Research Article

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Preparation and characterization of corn starch/PVA/glycerol composite films incorporated with ϵ -polylysine as a novel antimicrobial packaging material

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Abstract: Corn starch/polyvinyl alcohol (PVA)/glycerol composite films incorporated with ϵ -polylysine were prepared, and their properties were investigated. The Fourier-transform infrared (FTIR) spectroscopy indicated that the interactions happened between the amino group of ϵ -polylysine and hydroxyl group starch/PVA composite films. X-ray diffraction (XRD) analysis showed that the addition of ϵ -polylysine decreased the intensity of all crystal peaks. Thermogravimetric (TGA) analysis suggested that ϵ -polylysine improved the thermal stability of composite films. Scanning electron microscopic (SEM) analysis showed that the upper surface of composite films incorporated with ϵ -polylysine presented more compact and flat surface. The antimicrobial activity of the composite film progressively increased with the increasing of ϵ -polylysine concentration ($P < 0.05$). The tensile strength, elongation at break and water absorption significantly increased, whereas water solubility decreased with the increasing of ϵ -polylysine concentration ($P < 0.05$). Therefore, the corn starch/PVA/glycerol composite films incorporated with ϵ -polylysine had good mechanical, physical and antimicrobial properties and could have potential application as a novel antimicrobial packaging material.

Keywords: ϵ -polylysine, corn starch, polyvinyl alcohol, glycerol, antimicrobial packaging material

1 Introduction

To reduce environmental pollution, starch, a natural, inexpensive and biodegradable polymer, has been widely

used as a replacement of petroleum-derived synthetic polymers (1). But pure starch lacks the strength, water resistibility and thermal stability (2). Therefore, to form a film with good packaging property, water-soluble starch commonly needs to be blended with a polymer such as PVA (3).

PVA is a synthetic polymer that can also be biodegradable in the natural environment (2,4). However, the relatively high cost and the low biodegradation rate are two major restrictions while using packaging materials made of pure PVA (5). However, these defects can be eliminated by blending starch in pure PVA (6). Therefore, blend films prepared with starch and PVA by using solution casting have been extensively studied as potential biodegradable packaging materials, and their properties such as mechanical properties, water barrier property and morphology property could be improved (7–10).

The antimicrobial property is also important for food packaging materials (11). The antimicrobial active packaging is different from the traditional packaging in its ability to reduce or inhibit the growth of spoilage and pathogenic microorganism on food surfaces (12). To confer the antimicrobial property, many antimicrobial substances such as sorbic acid, chlorine dioxide, nisin and pectin have been successfully incorporated in food packaging materials (13–15). Among these antimicrobial substances, antimicrobial peptides that act as biological preservatives have received extensive attention due to their safety. ϵ -Polylysine is a natural antimicrobial peptide and has a broad antimicrobial activity against many fungi, yeast and bacteria (16,17). The antimicrobial effects and the mechanism of ϵ -polylysine against *Staphylococcus aureus*, *Listeria monocytogenes* and *Saccharomyces cerevisiae* have been intensively researched (18–21). Moreover, there are some reports about the preparation of food packaging films containing ϵ -polylysine for controlling spoilage and pathogenic microorganisms (21–23).

However, there is a lack of available scientific literature about the preparation and the characteristics of the starch/PVA composite film incorporated with ϵ -polylysine.

This study aims to develop novel corn starch/PVA/glycerol/ ϵ -polylysine composite films with antimicrobial

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activity and to evaluate their mechanical properties, physical properties and antimicrobial activity.

2 Materials and methods

2.1 Materials

Corn starch of analytical grade was purchased from Shanghai Yuanye Bio-Technology Company (Shanghai, China), which is composed of 74.3 wt% amylopectin and 25.7 wt% amylose, and the moisture content is 11.7 wt%. PVA with $1,750 \pm 50$ of polymerization degree was obtained from Shanghai Zhanyun Chemical Co. Ltd (Shanghai, China). Glycerol (PubChem CID: 753) was obtained from Beijing Aoboxing Bio-tech Co. Ltd (Beijing, China) and was of analytical grade. ϵ -Polylysine (PubChem CID: 118705389) was obtained from Kuer Chemical Science and Technology Co. Ltd (Beijing, China), with molecular mass of 3,980.

