Preparation and Properties of Functionalization for PLA Film

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Abstract: Functionalized PLA films were prepared by extrusion blow molding. The tensile strength (TS), elongation at break (E), water vapor permeability (WVP), Oxygen permeability (OP), antimicrobial rate (AR), thermal properties and rheological properties were tested. The results showed that glass transition temperature (T_g) of the modified PLA material was 42.52 ℃，while that of the pure PLA was 65.6℃, and elongation at break of the prepared film reached up to 314%,but the TS is decrease from 64 MPa to 26.9 MPa. The antibacterial rate of PLA films to Escherichia coli, Staphylococcus aureus and Mildew were exceeded 95% by adding a copy of inorganic nano-titania/silver (TiO_2/Ag^+). The thermal stability of modified PLA was decreased, but rheological property was improved and the shaping process was modified.

Key words: Polylactic acid; Antimicrobial rate; Plasticizers; Nano-TiO_2/Ag^+

1.Introduction

Poly (lactic acid), which is the most promising synthetic biodegradable polymer materials currently, is a fully degradable polymer material [1]. In addition, non- toxic poly-lactic acid makes it possible for directly use in food contact packaging [2]. It is known that PLA belongs to linear thermoplastic polyester produced by the ringopening polymerization of lactide. Lactide is a cyclic dimmer prepared by the controlled depolymerization of lactic acid, which is obtained from the fermentation of sugar feedstocks, corn, etc [3]. However, the cost of synthesis of high molecular weight PLA is high, and most biodegradable plastics currently on the market are two and ten times as much as the traditional plastics [4]. What's more, there are properties such as flexural properties, gas permeability, impact strength, processability, etc. that are often not good enough for some and use applications, which led to the application of PLA in the field of packaging be restricted. In resent years, many literatures have been reported about improving the flexibility and impact resistance of PLA by blending with various additives such as lubricant, plasticizer or a second polymer [5-8]. The objective of this paper is to modify the properties by blending PEG and DOA, etc because of brittle of PLA. On the basis of modified, inorganic nano- TiO_2/Ag^+ was added into the composites to prepare degradable functional packaging films with antibacterial property.

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2.Experimental

2.1.Materials

PLA ($Mn=1\times10^5$) was purchased from Shenzhen, China. It was dried in a vacuum at 80℃for 12h before using. PEG (Mn=400), DOA, and Epoxidized Soybean Oil (ESO) were purchased from Tianjin, China. The nano-TiO_2/Ag^+ (VK-T07) was purchased from Wan Jing New Material Co. Ltd, Hangzhou, China. The Coli bacillus, Staphylococcus aureus and Mildew were kindly provided by the College of Food Engineering and Biotechnology, Tianjin University of Science & Technology.

2.2.Preparation of PLA films

The pure PLA films and modified PLA films were prepared by extrusion blow molding method to evaluate their mechanical, water vapor permeability (WVP), Oxygen permeability (OP), antimicrobial rate (AR) and thermal properties. Before mixing nano- TiO_2/Ag^+ with PLA, plasticizers were blended with nano-TiO_2/Ag^+ to disperse in ultrasound for 30min. Then the blended materials were use to granulate in a single-screw extruder (Model RM-200A, Harbin, China), and the temperatures of processing were 150℃, 165℃, 175℃, 170℃. At last, the PLA films were prepared by extrusion blow molding method and the temperatures were 145℃, 165℃, 170℃, 165℃.

2.3.Mechanical properties of PLA films

The tensile strength (TS) and elongation at break (E) of each film were determined with an Electronic Universal Testing Machine (Model RG T-3, REGER instrument Corporation, Shenzhen, CHINA) according to GB/T

13022-91. Dumbbell specimens of 12×1.5cm were cut using a precision dumbbell cutter. Initial grip separation was set at 50mm and the cross-head speed was set at 100 mm/min. TS was calculated by dividing the maximum load to break the film by the cross-sectional area of the film and E was calculated by dividing film elongation at rupture by the initial gauge length of the specimen and multiplying by 100. Each type of film was prepared and evaluated in triplicate. For each film sample, TS and E measurements were made on three specimens taken from the same film, and reported as the mean for the replicate.

