

Barrier and Mechanical Properties of Biodegradable Poly(ϵ -caprolactone)/Cellophane Multilayer Film

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ABSTRACT: In this study, cellophane (PT) multilayer films were prepared by coating with different thickness of poly(ϵ -caprolactone) (PCL) and chitosan (CH), and its effects on barrier and mechanical properties were evaluated. It was shown that the PCL/PT/PCL and PCL/CH/PT/CH/PCL multilayer films exhibit much better water vapor barrier than PT, and these films still keep the high oxygen barrier. And the barrier properties of multilayer film were improved with the increase of the thickness of coating materials. The Young's modulus and tensile strength of PT multilayer film were slightly decreased, and their elongations at break were increased by coating. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 1805–1811, 2013

KEYWORDS: biodegradable; mechanical properties; packaging; films; coatings

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INTRODUCTION

With the development of the technology, the plastic has become one of the most important materials which we use in our daily life. Compared with other materials, plastic has many excellent characters, such as light, easily plastic, and low price compared to other materials. However, how to deal with the waste plastics is a difficult problem, because plastics may result environmental pollution when they are discarded at will.^{1,2} Therefore, a number of theoretical and experimental research groups have paid considerable attentions to biodegradable materials to replace the non-degradable plastics.^{3–5}

Biodegradable material is defined as the deterioration of its physical and chemical properties and a decrease of its molecular mass down to the formation of CO₂, H₂O, and other low molecular-weight products under the influence of micro-organisms in both aerobic and anaerobic conditions aided by abiotic chemical reactions like photodegradation, oxidation, and hydrolysis.⁶ Despite its advantages, compared with non-degradable plastics, biodegradable materials also have some shortages, such as low barrier and mechanical properties which limit its application in many areas. Therefore, a number of works have been performed to improve the barrier and mechanical properties of biodegradable materials,^{7–10} and the coating techniques of membrane materials are well reviewed in literature.¹¹ Strange

et al.¹² had made a biodegradable poly(L-lactic acid) (PLLA) substrate loaded with nanoclay to improve the thermal properties and possibly reduce permeation of water and oxygen. And a patent called “multilayer structures containing biopolymers” (Publication date: December 27, 2012; Patent application number: 20120328808) introduce a multilayer film which inner layer containing a biopolymer gains significantly improved UV resistance, abrasion resistance, and surface appearance, when covered with an outer acrylic layer.

In this study, the multilayer films were prepared using poly(ϵ -caprolactone) (PCL), cellophane (PT), and chitosan (CH) with surface coating method in an attempt to improve the barrier and mechanical properties. PCL is hydrophobic, biodegradable aliphatic polyester, which has been thoroughly studied as medical devices, pharmaceutical controlled release systems and degradable packaging. However, PCL is not a perfect material which has some drawbacks, such as low modulus. Therefore, PCL is generally grafted, blended nanoreinforced, or modified with other materials to improve its performance.^{13–20}

Cellophane is a very well-known material due to its good mechanical properties and hydrophilicity which made from cellulose. Cellophane is used in packaging and as a membrane for dialysis. However, the application of cellophane is limited by its hydrophilicity character. For example, food and medical

Table I. Composition, Thickness, and DSC Results of PCL and Multilayer Film

Code	Concentration of PCL (wt %)	Concentration of CH (wt %)	Thickness (μm)	Weight fraction of PCL (%) ^a	T_m for PCL ($^{\circ}\text{C}$)	ΔH_m for PCL (J/g) ^b	Crystallinity of PCL (%)
PCL	12	-	11.0 ± 0.6	100	63.2	71.8	43.3
PT	-	-	15.0 ± 0.1	-	-	-	-
CH/PT/CH	-	1.5	20.7 ± 0.7	-	-	-	-
PCL/PT/PCL (1)	1	-	17.7 ± 0.5	11.6	57.4	16.8	10.1
PCL/PT/PCL (2)	3	-	22.3 ± 0.3	26.2	57.5	29.8	18.0
PCL/PT/PCL (3)	6	-	26.0 ± 0.3	34.9	58.7	61.9	37.3
PCL/CH/PT/CH/PCL(1)	1	1.5	26.4 ± 0.6	16.7	57.4	13.8	8.3
PCL/CH/PT/CH/PCL (2)	3	1.5	31.7 ± 0.5	27.9	57.5	31.4	18.9
PCL/CH/PT/CH/PCL (3)	6	1.5	38.4 ± 0.4	38.4	58.5	54.6	32.9

^a The weight fraction of PCL was carried out with following the method. First, weighting multilayer films with area is 100 mm^2 (M_0), then dip them to chloroform solution, dry the films, and weight them after dissolving (M_1). The weight fraction of PCL was calculated as follows: Weight Fraction of PCL = $\frac{M_0 - M_1}{M_0} \times 100\%$.