2.2 Preparation of composite films

Composite films were prepared by the casting method. First, 12 g of corn starch, 9 g of PVA and 6 g of glycerol were mixed in 300 ml distilled water. ϵ -Polylysine was dissolved in distilled water to form the 20 wt% of solution. Then, the ϵ -polylysine solution was added to this mixture at different final concentrations of 0, 5, 10, 15 and 20 wt% (of corn starch). By using a mechanical stirrer (JB60-SH, Lichen science and Technology Co. Ltd, China), the mixture was stirred at 300 rpm and 40°C for 30 min, at 500 rpm and 60°C for 30 min and at 500 rpm and 95°C for 60 min. After 100 g of the film-forming solution being poured on the glass plate (20 cm $\times$ 20 cm), the mixture was dried in a ventilated oven at 45°C for 12 h. After equilibrated at 50% relative humidity and 20°C for at least 3 days, the measurements were carried out. The prepared composite films containing ϵ -polylysine at the final concentration of 0, 5, 10, 15 and 20 wt% (of corn starch) were marked as SPG, SPG-L5, SPG-L10, SPG-L15 and SPG-L20, respectively.

2.3 Characterization of composite films

FTIR analysis of composite films was conducted using a Spectrum one Model FTIR Infrared Spectrometer

(PerkinElmer, USA). After equilibrated for 24 h at 50°C, the samples were recorded using the KBr pellets method with a total of 50 scans at a resolution of 4 cm⁻¹ in the range between 400 and 4,000 cm⁻¹.

XRD patterns of the composite films were evaluated with a D8 Advance diffractometer (Bruker-AXS, German) through CuK α radiation at room temperature, 40 kV and 40 mA, an integration time of 1 s and with the 2θ range of 0°–60°.

The TGA analysis of composite films was carried out using a NETZSCH TG Analyzer (Star 449F3, Germany) under a dynamic nitrogen atmosphere in aluminum pans at a heating rate of 10°C min⁻¹ from 25 to 600°C.

The surface morphology of the composite films was analyzed by the method described in the study by Espitia et al. (24) using an SEM (S-4300, High-Technologies Corporation, Tokyo, Japan).

The mechanical properties of the composite films including the tensile strength and the elongation at break were determined using a texturometer (Texture Technologies Corp, New York, USA) according to the standard test method for tensile properties of thin plastic sheeting (25). Six replicate measurements were carried out for each treatment (10 cm $\times$ 2 cm).

Water absorption and water solubility of composite films were determined according to the method described by Bourtoom (26).

The antimicrobial activity of the composite films was assayed according to the method described by Ko et al. (27) with some modification. Composite films were first cut into square chips (1 cm $\times$ 1 cm). Twenty microlitres of the cell suspension or the spore suspension (5×10^6 CFU ml⁻¹) of *S. aureus* ATCC 63589, *Escherichia coli* ATCC 25922 and *Aspergillus oryzae* ATCC 42149 was placed on the prepared composite films chips containing ϵ -polylysine (SPG-L5, SPG-L10, SPG-L15 and SPG-L20), and the composite film without ϵ -polylysine (SPG) was used as a control. The initial viable cells of each chip of the composite film were about 10^5 CFU. The chips of films were incubated at 37°C for *S. aureus* and *E. coli* and at 30°C for *A. oryzae*. After 2 h of incubation, the chips of composite films were put in stomacher bags containing 1 mL of sterile normal saline (0.85 wt%). After being stomached for 2 min, the solution was then decimally diluted with sterile normal saline and plated in duplicate onto the nutrient broth agar plate for *S. aureus* and *E. coli* and onto the potato dextrose agar plate for *A. oryzae*. After being incubated for 24 h at 37°C for *S. aureus* and *E. coli* and for 48 h at 30°C for *A. oryzae*, the viable counts (log CFU cm⁻²) on the composite film chip were determined.

