

Biodegradable high oxygen barrier membrane for chilled meat packaging

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ABSTRACT: “Chilled” meat is more nutritional, healthy and hygienic than the meat kept at ambient temperature. “Poly(propylene carbonate) (PPC) and poly(vinyl alcohol) (PVA) were used to prepare biodegradable three-layer PPC/PVA/PPC films with high barrier and tensile properties. The potential benefits of the developed films were also evaluated on the shelf life of chilled meat products. Compared to PPC film, using 20 wt % PVA as an intermediate layer in PPC/PVA/PPC film remarkably enhanced oxygen barrier performance at 0 and 50 RH % by about 500 times, tensile strength by about 8 times, and Young’s modulus by nine times, but no beneficial effect on water vapor barrier performance has been observed. A new “sandwich” type of completely biodegradable material with high barrier was obtained. The application of PPC/PVA20/PPC film as the packaging material of chilled meat was effectively kept the total viable count (TVC) and total volatile basic nitrogen (TVB-N) to acceptable levels in chilled meats until 19th day of storage at 4°C, however, the spoilage occurred within 11th and 14th days of refrigerated storage in term of TVC and TVB-N, respectively, in the chilled meats packed with only PPC. Herein, we report that PPC/PVA/PPC three-layer film can be a promising well-defined biodegradable material with excellent potential in chilled meat packaging. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41871.

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INTRODUCTION

There has been great consumer demand for perishable chilled meat that is perceived as being fresh, healthy and convenient. Many packaging technologies have been established for extending chilled food shelf-life, such as modified atmosphere packaging, vacuum packaging,¹ vacuum skin packaging and active packaging. In early 1979, Newton and Rigg studied the effect of the permeability of polyethylene/polyamide (PE/PA) film on the storage life of vacuum-packed meat and found that both multiplication rates and final counts of the obligately aerobic *Pseudomonas* spp. increased dramatically with increasing film permeability.² In order to maintain the quality of the meat in chilled cabinets, the food-packaging industry has put high priority on improving the performance of the packaging materials, especially in terms of the barrier requirement.³ The commercial semi-rigid plastic containers used for chilled food packaging are predominantly made from PE, poly(propylene) (PP), poly(styrene) (PS), poly(vinyl chloride) (PVC), Acrylonitrile-butadiene-styrene (ABS) and poly(ethylene terephthalate) (PET), and most of these materials are oil dependent, which would cause environmental pollution.

Biodegradable polymers and plastics can be quantitatively converted by action of microorganisms either to CO₂ and H₂O or

to CH₄ and H₂O under aerobic or anaerobic conditions.⁴ They are more environmental friendly and better suited for a number of applications such as shopping bags, food-service packaging materials, and agricultural mulch films.^{5,6} Developing a nontoxic biodegradable package material will have great importance in chilled food-packaging. Oxygen barrier property of materials is especially important for atmosphere and vacuum packaging. The oxygen barrier of materials used presently is far better than most biodegradable materials.⁷ Therefore, improving the oxygen barrier performance of the biodegradable packaging materials is the key for the application of biodegradable materials in chilled meat packaging.

Poly(propylene carbonate) (PPC) is one of the most promising biodegradable materials in the future,⁸ owing to its widespread availability, low cost, and nontoxicity.⁹ It has applications in areas such as coatings, and electronics. PPC can be synthesized from CO₂ with cyclic ether compounds, such as propylene oxide.^{10,11} Considerable effort has been made by the packaging industry to extend the application of PPC as a new packaging materials based on its good packaging property.¹² But PPC has limitations as an individual packaging material due to its poor mechanical properties.^{13,14} Thus great effort has been devoted to improve the poor thermal and mechanical property of PPC

Table I. Mechanical Properties of PPC, PVA, and PPC/PVA/PPC Films

Sample	PVA content in PPC/PVA/PPC film (wt %)	Yield stress (MPa)	Elongation at break (%)	Young's modulus (MPa)
PPC	–	4.3 ± 0.9 ^f	245.4 ± 35.5 ^a	282 ± 83 ^f
PPC/PVA10/PPC	10	18.5 ± 0.5 ^e	31.3 ± 2.9 ^b	1503 ± 229 ^e
PPC/PVA20/PPC	20	34.5 ± 0.7 ^d	10.0 ± 3.1 ^c	2594 ± 122 ^d
PPC/PVA30/PPC	30	52.7 ± 2.2 ^c	4.5 ± 2.8 ^c	5364 ± 898 ^c
PPC/PVA40/PPC	40	76.0 ± 2.7 ^b	4.3 ± 2.2 ^c	7342 ± 768 ^b
PVA	100	145.9 ± 13.1 ^a	2.1 ± 1.1 ^c	17849 ± 859 ^a