2.4.Water vapor permeability (WVP)

WVP (g·cm/cm^2·s·Pa) was calculated as WVP= (1.157×10^{-9}×WVT·d)/△p, where WVT was the measured water vapor transmission rate (g/m^2·24h) through a film, d was the mean film thickness (cm) and △p was the partial water vapor pressure difference (Pa) between the two sides of the film. WVT was determined gravimetrically with a modified procedure in accordance with GB/T 1037-88 using a cup containing Silicone as absorbent. The film-covered cups were sealing by sealing wax and weighing ,then placed in constant humidity and temperature chest with 38℃and 90% RH. The cups were removed from the chest after 16 h, put at 23 ± 2 ℃ environment of the dryer, waited for 30 min and weighed. The cups were re-placed in constant temperature and humidity chest, and weighed once every 24h. The experiment was end until the difference of before and after quality increments was no more than 5%. Silicones moisture at the film undersides during test was less than 10% of the total increment absorbent.

2.5.Oxygen permeability (OP)

OP (cm^3·cm/cm^2·s·Pa) was calculated as OP= 1.1574×10^{-14}×Q·D, where Q was the measured Oxygen transmission rate (cm^3 /m^2·d·bar) through a film, D was the mean film thickness (cm). Q of each film was determined with gas permeability testing machine (Model GDP-C, BRRUGER Corporation, Germany) according to GB/T 1038-2000.

2.6.Antimicrobial test

The antibacterial rate of PLA films to Escherichia coli, Staphylococcus aureus and Mildew were determined by employing the standard discs diffusion method. Pouring about 15 ml medium into Petri dishes according to sterile operation. After the solidification of the medium, the suspension (100μL) was spread onto the surface of medium. The sample (6 mm diameter) were placed in the centre of the inoculated Petri dishes, then the Petri dishes of Escherichia coli and Staphylococcus aureus were incubated at 37 ℃ for 24 hours and the Petri dishes of Mildew were incubated at 28 ℃ for 48 hours and the growth inhibition zone diameter was measured to the nearest mm[6-8].

2.7.DSC analysis

The glass transition temperature (T_g) and melting temperature (T_m) of PLA films were performed on a Differential Scanning Calorimeter (Model DSC-141, SETARAM Corporation, France). For each film type, about 8mg of film sample was sealed in an aluminum pan and heated from 25 to 150℃ at a rate of 10℃/ min, held at that temperature for 3 min, then cooled to -40℃ with liquid nitrogen (cooling rate of 25℃/min) before a second heating scan to 200 ℃ at a 10℃/min scan rate. A nitrogen flow (50 ml/min) was maintained throughout the test. The first scan was meant to discard the thermal history of the samples.

2.8.Scanning electron microscopy

The films were brittle in liquid nitrogen, subsequently, the samples were coated with an approximative10 nm-thick gold film and then examined under a scanning electron microscope (JSM 6380) using a lens detector with an acceleration voltage of 20 kV at 5000 and 10000 magnification.

2.9.TGA analysis

Thermal stability of PLA films were measured by a Thermogravimetric Analyzer (Model TAQ50, TA Corporation, USA). For each film type, about 5mg of film sample was heated from environment temperature to 600 ℃ at a rate of 10℃/min. Experiment using a high-purity nitrogen carrier gas flow (40 ml/min) was maintained inert atmosphere furnace and be able to promptly produce the volatile pyrolysis products away from the sample throughout the test, thereby reducing the impact brought to the instantaneous weight of the sample due to the secondary reaction.

2.10.Rheology analysis

The sample material was dried under vacuum at 60 ℃ for 12h before measurements. Rheology properties of each sample were determined with Capillary Rheometer (Model RH2000, BOHLIN instrument, UK). The radius of capillary was 1 mm and length-diameter ratio was 16. Each film sample was about 15g. The rheology experiments were carried at 185℃.

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3.Results and discussion

3.1.Properties of PLA films

The results for tensile testing (TS), elongation at break (E), water vapor permeability (WVP), Oxygen permeability (OP) and antimicrobial rate (AR) of PLA films are shown in Table 1, E for the modified PLA films increased dramatically from 3.6% up to 314% for pure PLA., however, TS decreased from 64 MPa to 26.9 MPa, which can be explained to be due to the introduction plasticizers. These values are comparable to those of widely used plastic films such as LDPE, for which TS values is known to be 13 MPa and E is 379%. WVP and OP of modified PLA files were greatly improved. The main reason is the effects of plasticizers, which can be led to the increasing gap between PLA molecules. After adding a copy of inorganic nano- TiO_2/Ag^+, the antibacterial rate of PLA films to Coli bacillus, Staphylococcus and Mildew were exceeded 95%.