^b ΔH_m was normalized with PCL fraction in multilayer film.

packaging need high water-absorption properties material. Because of cellulose is the mainly component of cellophane, many experiments used polymeric blends or modified method to improve its hydrophilic property.^{10,21} Cellulose fibers can graft PCL and PLLA by ring-opening polymerization.²² Cellophane membranes modified with fatty acids also had improved surface and barrier properties.²³ Chitosan is derived from naturally occurring sources, which is the exoskeleton of insects, crustaceans, and fungi. It is biocompatible and biodegradable²⁴ and shows a good compatible property with PCL, cellulose, and other nature materials.^{8,25–30}

Improvements in the barrier properties and mechanical properties of biodegradable polymers will be beneficial to widen applications in the packaging products. Yoshio Makino and Takashi Hirata³¹ used a chitosan–cellulose and PCL to make a biodegradable laminate film for modified atmosphere packaging. To the best of our knowledge, up to date, there is no research on biodegradable PCL- and CH-coating PT film to enhance its properties. In this study, the biodegradable multilayer films were prepared into different thicknesses by coating technique and their barrier and mechanical properties were evaluated. In order to improve the compatibility between PT and PCL, CH had been coated as a compatibilizer between PT and PCL layers.

EXPERIMENTAL

Materials

PCL sample ($M_n = 1.3 \times 10^5$) was purchased from Shenzhen Esun Industrial Co. and cellophane was purchased from Zhejiang Xinyang Polymer Materials Co. Chitosan sample was provided by Sangon Biotech (Shanghai) Co. and used as received without further purification.

Sample Preparation

PCL (1, 3, 6, and 12 wt %) solution was prepared by dissolving PCL in chloroform solution with stirring for 3 h at 25°C . Chitosan (1.5 wt %) solution was prepared by dissolving Chitosan in the 0.5 wt % acetic acid solution and stirring for 48 h at ambient temperature.

Preparation Monolayer PCL Film

Poly(ethylene) (PE, $150 \text{ mm} \times 150 \text{ mm}$) was immersed into the 12 wt % PCL chloroform solution for 2 min, then the film was hanged in fume hood about 24 h, then allowed to dry in vacuum oven for 48 h at 40°C . After drying, PCL monolayer film would be separated from the PE.

Preparation of Multilayer Film

- PCL/PT/PCL film. Cellophane ($150 \text{ mm} \times 150 \text{ mm}$) was separately immersed into the 1, 3, and 6 wt % PCL solution for 2 min, then the films were hanged in fume hood about 24 h and allowed to dry in vacuum oven for 48 h at 40°C .
- CH/PT/CH film. Cellophane ($160 \text{ mm} \times 160 \text{ mm}$) was immersed into the 1.5 wt % chitosan solution, affixed to the upper edge of a glass petri dish with a diameter of 150 mm and dried at room temperature. The multilayer film was cut with a graver after being dried, then placed in vacuum oven for 72 h at 40°C .
- PCL/CH/PT/CH/PCL film: CH/PT/CH film was immersed into the 1, 3, and 6 wt % PCL solution for 2 min, respectively. Then the film was hanged in fume hood about 24 h and allowed to dry in vacuum oven for 48 h at 40°C .

The thicknesses of the film were measured at five locations (center and four corners) using a micrometer and the mean thickness was calculated. The measurement of thickness was repeated five times. The codes and thickness of samples were summarized in Table I.

ATR-FTIR Measurement

The attenuated total reflectance Fourier transformed infrared (ATR-FTIR) spectra were recorded on the IR Affinity-1 spectrometer (Shimadzu, Japan) to analyze the chemical composition of the film surfaces. The spectra were recorded from 700 to 4000 cm^{-1} with the sum of 64 scans at a resolution of 4 cm^{-1} .