Column data marked with different superscripts differ significantly ($P < 0.05$).

by means of chemical modification such as “grafting”¹⁵ and the physical modification such as “filling” and “compositing.”¹⁶ Poly(vinyl alcohol) (PVA) is one of the few completely biodegradable synthetic polymers. It is a synthetic polyhydroxy polymer, having very good water absorption and high gas barrier properties.¹⁷

In the present work, biodegradable PPC/PVA/PPC three-layer films were prepared by a solution casting method. The developed films were characterized by attenuated total reflectance Fourier transformed infrared (ATR-FTIR) and investigated in terms of oxygen and water vapor barrier and mechanical performances. The potential benefits of the packaging treatment on total viable count (TVC), total volatile basic nitrogen (TVB-N), and sensorial changes in chilled meats were also evaluated.

EXPERIMENTAL

Materials

PPC ($M_n = 1.17 \times 10^{-5}$, $M_w/M_n = 4.21$) was purchased from Inner Mongolia Melic See High-Tech Group company, and purified by precipitation in ethanol from chloroform solution. PVA (1788) was provided by Shanxi three-dimensional company. PE was provided by Zhongchuang packing material Co. The fresh pork was purchased from Xiyuan meat Co. (Hohhot, China). Plate Count Agar (PCA; Sangon Biotech Co., Shanghai).

Film Preparation

a. PVA film: PVA (5, 9.5, 14.3, 19.5, and 48 g) was dissolved in the distilled water (1000 mL) with stirring for 3 h at room temperature. Then, 15 mL of the film solution was poured into a plastic Petri dish (diameter: 90 mm) and was dried at 35°C for 48 h in the vacuum oven. The prepared films were used as the PVA layers and the PVA single films were prepared by the maximum concentration solution.

b. PPC/PVA/PPC and PPC films: in order to keep the weight ratio of PPC : PVA at 9 : 1, 8 : 2, 7 : 3, and 6 : 4, different concentrations of PPC solutions were prepared as follows: PPC (65, 57, 50, 42, and 72 g) were dissolved in chloroform (1000 mL), with stirring for 3 h at room temperature.

PPC solution (5 mL) was transferred into a plastic Petri dish containing the corresponding proportion of PVA film. After the film dried, another equal amount of PPC solution (5 mL) was added to treat another side of the PVA film. PPC/PVA/PPC

films with different weight percentage of PVA were named as PPC/PVA10/PPC, PPC/PVA20/PPC, PPC/PVA30/PPC, and PPC/PVA40/PPC films as shown in Table I.

The PPC single membrane was prepared by pouring amount of PPC solution (maximum concentration; 10 mL) into the glass Petri dishes (diameter = 90 mm) and dried. The films were placed into vacuum drying oven at 35°C for a week before measurements. The thicknesses of the film (about 86.8 ± 7.8 μm) were measured using a micrometer (0.001 mm, Shangshen, Shang Hai, China) repeated ten times in different positions, the mean thickness was calculated.

ATR-FTIR Measurement

The ATR-FTIR spectra were recorded on the IR Affinity-1 spectrometer (Shimadzu, Japan) with two 4.5 cm \times 0.8 cm films to analyze the chemical composition of the film surfaces. The spectra were recorded from 750 to 4000 cm^{-1} with the sum of 64 scans at a resolution of 4 cm^{-1} .

Tensile Test

The tensile testing of the sample was carried out on a texture analyzer (QTS-250, Stable Micro System, UK) followed by ASTM-D882-09. Each level 10 films were tested at room temperature, RH \approx 28%.

Oxygen Barrier Property

Oxygen transmission rate (OTR) was measured with 100% oxygen followed by ASTM F-1927 at 25, 35, and 45°C, and four relative humidity (0, 50, 60, and 70%) were set under each temperature. The tests were carried out on an oxygen permeation analyzer (Model 8001 Illinois Instruments) with a 5-cm² mask. Each test had two repetitions. The oxygen permeability (OP) was calculated according to the following equation:

$$OP = \frac{OTR \times D}{\Delta P} \quad (1)$$

OTR: oxygen transmission rate ($\text{cm}^3/\text{m}^2\cdot\text{d}$). D : thickness of the film (m). ΔP : ΔP is oxygen partial pressure (1 atm), corresponding to the gas permeation chamber side oxygen partial pressure, while the oxygen partial pressure on the carrier gas side was zero.

