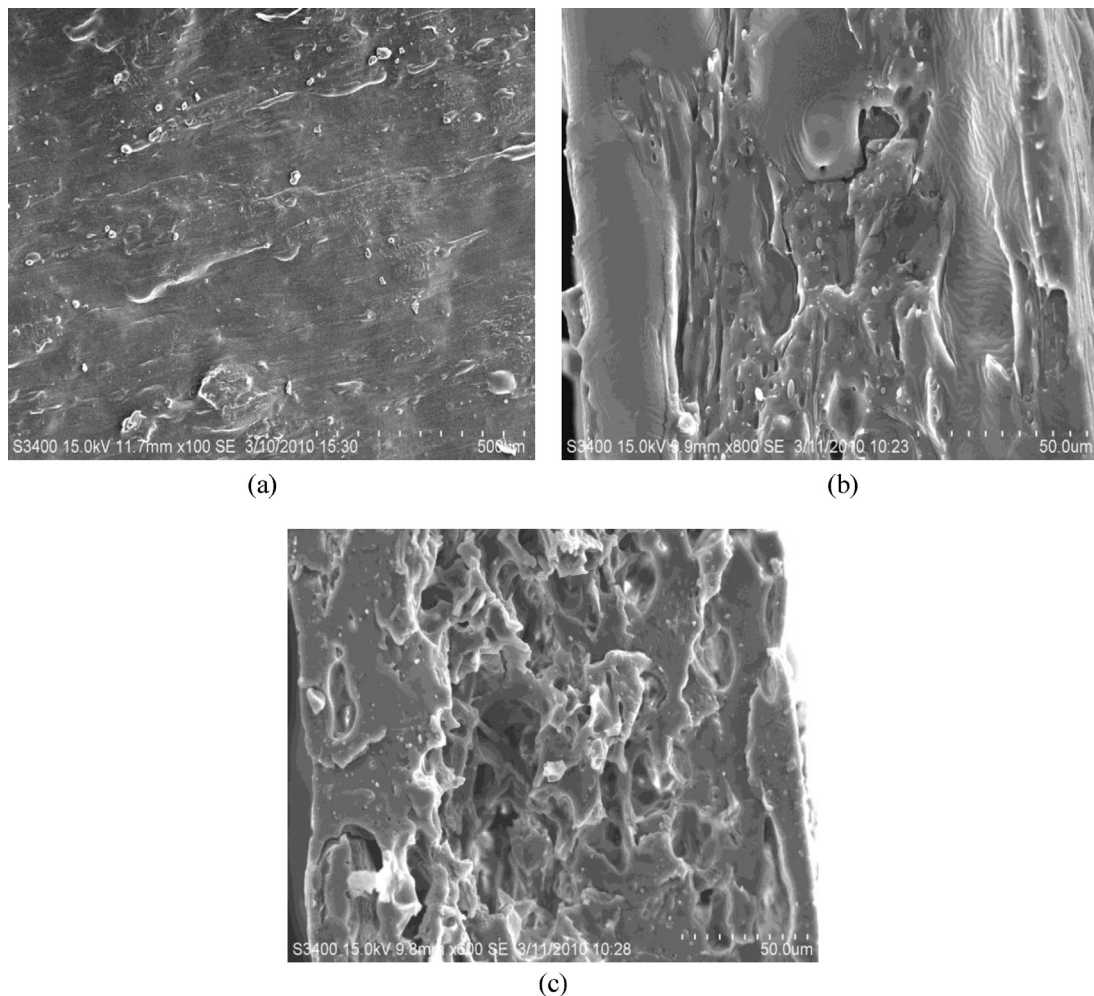


Fig. 2. The morphologies of the surface and fracture of PLA/starch/chitosan antimicrobial materials (S-40/5) before and after releasing: (a) is the surface before releasing; (b) is the fracture before releasing; and (c) is the fracture after releasing.