2.4 Statistical analysis

Experiments were repeated three times for each sample, and means were calculated. Software SAS8.1 (SAS Institute Inc., Cary, NC, USA) was used to analyze the data, and $P < 0.05$ is regarded as a statistically significant difference.

3 Results and discussion

3.1 FTIR analysis

Figure 1 shows the FTIR spectroscopy of ϵ -polylysine and starch/PVA/glycerol composite films with and without ϵ -polylysine. In the spectroscopy of ϵ -polylysine, the band

at $3,263\text{ cm}^{-1}$ was due to the nitrogen hydrogen single bond (NH_2) asymmetric stretching vibration in NH_2 groups, while the bands at $3,079$, $2,993$ and $2,923\text{ cm}^{-1}$ were due to the C–H stretching vibration. In addition, the bands at $1,678$ and $1,656\text{ cm}^{-1}$ were due to the C–O bond (amide I) in the carbonyl group and CH_2 bending vibration, respectively. The bands at $1,590$ and $1,405\text{ cm}^{-1}$ were due to the NH (amide II) of the primary amine group and the C–N stretching vibration in the amido group, respectively. The bands from 800 to $1,200\text{ cm}^{-1}$ were due to C–O stretching vibration.

In the spectroscopy of the starch/PVA/glycerol composite films, the band at $3,283\text{ cm}^{-1}$ was due to the hydrogen bond (O–H) stretching vibration in hydroxyl groups. The band at $1,655\text{ cm}^{-1}$ was due to the CH_2 plane bending vibration. The band at $1,417\text{ cm}^{-1}$ was due to the C–N deformation vibration.

Figure 1: FTIR spectroscopy of ϵ -polylysine (a) and starch/PVA/glycerol composite films without and with 10% and 20 wt% of ϵ -polylysine (b).

Changes of the spectra peaks in the FTIR spectroscopy can reflect the chemical interactions when substances are mixed (28). After ϵ -polylysine was incorporated into the starch/PVA/glycerol composite films, the band at $3,263\text{ cm}^{-1}$ resulting from NH_2 asymmetric stretching in the spectrum of ϵ -polylysine shifted to $3,283\text{ cm}^{-1}$. The bands at $3,079$ and $2,993\text{ cm}^{-1}$ in the spectrum of ϵ -polylysine were missing, and the band at $2,923\text{ cm}^{-1}$ shifted to lower frequency of $2,909\text{ cm}^{-1}$. The band at $1,678\text{ cm}^{-1}$ resulting from the C–O bond (amide I) in the carbonyl group shifted to the lower frequency. The band at $1,590\text{ cm}^{-1}$ resulting from the NH (amide II) blending vibration in amido group shifted to the frequency of $1,601\text{ cm}^{-1}$, and this phenomenon was similar to the band of NH (amide II) in the amino group of chitosan shifting to higher frequency after chitosan being mixed with starch (29). The band at $1,405\text{ cm}^{-1}$ resulting from the C–N stretching vibration in the amido group was shifted to the lower frequency of $1,381\text{ cm}^{-1}$. These results indicated that the interactions happened between the amino group of ϵ -polylysine and hydroxyl group in the matrix of starch/PVA/glycerol composite films. Zhu et al. also found that the characteristic absorption peak of $3,200\text{--}3,500\text{ cm}^{-1}$ shifted to the higher frequency after ϵ -polylysine being mixed with bacterial cellulose and reflected the interactions between ϵ -polylysine bacterial cellulose (30).

3.2 XRD patterns

XRD patterns of the starch film, the PVA film and the composite films with and without incorporation of ϵ -polylysine are shown in Figure 2. XRD patterns can reflect the crystallinity of composite films. Figure 2 shows that the addition of ϵ -polylysine in the composite films decreased the intensity of all crystal peaks ($2\theta = 18^\circ$, 20° and 23°) of starch/PVA/glycerol, while with the addition 20 wt% of ϵ -polylysine, the crystallization peak at $2\theta = 18^\circ$ and $2\theta = 23^\circ$ nearly disappeared. These results indicated that ϵ -polylysine had certain plasticizing and cross-linking effects and could reduce the crystallinity of corn starch/PVA/glycerol composite films. This reduction in the crystallinity may result from the interaction between the amine groups in the molecules of ϵ -polylysine and the –OH groups in the starch and PVA, and this may also make composite films more elastic and tough. This result agreed with the conclusion of Zhu et al., and they reported that the XRD pattern of ϵ -polylysine also changed after composite

films formed by ϵ -polylysine mixing with bacterial cellulose. This suggested that ϵ -polylysine had been incorporated into the networks of bacterial cellulose (30).