Water Vapor Barrier Property

Water vapor transmission rate (WVTR) was measured using a Permatran-W Model 3/61 water vapor permeability meter

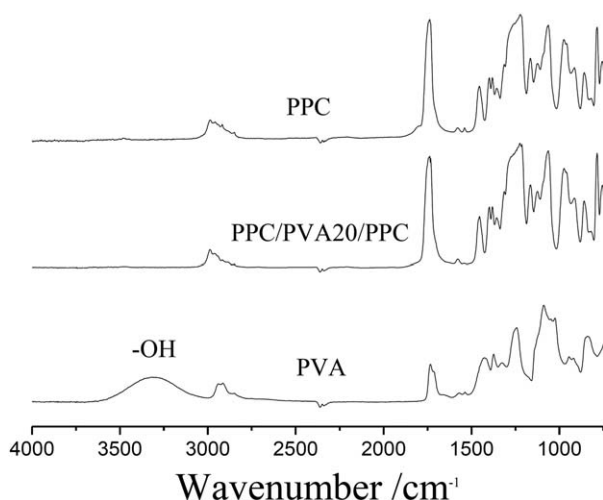


Figure 1. ATR-FTIR spectra of PPC, PVA, and PPC/PVA20/PPC films.

(Mocon) with six test chambers (six parallel samples) followed by ASTM E96 (Default Method) with a 1-cm² mask. The samples were cut from without any damage, fold and crease film. Measurements were carried out at 25, 35, and 45°C with three relative humidity (50, 60, and 70%) under each temperature. Water vapor permeability (WVP) values were calculated from the following equation:

$$WVP = \frac{WVTR \times D}{\Delta P} \quad (2)$$

WVTR: water vapor transmission rate (g/m²·d). *D*: thickness of the film (m). $\Delta P = S \times (RH_2 - RH_1)$

In the formula, *S* is saturated water vapor pressures (Pa) at a certain temperature (25, 35, and 45°C), and *RH*₁ (%) is the relative humidity of top test chamber and *RH*₂ (%) is the relative humidity of bottom test chamber. The top test chamber flowed with dry nitrogen so we consider *RH*₁ is 0, and the bottom chamber was flowed *RH*₂ is 50, 60, and 70%.

Chilled Meat Packaging

A 2-cm thick steak was cut from the fresh pork after storage at 4°C for 24 h, and then the meat was divided into several groups after getting rid of fat. Each group had thirty meat samples and each sample weighed about 30 ± 2 g. All of the cuttings were performed under aseptic conditions. Finally, one group of the meat samples was packed with the PPC and PPC/PVA20/PPC films on a vacuum packer (DZ-400; Shanghai Jia Cheng Packaging Machinery and Equipment CO.) for 30s. The other group was simple wrapped by ordinary PE film and contact with air directly, which acted as blank control group. All samples were kept in a chilled cabinet at 4°C. The sensory evaluation, TVCs, and TVB-N of chilled meat samples were measured every other day.

Sensory Evaluation

The Criteria for sensory evaluation of chilled meat was given in Table IV. These marks were given to at least 12 people and their evaluations for the meat qualities were averaged and summarized in Table V.

Microbiological Analysis

The meat sample was chopped with a knife in the bio-safety cabinet; all the tools used had been decontaminated, autoclaved. Moreover, the UV light in the biosafety cabinet was turned on for the first 30 minutes before operation to kill bacteria in the environment. Chopped meat sample (25 g) was transferred aseptically to a beaker with 225 mL of 0.85% physiological saline, and the mixture was stirred for 5 min with a glass rod. For microbial enumeration, 1 mL of sample with variable dilutions (1 : 10, diluent, 0.85% physiological saline) was added into dry Sterile Petri dishes and 15–20 mL Plate Count Agar was added into each dish afterward. TVCs were determined using Plate Count Agar. Briefly, after incubation for 48 ± 2 h at 36°C with a colony counter (Yulangnuo technology Co., Beijing, China). Each test had three repetitions, two plates in each repetition. Microbiological data were recorded every other day during storage at 4°C.

Total Volatile Basic Nitrogen

TVB-N value was evaluated as a quality index for fresh pork using the half minim nitrogen determination method. Each test had two repetitions. A chopped meat sample (10 g) was homogenized for 30 min in 100 mL of 0.85% physiological saline. A 5-mL supernatant of the mixture was combined with 5 mL of 1% MgO solution in the glass Conway unit to produce ammonia, which in turn was absorbed into 10 mL of 2% H₃BO₃ solution. TVB-N was then determined as mg per 100 g by titration with 0.01 mol/mL HCl solution.

Statistical Analysis

The results from tensile test, sensory evaluation, TVCs, and TVB-N measurement were analyzed using analysis of variance and Fisher's least square deviation test by using IBM SPSS Statistics (version 20.0). A *P* value < 0.05 was considered as statistically significant.