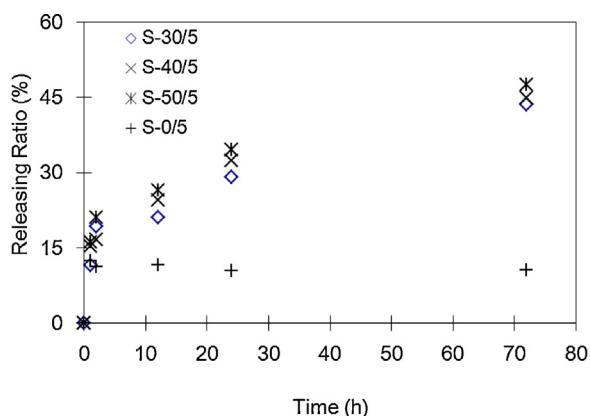


Fig. 3. The chitosan releasing ratio in starch/PLA antimicrobial materials as a function of time (for S-30/5, the standard deviations are $\leq 9\%$ of the experimental value; for S-40/5, $\leq 10\%$; for S-50/5, $\leq 8\%$; for S-0/5, $\leq 20\%$).

released gradually. Nonetheless, only limited channels could be formed as there were fewer aggregations near the surface. Therefore, it can be deduced that the release rate of chitosan should be slow.

3.3. Release behavior

The percentage of release of chitosan from the blends could be seen in Fig. 3. For the sample S-0/5 (PLA matrix with chitosan), there were two release stages, namely an initial fast stage and a following stable stage. In the former one, the release was mainly ascribed to the chitosan that located on or near the film surface. In this case, when the chitosan contacted water, they could diffuse out immediately. Only within an hour, its release percentage reached about 15%. But in the later stable stage, the release percentage was kept at about 15%, suggesting that no further diffusion of chitosan. These results indicate that the hydrophobic PLA matrix blocked the diffusion of chitosan that located in the inner of the material.

The release process of the samples S-30/5, S-40/5 and S-50/5 could also be divided into two stages, an initial fast stage and a following slow stage. The first stage was similar to that of S-0/5, involving the release of chitosan locating near the surface. In the second stage, the release percentage also increased with time, but at a slower rate. During the period from 12 h to 72 h, the release percentage only increased from 24.5% to 47.5% for the sample S-40/5. This means that chitosan could diffuse out gradually and slowly, which was in accordance with the deduction from Fig. 2. These release percentage results directly demonstrate the slow release of chitosan from the blends.

Moreover, since chitosan was used as the antimicrobial agent in the blends, its release behavior could be used to forecast the antimicrobial behavior of the blends. Namely, in the initial fast stage, the chitosan could diffuse out quickly with the effectiveness in the antimicrobial ability. In the slow stage, chitosan could diffuse out slowly but durably and thus its antimicrobial activity could be kept for a long period. Therefore, the antimicrobial property of the blends could be both effective and durable.

3.4. Antimicrobial behavior

Both the effectiveness and long residual action of antimicrobial property of the blends were evaluated as shown in Figs. 4 and 5.

The effectiveness of antimicrobial activity was evaluated using the agar diffusion method (Fig. 4). The *E. coli* and *S. aureus*, which are the common putrefying bacteria for fresh meat, were used as the indicator bacteria. In Fig. 4, all the central film in the agar media was

the control sample. Namely, in Fig. 4a and b, the central film was the pure PLA film (S-0), and, in Fig. 4c and d, it was the sample S-40. The behavior of these control samples could contrast the antimicrobial properties of blends. From Fig. 4a and b, no antimicrobial zones were seen for S-0/10, meaning that not enough chitosan diffused out to restrain the growth of bacteria. This ineffectiveness was the main drawback of the PLA/chitosan antimicrobial blends. In Fig. 4c and d, the antimicrobial zones surrounding the circular film strips were very clear compared with those of the controls, indicating the effectiveness of PLA/starch/chitosan blends.