Figure 2: XRD patterns of starch/PVA/glycerol composite films (a), composite film containing 5 wt% of ϵ -polylysine (b), 10 wt% of ϵ -polylysine (c), 15 wt% of ϵ -polylysine (d) and 20 wt% of ϵ -polylysine (e).

3.3 TGA analysis

TGA analysis curves of starch/PVA/glycerol composite films incorporated with 0, 5, 10, 15 and 20 wt% of ϵ -polylysine are shown in Figure 3, and the data of the initial decomposition temperature (IDT), the final decomposition temperature (FDT) and the mass residual rate at 600°C are listed in Table 1. The weight loss curves of several composite films were similar, and three distinct stages can be seen from their TGA curves. It can be seen from Figure 3 that the first stage of mass loss was in the range of $25\text{--}200^\circ\text{C}$ and was mainly due to the evaporation of adsorbed water for all film samples (2). The weight loss at the second stage ($200\text{--}350^\circ\text{C}$) was mainly due to the polymer chain decomposition of PVA and starch (8,10). The third stage ($350\text{--}600^\circ\text{C}$) was mainly due to the decomposition of polymer chains, and small carbon and hydrocarbon molecules are the final products (31). From Table 1, it can be seen that both the initial decomposition temperature and the final decomposition temperature of major mass loss gradually increased with the increasing addition of ϵ -polylysine from 0% to 20 wt% (of corn starch) ($P < 0.05$). Moreover, the addition of ϵ -polylysine also

significantly increased the final residual mass rate at 600°C ($P < 0.05$). These results strongly suggested that the addition of ϵ -polylysine improved the thermal stability of composite films. This increase in thermal stability may also result from the cross-linking action between the $-OH$ groups of starch and PVA molecules and the amine groups of ϵ -polylysine molecules. Pour et al. also reported that the addition of citric acid significantly increased the thermal stability of the starch/PVA composite film and suggested that this increase could be from the cross-linking interaction of citric acid molecules with starch and PVA chains (10).

Figure 3: TGA analysis curves of composite films.

3.4 Surface morphology of the composite films

SEM photographs have been widely applied to the surface morphology analysis of a variety of composite films (2,18). The upper surface photographs revealed that ϵ -polylysine had a significant influence on the surface morphology of

starch/PVA/glycerol composite films (Figure 4). The surface of the composite films incorporated with ϵ -polylysine was more compact and flat than the surface of the film without ϵ -polylysine. When 20 wt% of ϵ -polylysine incorporated into the composite film, the upper surface of the film was relatively smooth and homogenous. These results indicated that ϵ -polylysine may help to distribute, interconnect and integrate throughout the matrix of the composite films. The result was similar to the study by Zhu et al. (2010). They revealed that the atomic force microscopic image of ϵ -polylysine/bacterial cellulose had more unique structure than bacterial cellulose and ϵ -polylysine, and ϵ -polylysine was evenly distributed inside the bacterial cellulose fibril networks with good compatibility (30). They concluded that the hydroxyl groups of cellulose could form hydrogen bonds with the amino groups in ϵ -polylysine (30). The result of the study by Xiong et al. indicated that the starch/PVA film showed a compact and smooth ultra-structure surface after the addition of nano-silicon dioxide and suggested that the hydroxyl group in nano-silicon dioxide can be form the hydrogen bond with starch and PVA (32).