RESULTS AND DISCUSSION

ATR-FTIR Observation

The ATR-FTIR spectra of PPC, PVA and PPC/PVA20/PPC films in the region of 750–4000 cm⁻¹ are given in Figure 1. The peak at 3294 cm⁻¹ was attributed to the -OH of PVA, and the peaks at 2915 and 1732 cm⁻¹ were due to the vibration of -CH₂ and C=O of a bit PVAC in PVA, respectively.¹⁸ The ATR-FTIR spectrum of PVA presented a smaller peak at 1732 cm⁻¹, which may be contributed from the non-hydrolytic PVAC in the presence of alcohol.

Comparing the spectra of pure PVA with pure PPC, the carbonyl stretching band of PPC appeared at about 1738 cm⁻¹ and the absorption band belonged to -CH₃ appeared at 2987 cm⁻¹ only in the spectrum of PPC and not of PVA.¹⁹ The ATR-FTIR spectrum of PPC/PVA20/PPC film presented a similar spectrum as the pure PPC, which indicated that the surface of the multilayer film was completely covered with PPC.

Mechanical Properties

Stress-strain curves for pure PPC, PVA and the PPC/PVA/PPC films are shown in Figure 2. The Yield stress, elongation at break and Young's modulus are summarized in Table I. The yielded points of PPC/PVA/PPC films shifted to the higher

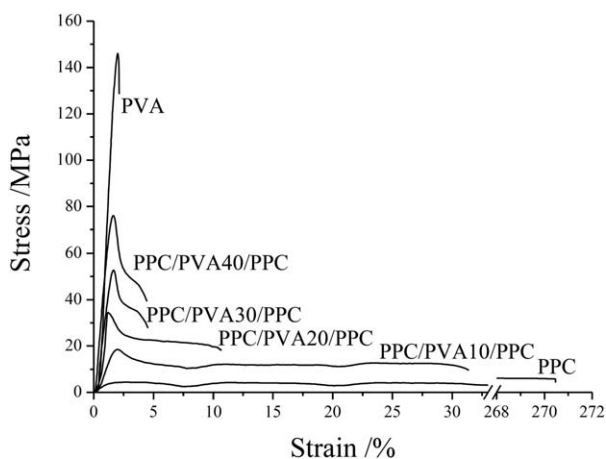


Figure 2. Stress–strain curves of PPC, PVA, and PPC/PVA/PPC films.

strain compared with PPC meaning that the addition of middle PVA layer had improved the yield strength of PPC.

PPC is a ductile polymer with lower yield stress and elongation at break.²⁰ While the PVA is a rigid material with a yield stress of 145.9 MPa at room temperature, which is about 30 times of PPC. After coating, with the addition of PVA, both the yield stress and Young's modulus increased remarkably compared with neat PPC film ($P < 0.05$). For the PPC/PVA10/PPC, the yield stress increased four times and Young's modulus improved about five times compared with pure PPC membrane. Similarly, both yield stress and Young's modulus of PPC/PVA/PPC films increased with the increase in the PVA content. This indicated that PVA can make a significant impact on modifying the mechanical property of PPC, even its resistance to deformation.

Although the elongation at break decreased with increasing PVA content, the multilayered film still kept a value at least two times more than pure PVA membrane, which showed that good ductility is maintained. PPC/PVA10/PPC and PPC/PVA20/PPC films already had mechanical properties similar to PE which are widely used in daily life.²¹ On the other hand when the PVA content increased to 30 or 40%, the elongation at break was less than 5%. These films do not have the performance of plastics and may suggest that too much PVA content was not suitable.

Oxygen Barrier Properties

Table II shows the OTR and OP values of samples at 25°C and in the humidity range of 0–70%. PPC film presented a small OTR value under dry conditions, and the OTR increased with increasing humidity. At 0% humidity, PPC/PVA/PVA films had OTR values far lower than PPC. Moreover, the OTR values of PPC/PVA/PVA films increased when humidity increased from 0 to 70%, which was same trend in pure PPC. This phenomenon can be due to the presence of moisture as moisture can significantly affect the permeability of gas and water vapor. In general, the water plays a role as a plasticizer to increase the free volume of the polymer, which is considered to be "empty" volume in the polymer chains. Therefore, the permeability will increase with the increase in the moisture adsorption amount. In our study, the OTR values decreased when the PVA content increased from 10 to 40%. That is, after coating with PVA, the

Table II. OTR (mL/m^2) and OP ($\times 10^{-15} \text{ mL}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$) Values of PPC, PVA, and PPC/PVA/PPC Films in Different Humidity at 25°C