The long residual action of antimicrobial property of the blends was evaluated by the accelerated-release method. From the growth curves of the control samples in Fig. 5, the OD_6 increased very fast, meaning that the microorganisms were active and the culture solutions were suitable. Besides, since the sterilized blends had already been immersed in bacteria-free water for 24 h before it was used to restrain the growth of microorganisms, the initial fast-release stage for chitosan had already passed, so it was the chitosan that located in the center of the materials diffused out to show an antimicrobial behavior. It can be seen that the growth curves of S-40/5 and S-40/10 located below that of the control while either of the microorganisms was used, suggesting that the blends samples still had the antimicrobial property. Consequently, these results proved that the diffusion of chitosan was slow but durable, and the antimicrobial ability of the blends could be maintained for a long period.

3.5. Discussion

From the above results, the slow-release property of chitosan offered the blends the effectiveness and the long residual action of antimicrobial property, which is advantageous in practical application. On the other hand, since water is the key issue for the diffusion of chitosan, the suitable application of such a blend material is protecting foods with high water activity, such as fresh meat.

When the PLA/starch/chitosan blend contacts fresh meat, the fast-release stage for chitosan takes place immediately. The chitosan at or near the surface of the material diffused out immediately to reach a certain concentration. Therefore, the most active putrefying bacteria, which accumulate on the surface of fresh meat, are restrained and the effectiveness of antimicrobial property can be achieved.

Besides the active bacteria, which directly cause the deterioration of meat, the inactive spores also exist in fresh meat, which influence the preservation of fresh meat as well. After the fast-release stage, the slow-release stage takes place, resulting in a continuous diffusion of the chitosan locating in the center of the material, for compensating the deactivated chitosan that is consumed by microorganisms, the environment, and the food components. Consequently, the chitosan concentration in the food can be maintained, the breeding of spores can be restrained, and the long residual action of antimicrobial property could thus be achieved.

In this paper, the water soluble chitosan played as the antimicrobial agent. It is worth to be mentioned here that, as the release and antimicrobial behaviors of chitosan are based on the hydrophilicity of PLA/starch matrix, addition of other hydrophilic antimicrobial agents other than chitosan into the PLA/starch matrix is expected to achieve similar behaviors.

3.6. Tensile properties

The elongation at break, tensile strength, and tensile modulus of the PLA/starch/chitosan antimicrobial materials could be seen in Table 2. As expected, without compatibilizer, the addition of starch and chitosan caused a decrease in the tensile strength and