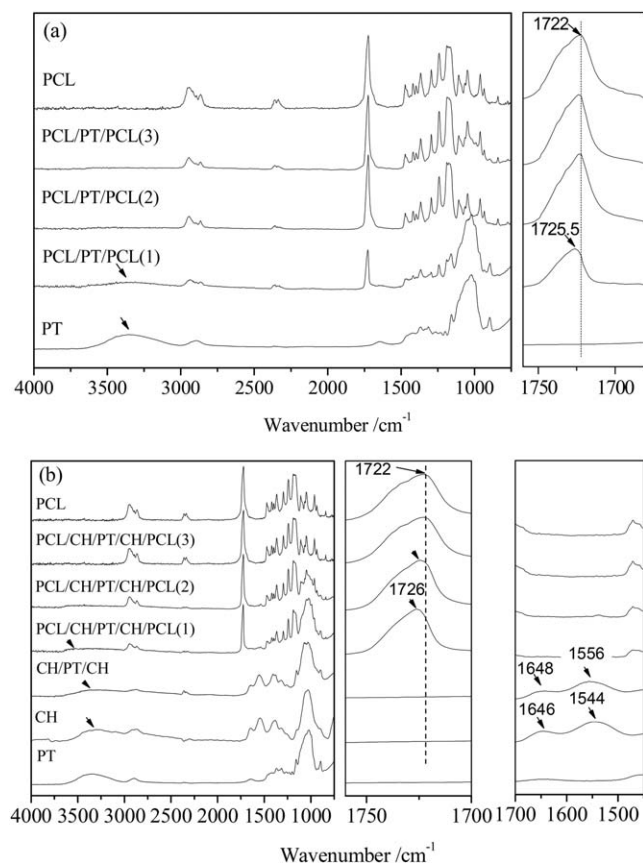


Figure 1. ATR-FTIR spectra for (a) PCL/PT/PCL and (b) PCL/CH/PT/CH/PCL multilayer films.

Tensile Test

The tensile testing of the sample was performed on a texture analyzer (QTS-250, Stable Micro System, UK). Referring to the ISO 527-3-1995, the film was cut into the samples with a dumb-bell shape (gauge length = 50 mm, parallel middle width = 10 mm), and test speed is 5 mm/min. Each sample film was tested at least five times at room temperature, respectively.

Differential Scanning Calorimetry

A calorimetric study both in isothermal and dynamic modes was performed by means of a microcalorimeter (DSC, TA Q20) with purge using extra pure nitrogen. Each sample, sealed in an aluminum pan, was heated from 10 to 80°C. The melting temperature (T_m) and melting enthalpy (ΔH_m) values of film were determined from the heating scan at a scanning rate of 10°C/min. The sample weight is 5 ~ 6 mg in this study.

Dynamic Mechanical Analysis

Dynamic mechanical analysis (DMA) was carried out in a DMA Q800 (TA) apparatus with a heating rate of 3°C/min. In this study, rectangular samples were prepared with 6.3 mm width and 30 mm length. DMA experiments were performed in the temperature range from -120 to 40°C.

Oxygen Barrier Property

Oxygen transmission rate (OTR) was measured with 100% oxygen at 23°C with an oxygen permeation analyzer (Model 8001 Illinois Instruments, Johnsburg, IL).

Water Vapor Permeability

Water vapor transmission rate (WVTR) was measured using a Permatran W3/31 water vapor permeability meter (by Mocon, Minneapolis, MN). Measurement was carried out at 23°C with 50% relative humidity across the film. Due to the high water vapor permeability of materials, which is beyond the test range of instrument, 2.5 cm² mask was used in test, while the normal test area is usually 10 cm².

RESULTS AND DISCUSSION

The Surface Characterization of Multilayer Composition

Both PCL/PT/PCL and PCL/CH/PT/CH/PCL multilayer film are coated with PCL by immersing the PT (or CH/PT/CH) films in the PCL/Chloroform solutions having different PCL concentrations. The thickness of PCL coated on the PT (or CH/PT/CH) film is determined by micrometer, and the results are summarized in Table I. The fraction of PCL coated on the PT (or CH/PT/CH) films increases with the increase in the PCL concentrations. The fraction of PCL coated on Chitosan surface to be more than that coated on PT surface, suggesting that the effect of CH/PT/CH coating PCL layer was better than PT. Apparently Chitosan layer improves interfacial adhesion between PCL and PT layers.