Sample	0%RH		50%RH		60%RH		70%RH	
	OTR	OP	OTR	OP	OTR	OP	OTR	OP
PPC	68.55 ± 0.92	750.16 ± 4.50	130.50 ± 7.78	1430.85 ± 74.52	131.50 ± 9.19	1440.74 ± 88.90	126.00 ± 8.48	1380.58 ± 82.71
PPC/PVA10/PPC	0.29 ± 0.03	3.05 ± 0.36	0.51 ± 0.02	5.49 ± 0.24	0.61 ± 0.06	6.54 ± 0.68	1.96 ± 0.02	20.90 ± 0.07
PPC/PVA20/PPC	0.14 ± 0.05	1.35 ± 0.42	0.23 ± 0.06	2.20 ± 0.50	0.41 ± 0.04	3.92 ± 0.48	0.65 ± 0.01	6.32 ± 0.12
PPC/PVA30/PPC	0.13 ± 0.05	1.11 ± 0.36	0.22 ± 0.06	1.98 ± 0.47	0.46 ± 0.05	4.12 ± 0.32	0.74 ± 0.06	6.56 ± 0.28
PPC/PVA40/PPC	0.10 ± 0.01	0.83 ± 0.07	0.07 ± 0.05	0.62 ± 0.39	0.14 ± 0.06	1.21 ± 0.53	0.23 ± 0.07	1.98 ± 0.23
PVA	0.04 ± 0.01	0.52 ± 0.02	0.03 ± 0.01	0.32 ± 0.04	0.05 ± 0.01	0.54 ± 0.01	0.08 ± 0.01	0.86 ± 0.05

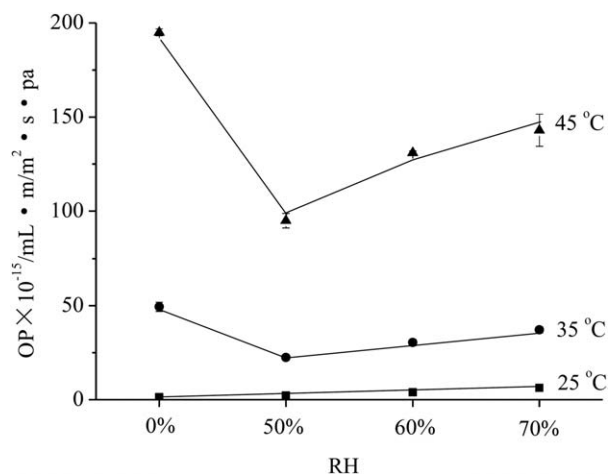


Figure 3. OP values of PPC/PVA20/PPC film depended on variation in temperature and relative humidity.

oxygen barrier property of PPC had greatly improved. The OP values with different humidity are presented in Table II. The OP values showed almost the same tendency to the OTR values with the changing humidity and increasing PVA content.

Generally, transparent films with an OTR of 25.4 μm film below 5 $\text{mL}/\text{m}^2\cdot\text{d}$ ($\text{OP} < 14.55 \times 10^{-15} \text{ mL}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$) are considered as the high barrier materials in food packaging.²² Our PPC/PVA10/PPC film meets the requirement when the humidity is below 70%. When the PVA content increases to 20%, the film satisfies the high barrier material requirement in the humidity range from 0 to 70%, as well as the PPC/PVA30/PPC, PPC/PVA40/PPC films. But when the percentage of PVA increases, the OP is compromised due to its sensitivity to humidity. Considering both mechanical and oxygen barrier properties, we chose the PPC–20%PVA as the chilled meat packaging material.

The OPs of PPC/PVA20/PPC under different temperatures and humidity are presented in Figure 3. At 25°C and initial RH of 0%, the OP increased only slightly with the increase in humidity. At 35°C, the OP decreased slightly, with the humidity increasing to 50%. This may be attributed to the fact that, in the presence of humidity, the film can absorb polar water molecules from the external environment forming a water layer on the surface, leading to the reduction in polar oxygen permeability. Therefore, with the increase in the moisture on the film surface, the oxygen permeability of the PPC/PVA20/PPC film will

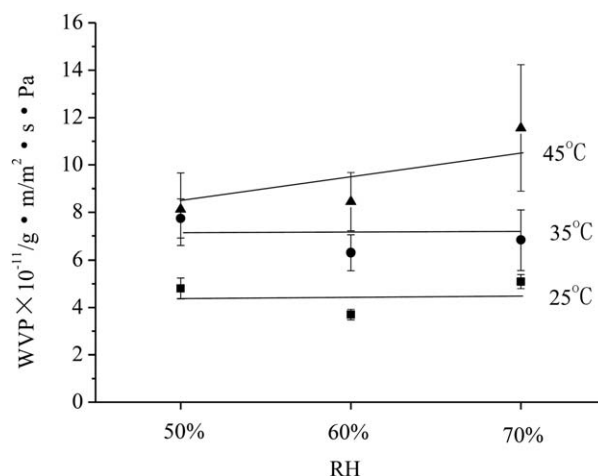


Figure 4. WVP values of PPC/PVA20/PPC film depended on variation in temperature and relative humidity.