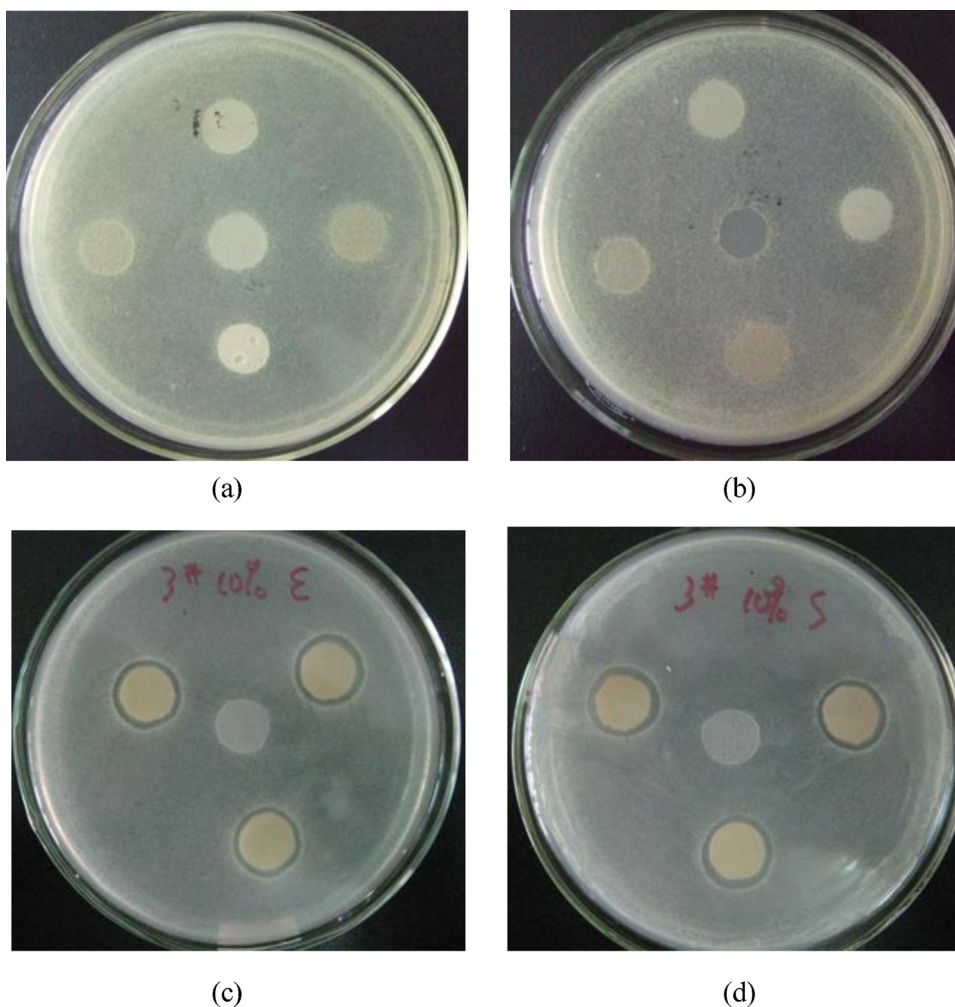


Fig. 4. The antimicrobial ability of blends against microorganisms. (a) and (b) S-0/10 blend versus *E. coli* and *S. aureus*, respectively; (c) and (d) S-40/10 blend versus *E. coli* and *S. aureus*, respectively.

an increase in the elongation at break of the blends. Specifically, the tensile strength of antimicrobial films was about only half of that of pure PLA film (S-0). A former paper has shown that, with the addition of a compatibilizer, the tensile properties of PLA/starch blends could be remained as those of pure PLA (Huneault & Li, 2007). Nevertheless, the current work shows that the tensile properties of the blends were consumed partly, with the release of chitosan and the maintaining of the antimicrobial property.

As the aggregations of starch/chitosan could migrate from the blends to water, only porous PLA matrices were left after the release. Namely, the physical state of the blend films was turned into a porous state. The films became more and more brittle during the release, as the blends turned into pure PLA which is inherently brittle. While this paper is focused on the a model of slow-release devices, future research is necessary to investigate the mechanical properties of the blends as influenced by the release which

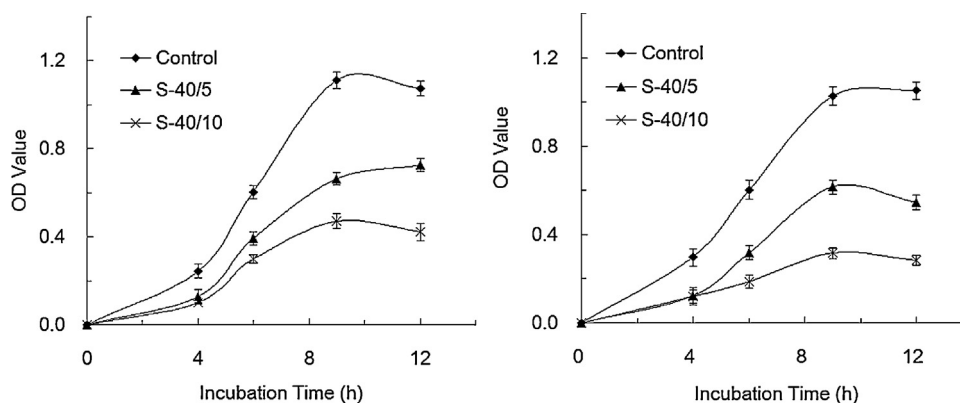


Fig. 5. The growth curves of microorganisms (*E. coli*, left; and *S. aureus*, right) that were restrained by the blends during the accelerated release.

Table 2
Tensile properties of blends.