ATR-FTIR can give information about the chemical composition of the sample film from the top surface into the depth of a few micrometers, and the interaction between layer matrixes can be identified by this information. Figure 1 shows the ATR-FTIR spectra of the PCL, PT monolayer film and PCL/PT/PCL multilayer film. The carbonyl stretching band of PCL appears at about 1722 cm⁻¹. For the PT film, the peaks at 1150 and 895 cm⁻¹ are assigned to the vibration of glycosidic bonds. A wide band ranged from 3025 to 3600 cm⁻¹ is assigned to symmetric and asymmetric vibrations of the hydroxyl groups. These characteristic peaks are used to monitor the compositional change of PCL and PT along the thickness direction of the multilayer film.

As shown in spectra of PCL/PT/PCL(1), all of the characteristic ATR-FTIR absorption peaks of PCL and PT are found in the spectra of multilayer film, confirming that the samples contain both PCL and PT. The relative intensity of ATR-FTIR peak corresponding to the carbonyl stretching band of PCL increases with increasing the PCL thickness. There is a little but distinctive difference spectra between pure components and multilayer films. The peak of carbonyl stretching band of PCL at 1722 cm⁻¹ shifts to higher wavenumber at 1725.5 cm⁻¹ in the PCL/PT/PCL(1). The most plausible reason in the present case is formation of interaction force between PT and PCL layer. However, both PCL/PT/PCL(2) and PCL/PT/PCL(3) are rich in PCL, which the infrared spectrums of and the main characteristic peaks and the wavenumber are similar to pure PCL state, which means PCL layer is too thick that the text light wave have not been get through the surface and reach to the layer of PT.

In Figure 1(b), the amide band II^{32,33} of Chitosan is observed at 1544 cm⁻¹, upon coating on the PT surface, this band shifted to higher wavenumber at 1556 cm⁻¹. This band should be attributed to the associated amide vibration, and confirm the

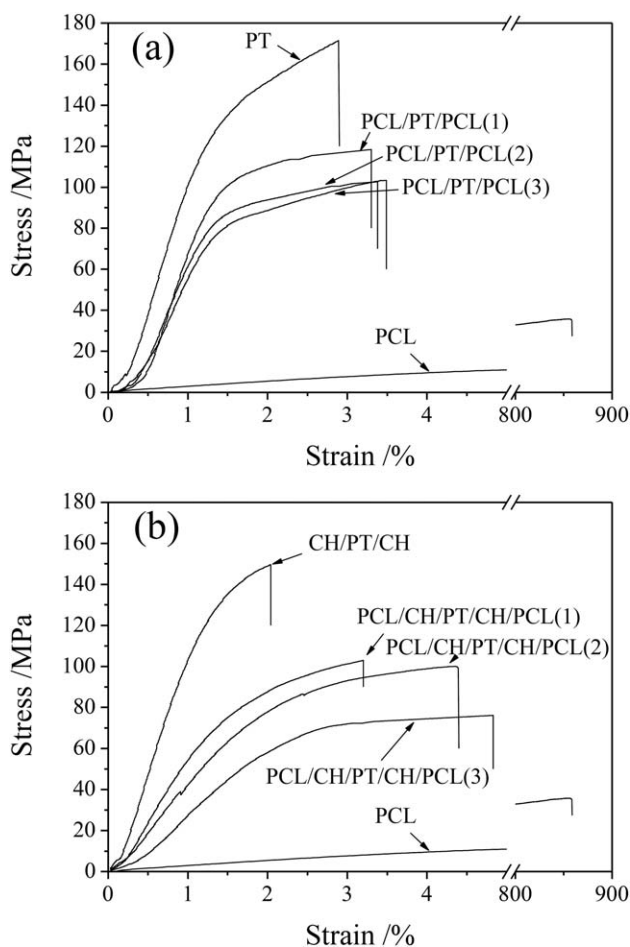


Figure 2. Stress–strain curves of PT, PCL, PCL/PT/PCL, CH/PT/CH, and PCL/CH/PT/CH/PCL multilayer films.

formation of interassociated hydrogen bonds between chitosan and cellophane. Upon coating, the peak of carbonyl band of PCL shifts from the lower wavenumber region at 1722 cm^{-1} toward the higher wavenumber region at 1726 cm^{-1} . In addition, the $-\text{OH}$ and $-\text{NH}$ stretching vibration band of chitosan^{32,33} locating at 3282 cm^{-1} shifts to the higher wavenumber at 3367 cm^{-1} . By coating with PCL, a new band appearing at about 3517 cm^{-1} , which should be induced by the formation of the intermolecular hydrogen bond between $-\text{OH}/-\text{NH}$ groups of Chitosan and carbonyl group of PCL, well accordant with the previously reported results.³⁴ These hydrogen-bonding interactions between Chitosan and PCL (or cellophane) should improve their miscibility and binding capacity of multilayers. This might prove the interfacial binding force of PT and PCL was improved by Chitosan.