decline slightly. With the increase in humidity, the OP starts to decrease. At 45°C, the OP value showed a sudden increase of about 28 times the value at 25°C and 3 times the value at 35°C. This indicated that the PPC/PVA20/PPC was more sensitive to humidity at high temperature, but had a much better and stable oxygen barrier property at low temperature. In the process of industrialization, chilled meat is usually packaged and stored at an environment within 0–4°C. PPC/PVA20/PPC film will keep high oxygen barrier at this temperature range according to the results of present study.

Water Vapor Barrier Property

The WVTR and WVP values of PPC, PVA and PPC/PVA/PPC films at 25°C in the humidity ranged from 50 to 70% are summarized in Table III. When the RH = 50%, the PVA had a low WVTR value of about 67.27 $\text{g}/\text{m}^2\cdot\text{d}$ and PPC kept its WVTR value about three times that of PVA. All the films had a trend of increasing WVTR with increase in humidity. This may be due to the vapor pressure increasing with the change in humidity, the result of the free diffusion speed of the water molecules increasing. In addition, the PPC/PVA/PPC multilayer films became more sensitive with the increase in the PVA content, especially the pure PVA films. This may be related to the strong hydrophilic of PVA.

As shown in Table III, the PPC exhibits good water vapor barrier property. But due to the strong hydrophilic properties of

Table III. WVTR ($\text{g}/\text{m}^2\cdot\text{d}$) and WVP ($\times 10^{-11} \text{ g}\cdot\text{m}/\text{m}^2\cdot\text{s}\cdot\text{Pa}$) Values of PPC, PVA, and PPC/PVA/PPC Films in Different Humidity at 25°C

Sample	50%RH		60%RH		70%RH	
	WVTR	WVP	WVTR	WVP	WVTR	WVP
PPC	67.27 ± 2.62	4.43 ± 0.29	113.90 ± 20.82	5.71 ± 0.10	147.10 ± 27.8	6.38 ± 0.11
PPC/PVA10/PPC	82.55 ± 16.71	4.75 ± 0.95	85.81 ± 14.79	4.65 ± 0.80	95.02 ± 11.98	4.71 ± 0.71
PPC/PVA20/PPC	76.14 ± 11.57	4.80 ± 0.44	99.79 ± 6.82	4.80 ± 0.41	118.50 ± 10.25	4.88 ± 0.85
PPC/PVA30/PPC	65.15 ± 8.76	4.05 ± 0.78	99.42 ± 6.89	4.87 ± 0.21	135.40 ± 5.25	6.55 ± 0.56
PPC/PVA40/PPC	51.63 ± 4.62	3.45 ± 0.23	78.19 ± 9.93	4.95 ± 0.86	128.00 ± 11.14	6.74 ± 0.49
PVA	24.50 ± 1.32	1.70 ± 0.23	120.90 ± 23.24	6.63 ± 0.14	205.00 ± 21.65	11.12 ± 0.33

Table IV. The Criteria for Sensory Evaluation of Chilled Meat

	Color	Smell	Organizational status
5 points	Shiny bright red color	Special smell of fresh meat, without odors	High elasticity after be being pressed rapid restorable
4 points	Shiny red color	Smell of meat without odors	Good elasticity can recovery after unloading.
3 points	Lackluster dark red color	A slight ammonia smell	Poor elasticity a slow recovery after be being pressed
2 points	Lackluster pale or gray color	Ammonia smell	Without elasticity irrecoverable
1 point	Dark color, unacceptable	Smell of rotting unacceptable	Without elasticity sag significantly after being pressed

PVA, when the humidity increased from 50 to 70%, the WVP value increased from 1.70×10^{-11} to 11.12×10^{-11} g·m/m²·s·Pa. For the PPC/PVA10/PPC, PPC/PVA20/PPC films, since the PVA content is low, the water barrier was mainly affected by the PPC layers. When the humidity increased, the WVP of PPC/PVA10/PPC film kept almost a fixed value about 4.70×10^{-11} g·m/m²·s·Pa, and the PPC/PVA20/PPC film demonstrated a slightly higher value of 4.80×10^{-11} g·m/m²·s·Pa. When the PVA content increased to 30–40%, the WVP increased with the increase in the humidity, Figure 4 shows the WVP of PPC/PVA20/PPC film at different temperatures and humidity. At 25°C, WVP did not change significantly as a function of relative humidity. The WVP values at 35°C showed the same trend similar as at 25°C, but increased slightly at 35°C. At 45°C, the WVP increased to a greater extent as the humidity increased. That is, the PPC/PVA20/PPC film is more sensitive to humidity under high temperatures. This is probably due the fact that as the temperature rises, the temperature more closely approaches the T_g s of polymers, the motion of segments became more intense and at the same time the water molecular diffusion also speeded up. In addition, the increase in humidity causes increasing of saturated vapor pressure, promoted the water molecules to permeate the film.