3.5 Mechanical property of composite films

To provide physical protection for a variety of foods, the mechanical properties of composite films incorporated with ϵ -polylysine are very important. Therefore, the elongation at break and the tensile strength were researched as a function of the ϵ -polylysine incorporated in the starch/PVA/glycerol matrix (Table 2). Both the tensile strength and the elongation at break significantly increased with the increasing addition of ϵ -polylysine from 0% to 20 wt% (of corn starch) ($P < 0.05$). Zhang et al. reported that both the tensile strength and the elongation at break of the starch/ ϵ -polylysine composite films significantly increased with the increasing ϵ -polylysine

Table 1: Thermogravimetric analysis of blend films

Sample	Initial decomposition temperature (°C)	Final decomposition temperature (°C)	Residual weight at 600°C (wt%)
SPG	251 ^a	345 ^a	11 ^a
SPG-L5	265 ^b	364 ^b	14 ^b
SPG-L10	282 ^c	382 ^c	15 ^c
SPG-L15	296 ^d	405 ^d	16 ^d
SPG-L20	315 ^e	426 ^e	18 ^e

The values presented here are means of three repeated examples, and a, b, c, d and e in values located in the same column express significant difference ($P < 0.05$).

Figure 4: SEM photographs of the surface of composite films: (a) without ϵ -polylysine, (b) containing 10 wt% of ϵ -polylysine and (c) containing 20 wt% of ϵ -polylysine.

Table 2: The effect of ϵ -polylysine concentration on the tensile strength and elongation at break

Samples	Tensile strength (MPa)	Elongation at break (%)
SPG	9 ^a	85 ^a
SPG-L5	11 ^b	92 ^b
SPG-L10	12 ^c	107 ^c
SPG-L15	14 ^d	122 ^d
SPG-L20	16 ^e	139 ^e

The values presented here are means of three repeated examples, and a, b, c, d and e in values located in the same column express significant difference ($P < 0.05$).

concentration (from 0% to 6%), and they concluded that the interaction formed between the amine groups of ϵ -polylysine and $-OH$ group of starch (33). The result was also similar to the report about the increase of the tensile strength and the elongation at break by the incorporation of chitosan into starch (34). ϵ -Polylysine has a similar property to chitosan in free positively charged amino groups. The increases in the tensile strength and the elongation at break may attribute to the hydrogen bonding interaction between the amine groups of ϵ -polylysine and the $-OH$ groups of starch and PVA. These results indicated that composite films incorporated with ϵ -polylysine possessed better mechanical property than those without ϵ -polylysine.

3.6 Water absorption and water solubility

The water absorption and water solubility of the composite films were important in indicating the combination degree among the components of the composite

films as well as the water resistance (35). It can be observed from Table 3 that water absorption of composite films increased, whereas water solubility decreased with the increasing addition of ϵ -polylysine ($P < 0.05$). When 20 wt% of ϵ -polylysine was incorporated into the film, the water absorption increased by 44.1%, whereas the water solubility decreased by 33.8% compared with the composite film without ϵ -polylysine. This result indicated that the incorporation of ϵ -polylysine into starch/PVA/glycerol films increased the water resistance of composite films. Moreover, this result might suggest that the combination of the substances in composite films was improved by the existence of interactions between the added ϵ -polylysine and the corn starch/PVA/glycerol mixture. Yoon et al. reported that the water absorption increased, whereas the water solubility decreased as the PMMA-CO-AAM (poly(methyl methacrylate-co-acrylamide)) nanoparticles content increased in the starch/PVA blend film and also suggested that it might resulted from the interactions between the added nano-sized PMMA-CO-AAM and the starch/PVA mixture (36).

Table 3: The effect of ϵ -polylysine concentration on the water absorption and solubility

Samples	Water absorption (%)	Water solubility (%)
SPG	127.3 ^a	6.5 ^e
SPG-L5	139.2 ^b	5.8 ^d
SPG-L10	156.5 ^c	5.2 ^c
SPG-L15	168.8 ^d	4.7 ^b
SPG-L20	183.4 ^e	4.3 ^a

The values presented here are means of three repeated examples, and a, b, c, d and e in values located in the same column express significant difference ($P < 0.05$).