Mechanical Properties

Mechanical properties of multilayer film, such as elongation at break (ϵ_b), Young's modulus (E), and tensile strength (σ_t), are evaluated from the stress–strain curves, and the results are summarized in Figure 2 and Table II. The PT film has a high Young's modulus, a low elongation at break and very high value of the tensile strength. The PCL film shows the low tensile strength, low Young's modulus and large elongation at break.

The mechanical properties of PT are changed after coating with PCL.

From the Table II, it can be seen that the tensile strength of PCL/PT/PCL multilayer films decreased with the thickness after increasing the PCL layer. As the addition of CH, compared with PT single film, the tensile strength of PCL/CH/PT/CH/PCL multilayer film is reduced obviously. Moreover, the higher the PCL layer thickness is, the lower the tensile strength is. The elongation at break of PT is about 2.9% because of its brittleness. Upon coating, the elongation at break of multilayer film is slightly increased.

It is obvious that the PT film shows the significantly high modulus than the pure PCL. The Young's modulus values of multilayer films fall in between PCL and PT. These results show CH layer has significantly affected Young's modulus of PCL/CH/PT/CH/PCL multilayer films, and they are lower than those PCL/PT/PCL multilayer films, which are much lower than PT.

Thermal and Dynamic Mechanical Properties

The melting behavior of PCL, PT, and their multilayer films are investigated by DSC heating process, and the results are shown in Figure 3 and Table I. The crystallinity of PCL is calculated from $\Delta H_m/\Delta H^0$, where ΔH^0 is the melting enthalpy expected for polymer with 100% crystallinity. Here, assuming the heat of fusion ΔH^0 of PCL is 166 J/g .³⁵

PT and CH do not show any thermal transition in the temperature range investigated, and only the enthalpy change of PCL is available by the DSC measurement. The PCL shows the melting point at 63.2°C , whereas the PT and CH/PT/CH film does not show distinct melting peak in the heating scans. The melting point of the PCL/CH/PT/CH/PT film shifts to lower temperature reduces with decreasing the thickness of the PCL layer. The crystallinity of PCL component decreases with decreasing PCL fraction. These changes of physical properties should be attributable to the existence of the interaction between PCL and PT or Chitosan layers.

Table II. Results of Tensile Tests of PCL, Cellophane, and Their Multilayer Films

Sample	Tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
PCL	35.8 ± 6.4	854.9 ± 23.6	246 ± 28.9
PT	171.3 ± 13.7	2.9 ± 0.54	5532 ± 814
CH/PT/CH	149.6 ± 10.3	2.0 ± 0.45	4923 ± 549
PCL/PT/PCL(1)	118.4 ± 12.3	3.3 ± 0.52	4754 ± 783
PCL/PT/PCL(2)	102.8 ± 16.7	3.4 ± 0.65	4267 ± 414
PCL/PT/PCL(3)	103.2 ± 17.0	3.5 ± 0.67	4057 ± 893
PCL/CH/PT/CH/PCL(1)	102.9 ± 18.9	3.2 ± 0.72	2109 ± 352
PCL/CH/PT/CH/PCL(2)	99.8 ± 8.9	4.4 ± 0.41	2194 ± 455
PCL/CH/PT/CH/PCL(3)	76.1 ± 8.4	4.8 ± 0.46	1738 ± 255