Table V. Sensory Evaluation of the PPC, PPC/PVA20/PPC, and Blank Control Groups

Storage time (day)	PPC	PPC/PVA20/PPC	Blank control group
1	14.7 ± 0.6 ^a	14.5 ± 0.4 ^a	14.9 ± 0.3 ^a
3	13.9 ± 0.8 ^a	13.6 ± 0.5 ^a	14.2 ± 0.5 ^a
5	13.3 ± 0.5 ^a	13.2 ± 0.6 ^b	13.1 ± 0.8 ^b
7	11.7 ± 0.5 ^a	12.3 ± 0.5 ^b	10.3 ± 0.7 ^b
9	10.1 ± 0.7 ^b	12.0 ± 0.7 ^a	9.7 ± 0.7 ^c
11	9.4 ± 0.8 ^b	11.6 ± 0.7 ^a	7.5 ± 0.8 ^c
14	7.3 ± 0.4 ^b	10.2 ± 0.8 ^a	4.3 ± 0.9 ^c
16	4.8 ± 0.9 ^b	8.2 ± 0.7 ^a	3.2 ± 0.4 ^c
19	3.5 ± 0.7	6.2 ± 0.5	-
21	-	4.3 ± 0.3	-

Line data marked with different superscripts differ significantly ($P < 0.05$).

Sensory Evaluation

PPC/PVA20/PPC film was used in chilled meat packaging and its preservation effect was compared with that of PPC packaging as well as the blank control group during storage time. The marking criterion of chilled meat sensory evaluation was according to the parameters described in Table IV, and the results were summarized in Table V. Results showed that although statistically distinctive differences were not all demonstrated between the two groups in the first 2 days, the blank control group had a tendency to score an overall higher mark than those packaged by PPC/PVA20/PPC three-layer film. This may be due to the difference of packaging technologies; the PPC/PVA20/PPC group was packaged by vacuum packing and normally dull red in color due to the oxygen started in the package system. Whereas the blank control group was simple wrapped and contact with air directly. Thus, it showed better coloring.

The PPC group had a tendency to score higher than the multi-layer group but slightly lower than the blank control group in the first 3 days. This may be due to the poorer oxygen barrier properties of PPC allowing the permeation of O₂ and affecting meat coloring.

Despite scoring higher based on the meat color, the scores of PPC and the blank control groups started to rapidly decrease from the fifth storage day and the meat samples were deemed unacceptable by the 11th day. Finally the meat had almost decayed on the 14th day. For the PPC/PVA20/PPC group, the meat samples kept a sleek appearance throughout the storage period, but by the 19th day, the meat was almost unacceptable and has completely decayed by the 20th day.

Total Viable Counts

The TVC values of meat samples packaged by PPC/PVA20/PPC, PPC films as well as the blank control group during 20 days of chilled storage at 4°C are shown in Figure 5 and Table VI. A critical limit often used to judge shelf life of meat is 7 log₁₀ CFU/g of microorganisms. Any values of 7 log₁₀ CFU/g and above indicate that the meat is not fit for human consumption.^{23–25} In the first 7 days, the TVCs of three groups were all below the 7 log₁₀ CFU/g. However, by Days 9–11, the meat packaged by PPC films and the blank control group exceeded the normal TVC consumption allowed for human consumption. The values were demonstrated significant differences on the

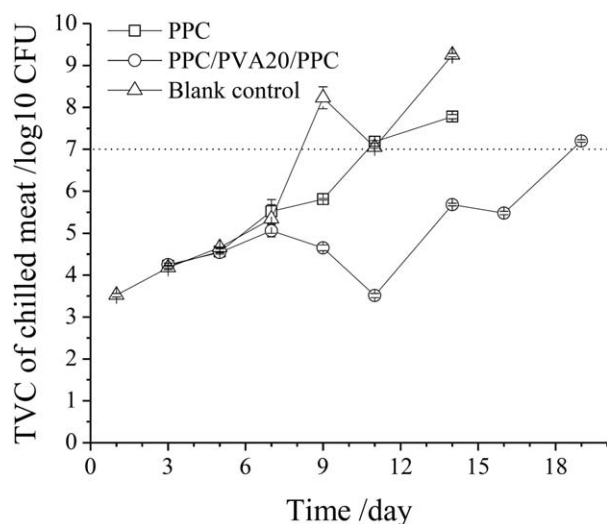


Figure 5. Total viable counts of chilled meat in the PPC, PPC/PVA20/PPC, and blank control groups.