The antibacterial mechanism of nano-TiO_2/Ag^+ was dual effect antibacterial of Ag^+ and TiO_2 [9-10]. Nano-antibacterial agent in a controlled release rate of positively charged Ag^+ ions, and firmly adsorbed and penetrated the bacteria, fungal cell walls and damaged to electronic transmission of microbial systems, respiratory, physical transmission system to rapidly kill the bacteria. The antibacterial particles contact the fungus cells and damage the cells wall and plasmolemma, and in some situation they can even penetrate the cell wall and plasmolemma to enter into the core to make cytoplasm agglomerate and thus cause the cells dead. The Ag+ ions can produce the greatest antibacterial effect induced by the light—catabolic action of Titania under the light，but the antibacterial effect can still continue while there is no light.

Thermal properties of modified PLA and pure PLA films were investigated using DSC and are shown in Fig. 1. The T_g of modified PLA films (42.52℃) was lower than the pure PLA (65.6℃), and the T_m of the modified PLA films was 160.70℃, which was lower than that of pure PLA films (175.19℃). Modified film displayed a cold crystallization exotherm, which the cold crystallization temperature was 73.58℃, and the crystallinity increased in comparison with the pure PLA. Those results may be due to the plasticizing effect of PEG and DOA et al. Generally, T_g is used as one of the most important criteria for the compatibility of a polymer blend [11]. It is known that usually only one T_g will appear in DSC thermograms at an intermediate temperature compared to that of the T_g value of each component polymer. The Fig.1 indicates that both plasticizers and PLA are fairly compatible for making films.

Table 1 Results of tensile strength (TS), elongation at break (E), water vapor permeability (WVP), Oxygen permeability (OP) and antimicrobial rate (AR) of pure PLA films (pPLA) and Modified PLA films (mPLA)

Properties	pPLA	mPLA
TS /MPa Vertical	64.0	26.9
Horizontal	44.7	21.8
E /% Vertical	3.6	314
Horizontal	2.7	282
WV/（×10-13(g•cm/(cm2•s•Pa))）	3.4	6.5
OP/（$\times10^{-15}$(cm^3·cm/(cm^2·s·Pa))）	46.1	62.6
AR (%)	<5	>95

AR determined was the antibacterial rate to Escherichia coli, Staphylococcus aureus and Mildew.