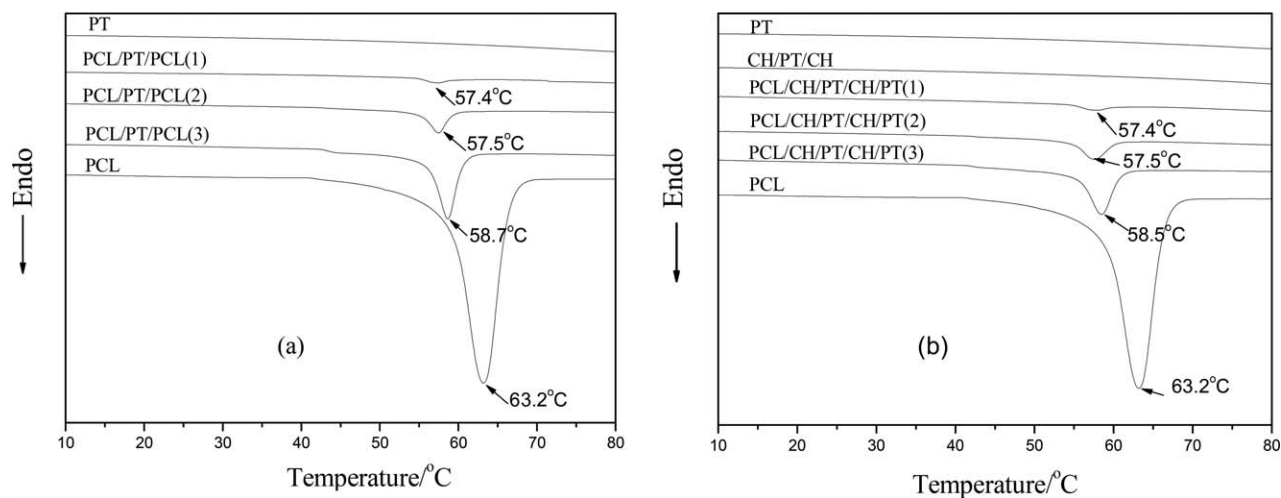


Figure 3. DSC thermograms of PT, PCL, PCL/PT/PCL, CH/PT/CH, and PCL/CH/PT/CH/PCL multilayer films.

Figure 4(a,b) depicts the storage moduli of the pure PCL, PT, and their multilayer films. The storage moduli decrease with increasing of temperature. From Figure 4(a), we can see that the storage modulus of the PCL/PT/PCL film is the maximum and the value of the PT film is close to that of the PCL/PT/PCL(1) film from -70 to -30°C . The PCL film has the lowest storage modulus. Figure 4(b) shows that the storage modulus

values of the multilayer film are between that of the PT and PCL film, and it is inversely proportional to the thickness of the film.

Figure 4(c,d) shows the temperature dependence of the loss tangent ($\tan \delta$) at 5 Hz, of the PCL, PT, and their multilayer films. From the PCL $\tan \delta$ curve, the PCL shows an α -transition from -65 to -20°C , this is related to glass transition temperature.