ninth day between three groups ($P < 0.05$). The TVC of meat packaged by PPC/PVA20/PPC film still remained around 3.5–5.8 log₁₀ CFU/g at 11 days. Only until the 19th day of storage, the PPC/PVA20/PPC film showed a CFU value of 7.2 log₁₀ CFU/g. This further indicated that the PPC/PVA/PPC films were more likely to contribute to optimizing meat quality and shelf life.

Total Volatile Basic Nitrogen

TVB-N value (Figure 6) was evaluated as a quality index for the shelf life of meat.²⁵ The meat is considered decayed when TVB-N > 20 mg/100 g. In the first 5 days, there were no significant differences ($P > 0.05$) among the TVB-N values of the three groups. But from the seventh day, the TVB-N values of meat samples packaged by PPC films and the blank control group increased rapidly and the meat decayed by the 11th day and 14th days, while the meat samples packaged by PPC/PVA/PPC films began to slowly increase and after the 19th day, the meat had completely decayed.

Table VI. TVC of the PPC, PPC/PVA20/PPC, and Blank Control Groups

Storage time (day)	PPC	PPC/PVA20/PPC	Blank control group
1	-	-	3.52 ± 0.04
3	4.22 ± 0.06 ^a	4.25 ± 0.04 ^a	4.18 ± 0.05 ^a
5	4.56 ± 0.06 ^b	4.54 ± 0.10 ^a	4.66 ± 0.01 ^a
7	5.52 ± 0.28 ^a	5.06 ± 0.15 ^a	5.34 ± 0.34 ^b
9	5.81 ± 0.02 ^b	4.65 ± 0.07 ^c	8.23 ± 0.26 ^a
11	7.18 ± 0.03 ^a	3.51 ± 0.05 ^c	7.05 ± 0.02 ^b
14	7.78 ± 0.05 ^b	5.68 ± 0.03 ^c	9.25 ± 0.04 ^a
16	-	5.48 ± 0.04	-
19	-	7.20 ± 0.03	-

Line data marked with different superscripts differ significantly ($P < 0.05$), unit: log₁₀ CFU.

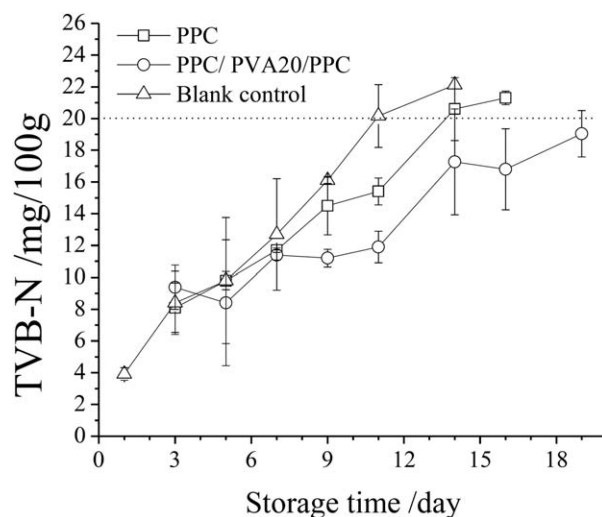


Figure 6. TVB-N of chilled meat in the PPC, PPC/PVA20/PPC, and blank control groups.

CONCLUSIONS

The PPC/PVA/PPC three-layer film was prepared improving the mechanical properties of PPC. The PPC/PVA20/PPC exhibited much better mechanical properties among the four PPC/PVA/PPC films prepared. In addition to improving the overall PPC mechanical properties, PVA also enhanced the relatively poor oxygen barrier of PPC and at the same time did not affect the water barrier performance of PPC in despite of hydrophilic nature of PVA. Furthermore, this biodegradable PPC/PVA20/PPC multilayer film with high barrier was tested in chilled meat packing and its performance was compared against PPC vacuum packaging and the blank control group was simple wrapped by common PE. The meat packaged in PPC/PVA20/PPC had a longer shelf life and overall better quality during storage time than those packaged with PPC films and the blank control group. These results show that the three-layer film with high barrier properties could be used as a new type of chilled meat packaging materials for a field that demands high-quality control.

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