3.7 Antimicrobial activity analysis

In food preservatives, bacteria (both Gram positive and Gram negative) and fungi were the very important spoilage and pathogenic microorganisms. Therefore, the antimicrobial activities of composite films incorporated with 0, 5, 10, 15 and 20 wt% of ϵ -polylysine against *S. aureus* ATCC 63589 (Gram-positive bacteria), *E. coli* ATCC 25922 (Gram-negative bacteria) and *A. oryzae* ATCC 42149 (fungi) were investigated and summarized in Table 4. The initial viable counts of *S. aureus*, *E. coli* and *A. oryzae* on the chips of the composite films were 4.92, 4.98 and 5.06 log CFU cm⁻², respectively. It can be seen that the viable counts of these three strains in composite films without ϵ -polylysine did not significantly decreased after exposure for 2 h ($P > 0.05$). However, the antimicrobial activity against these three strains progressively increased with the increase of the final concentration of ϵ -polylysine in composite films ($P < 0.05$). The inhibition of the composite film incorporated with ϵ -polylysine against Gram-positive bacteria *S. aureus* was the strongest, and the inhibition against fungi *A. oryzae* was the weakest. Compared with the composite film without ϵ -polylysine, the viable cell counts of *S. aureus*, *E. coli* and *A. oryzae* in composite film chips containing 20 wt% of ϵ -polylysine were reduced by 2.06, 1.86 and 0.97 log CFU cm⁻², respectively, after exposure for 2 h. These results indicated that the composite film without ϵ -polylysine had no antimicrobial activity, whereas those incorporated with ϵ -polylysine showed considerably stronger antimicrobial activity. The results of the study by Zhang et al. indicated that the starch films incorporated with ϵ -polylysine showed the inhibitory effect on *E. coli*, *Bacillus subtilis* and *Aspergillus niger* (33). Zhu et al. reported that the ϵ -polylysine/BC blend film exhibited a broad-spectrum antimicrobial activity (30). These results strongly suggested

that the blend films incorporated with ϵ -polylysine have good potential as antibacterial packaging materials. Other antimicrobial peptides such as nisin and pediocin also had similar antimicrobial action after being incorporated into the film (15,24,27).

4 Conclusions

Corn starch/PVA/glycerol composite films incorporated with ϵ -polylysine were prepared, and their mechanical, physical and antimicrobial properties were investigated. The FTIR spectroscopy indicated that the interactions happened between the amino group of ϵ -polylysine and the hydroxyl group in the matrix of starch/PVA/glycerol composite films. The XRD patterns of composite films showed that the addition of ϵ -polylysine decreased the intense of all crystal peaks of starch/PVA/glycerol composite film. The TGA analysis suggested that the addition of ϵ -polylysine improved the thermal stability of composite films. The surface of the composite film incorporated with ϵ -polylysine was more compact and flat than the surface of the film without ϵ -polylysine. The tensile strength and the elongation at break of composite films significantly increased with the increasing addition of ϵ -polylysine ($P < 0.05$). The water absorption of the composite film increased, whereas the water solubility decreased with the increasing addition of ϵ -polylysine ($P < 0.05$). The starch/PVA/glycerol composite film without ϵ -polylysine had no antimicrobial activity, and the antimicrobial activity of the composite film against *S. aureus*, *E. coli* and *A. oryzae* progressively increased as the increasing of ϵ -polylysine concentration ($P < 0.05$). Therefore, corn starch/PVA/glycerol composite films incorporated with ϵ -polylysine had good mechanical, physical and antimicrobial properties and could be applied as a novel food packaging material with antimicrobial activity.

Table 4: Effect of ϵ -polylysine on viable count (log CFU cm⁻²) of composite films

Composite films	<i>Staphylococcus aureus</i>	<i>Escherichia coli</i>	<i>Aspergillus oryzae</i>
SPG	4.88 ^a	4.92 ^a	4.98 ^a
SPG-L5	4.01 ^b	4.25 ^b	4.72 ^b
SPG-L10	3.64 ^c	3.87 ^c	4.46 ^c
SPG-L15	3.27 ^d	3.56 ^d	4.23 ^d
SPG-L20	2.82 ^e	3.06 ^e	4.01 ^e

The values presented here are means of three repeated examples, and a, b, c, d and e in values located in the same column express significant difference ($P < 0.05$).

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