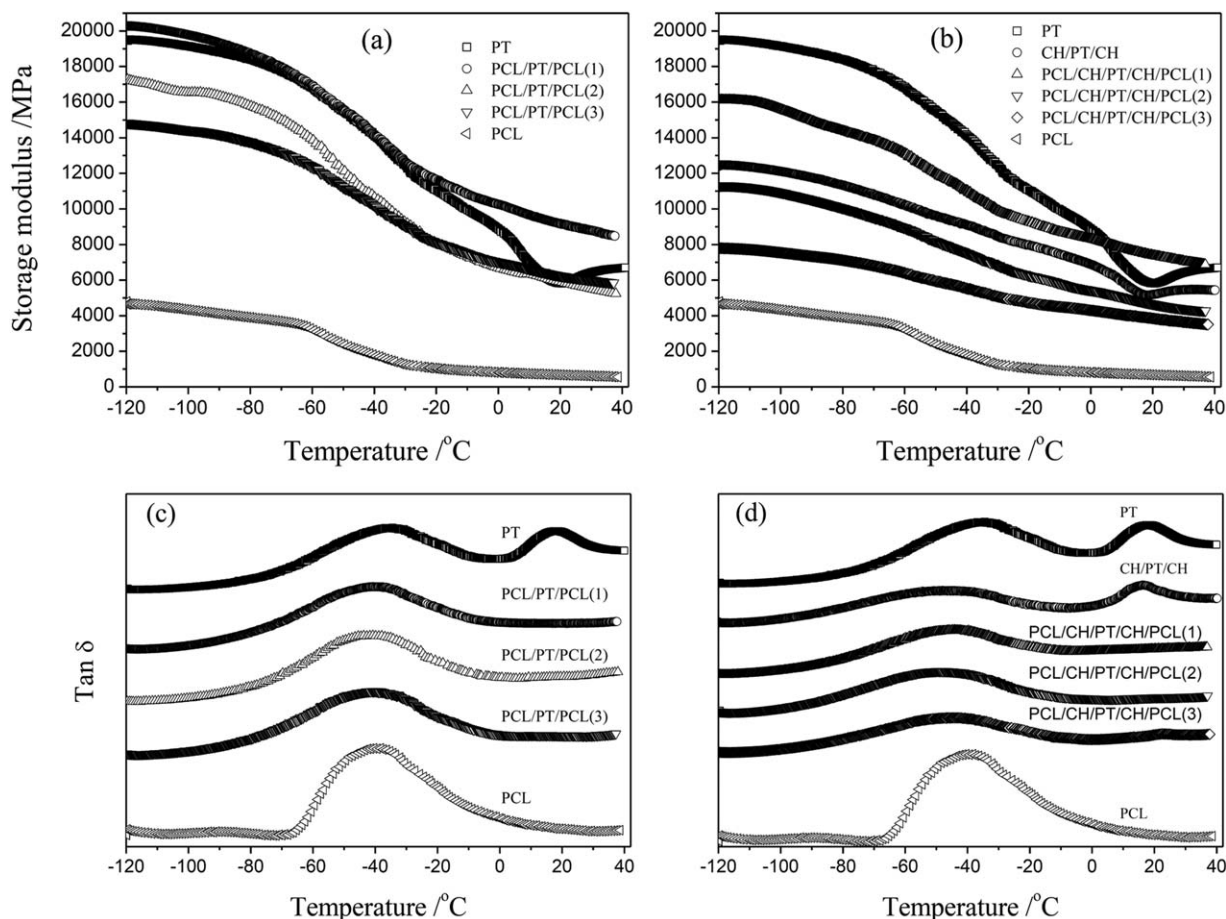


Figure 4. Dynamic mechanical properties of PT, PCL, PCL/PT/PCL, CH/PT/CH, and PCL/CH/PT/CH/PCL multilayer film.

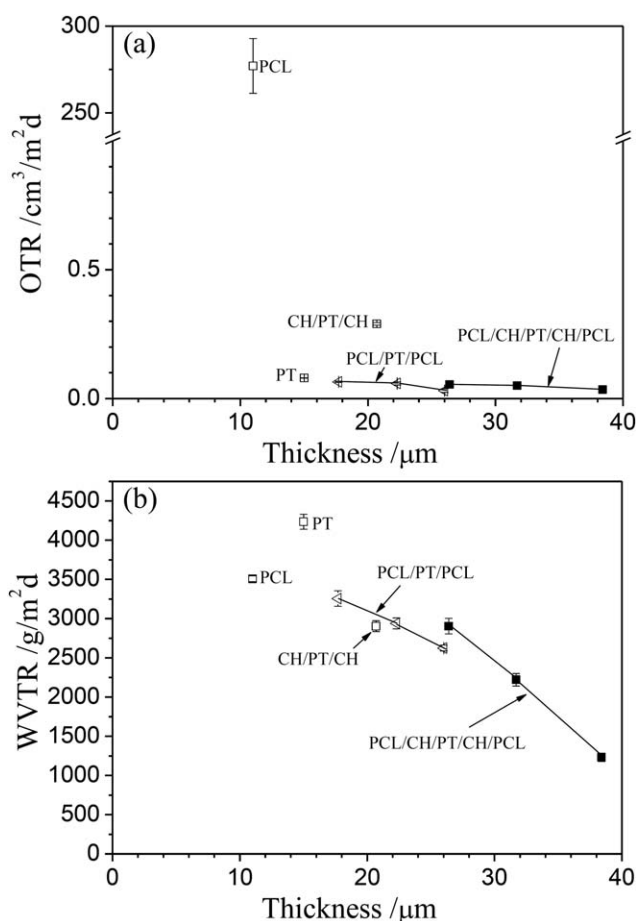


Figure 5. (a) Oxygen transmission rate and (b) water vapor permeability of PCL, cellophane, and their multilayer films.

PT exhibits two $\tan \delta$ peak at around $-100 \sim 40^\circ\text{C}$, the former peak may be characterized as the β -relaxation attributed to the hydration of side groups of cellulose molecules, and the later one may be motion of water molecules. For the PCL/PT/PCL multilayer films, the α -transition peak becomes broader than that of PCL and it slightly shifts to the lower temperature region, indicated that the glass transition temperature of PCL in its multilayer film decreases. The intensity of α -transition peak is slightly reduced of the PCL/PT/PCL film.