	Elongation at break (%)	Tensile strength (MPa)	Tensile modulus (GPa)
S-0	2.5 ± 1.0	34.1 ± 3.8	3.3 ± 0.3
S-0/5	1.8 ± 0.7	19.3 ± 7.0	2.6 ± 0.7
S-30/5	4.5 ± 1.4	14.5 ± 1.9	1.4 ± 0.1
S-40/5	7.3 ± 1.7	13.3 ± 0.6	1.2 ± 0.1
S-40/10	9.9 ± 1.4	14.6 ± 3.9	1.0 ± 0.1

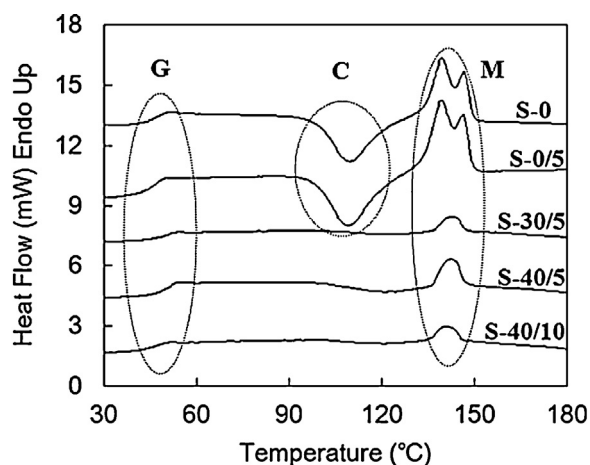


Fig. 6. The DSC heat flows of blended materials.

are important for the actual application period of such materials.

Although the results here show that the tensile properties of the antimicrobial blends became less strong with the addition of starch and chitosan, the remaining PLA was still in a continuous phase and thus its tensile properties could be expected to be better than some other materials based on protein or polysaccharides (Yu et al., 2006).

3.7. Thermal property

The DSC heat flow curves of the samples could be seen in Fig. 6. For all curves, a clear step change (peak G) could be observed in the range of 40–60 °C, signifying the glass transition. Besides, for the samples S-0 and S-0/5, an obvious exothermic peak (peak C) emerged in the range of 100–120 °C, which was the signal of annealing. But this peak did not appear for the samples S-30/5, S-40/5, and S-40/10. The reasons for this might be that, after the glass transition, the recrystallization occurred for the continuous PLA matrix due to the elimination of the stress between molecular chains, while the addition of starch and chitosan destroyed the continuous PLA matrix, which compressed the recrystallization process. Moreover, an apparent endothermic peak (peak M) emerged in the range of 140–150 °C, which represents the melting of PLA crystallinity. As expected, the M peaks of the samples S-0 and S-0/5 were much larger than those of the blends, which can be explained by the thermal event of annealing.

On the other hand, it should be noted that the glass transition temperature (T_g) of antimicrobial blends was around 50 °C. As the application of the blend material is for fresh meat as mentioned before, the thermal property shown here supports such application.

4. Conclusions

Food antimicrobial packaging materials require not only the effectiveness of antimicrobial ability, but also the long-lasting

performance of such ability. Based on this requirement, an antimicrobial material with a slow-release property was developed based on PLA/starch/chitosan blends.

Specifically, the DCA results showed that the addition of starch into the PLA matrix obviously improved the hydrophilicity of the blends, which was favorable for the diffusion of the embedded chitosan. The microstructure of the blends illustrated that the embedded aggregations of starch/chitosan could diffuse out from the surface. Moreover, the release procedure for chitosan could be divided into two stages, an initial fast stage and a following slow stage. In the first stage, the release rate of chitosan was very fast, while in the slow-release stage, chitosan was released slowly but durably. These two stages exhibited the effectiveness and long residual action of the antimicrobial property of blends respectively, and showed that the blend material was very suitable for foods with high water activity, such as fresh meat. At last, the tensile and thermal properties also supported the suitability of the PLA/starch/chitosan antimicrobial material for application.

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