The β -relaxation of Chitosan is between -50 and 20°C , which is associated with the local motions of side groups in chitosan superposed on other non-identified transitions.³⁶ Adding chitosan layer, the PCL/CH/PT/CH/PCL multilayer film shows the one relaxation peak between -120 and 0°C . The relaxation peak becomes very broader, and shifts to the lower temperature region obviously. Those results reveal that chitosan has a good compatible property which improved the composite properties of PCL and PT.

Barrier Property of Multilayer Film

The measurements of oxygen permeability were carried out based on the equal pressure method at 23°C , and the oxygen transmission rate (OTR) are summarized in Figure 5(a). The OTR values of each film is presented as the average value of the last 10 data points observed in the plateau region of OTR versus

time graph, and the standard deviation is reported as less than 3%. OTR of PT is only $0.080 \text{ cm}^3 \text{ m}^{-2} \cdot \text{d}^{-1}$, whereas the PCL value is $277 \text{ cm}^3 \text{ m}^{-2} \cdot \text{d}^{-1}$. After coating, the OTR values of PCL/PT/PCL are significantly decreased from 0.065 to $0.031 \text{ cm}^3 \text{ m}^{-2} \cdot \text{d}^{-1}$ with increasing of the PCL layer thickness. OTR of the CH/PT/CH film is $0.290 \text{ cm}^3 \text{ m}^{-2} \cdot \text{d}^{-1}$, which is greater than that of the PT film. Acetic acid maybe the main influential factors for this phenomenon. Because the oxygen barrier of Cellophane is destroyed by the acetic acid solution after coating with Chitosan and the residual acetic acid molecule of the CH/PT/CH multilayer film maybe recognized as oxygen molecule. For the PCL/CH/PT/CH/PCL films, their OTR values decrease from 0.054 to $0.035 \text{ cm}^3 \text{ m}^{-2} \cdot \text{d}^{-1}$ with increase of the PCL layer thickness. The OTR value of multilayer films was close to the value for typical synthetic polymer films such as Poly(ethylene-vinyl alcohol) copolymers that generally considered to be one of the best food-packaging polymers.

The water vapor barrier property of multilayer film can be observed in Figure 5(b). Both PCL and PT film have the high WVTR values. After coating, water resisting ability of the PCL/PT/PCL multilayer film is obviously improved with the thickness of the PCL layer, and the WVTR decrease significantly. CH/PT/CH film has a better water resisting ability than the PT film, and its WVTR is $2904 \text{ g m}^{-2} \cdot \text{d}^{-1}$. PCL/CH/PT/CH/PCL multilayer films with CH and higher thickness of PCL layers present the low WVTR value. Compared with PT, the WVTR value of the PCL/CH/PT/CH/PCL(3) film decrease by 71%, namely, $1232 \text{ g m}^{-2} \cdot \text{d}^{-1}$. Meanwhile, the thickness of the PCL/CH/PT/CH/PCL(3) film just grown by 61%, that is, the advance of water resisting ability is not only because of the increase of film thickness, and the growth rate of film thickness is less than the decrease rate of the WVTR value. The PCL/CH/PT/CH/PCL multilayer films show better water resisting properties than the multilayer films without chitosan. This can be attributed to the chitosan, which used as a binder, eliminated the interspace between PCL and PT.

However, these multilayer films have a good oxygen barrier property, compared with other high barrier materials, the water vapor barrier property of multilayer films is still need to be improved. Further developments include finding effect methods, and new environmentally friendly polymer materials to make the multilayer film with a high water vapor barrier property.

CONCLUSIONS

The biodegradable PCL/PT/PCL and PCL/CH/PT/CH/PCL multilayer films with different thickness were prepared by the coating method. The ATR-FTIR results showed that the multilayer films are composited pretty good. Compared with PT, the tensile strength and Young's modulus of multilayer films shifted to lower value, which means multilayer films are softer than PT, and PCL/CH/PT/CH/PCL multilayer films are softer than PCL/PT/PCL. Both of these two kinds of multilayer films showed substantially higher oxygen barrier and better water vapor barrier property. Thus, the biodegradable film with the high oxygen barrier property can be obtained by coating PCL on the

cellophane surface with chitosan as a middle layer to enhance the miscibility between PCL and cellophane.

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