3.2.Thermal properties

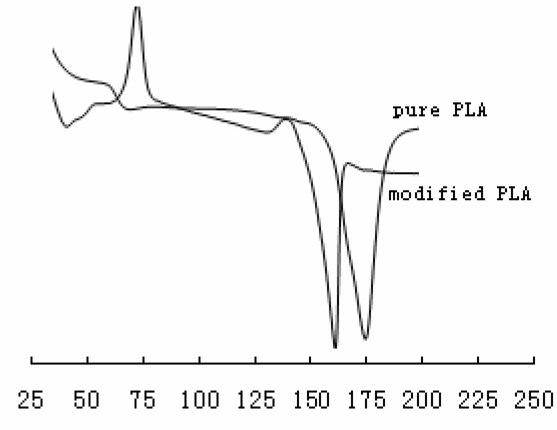

Fig.1 DSC curves of modified PLA and pure PLA

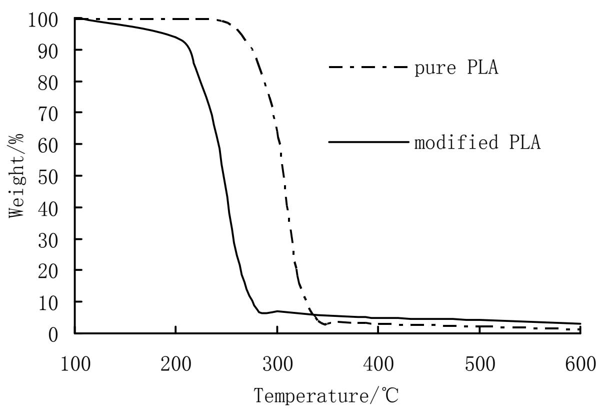

Fig.2. TGA curves for modified PLA and pure PLA

Fig. 2 depicts TGA mass loss curves for the modified PLA as well as for the pure PLA. The thermal stability of the modified PLA is lower than the pure PLA, and the thermal weight loss temperature of modified PLA and pure PLA occurred in the 240 ~ 330 ℃ and 180 ~ 270 ℃, respectively, as can be seen in detail in Fig. 2. This significant decrease in thermal stability for the modified PLA in comparison with the pure PLA can be due to the thermal stability of Plasticizers are lower than pure PLA, in addition, the reduction of *M*w of PLA during extrusion blow molding led to a decrease in thermal stability.

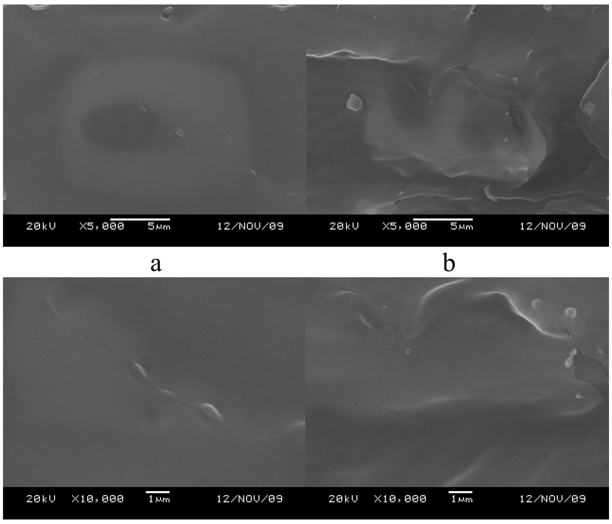

Figure 3. SEM images of modified PLA and pure PLA films; (a) pure PLA×5000 (b) modified PLA×5000; (c) pure PLA×10000 (d) modified PLA×10000.

3.3.Scanning electron microscopy

In order to investigate the reactive compatibility of modified PLA system, the fracture surface of PLA films was observed by using SEM, operated at an acceleration voltage of 20 kV. The SEM images of the fracture of modified PLA films and pure PLA films is shown in Fig. 3 .a ,b, c and d. Crazing, cavitation, shear banding, crack bridging, and shear yield have been identified as important energy dissipation processes involved in the fracture of toughened polymer systems [12]. In Fig. 3 b, d, modified PLA system showed better miscibliity and more shear yielding when it was fractured.

3.4.Rheology properties

The experimental data indicated that shear rate affected apparent shear viscosity of the melt greatly. As shown in Fig. 4, modified PLA has a lower apparent shear viscosity in comparison with pure PLA. This results is attribute to the introduction of plasticizers, the increase of mobility of molecule chain, the enlargement of distance among molecules and the decrease of fiction among molecules, which led to the drop of flow obstacle, the reduction of apparent shear viscosity, and the improvement of flow properties. And all of this is favorable for molding process. Apparent shear viscosity decreased drastically as the shear rate increased for modified PLA and pure PLA. Such flow behavior was called shear thinning. The relationship between apparent shear viscosity and shear rate exhibited typical non-Newtonian pseudoplastic behavior [13]. There were the linear relationships between apparent shear viscosity and shear rate in a bi-logarithmic coordination system in the studied shear rate range, indicating that the melt shear flow of the systems obeyed the power law relationship.

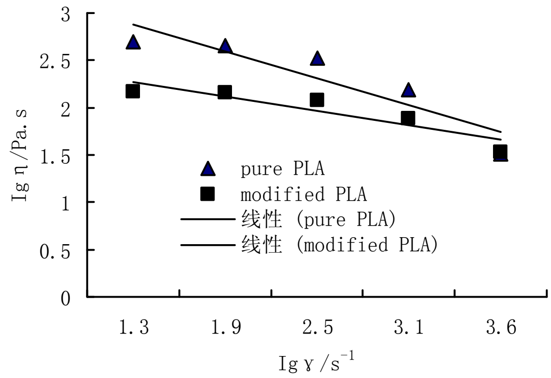

Figure 4. Rheology curves for modified PLA and pure PLA.

4.Conclusions

In summary, flexible and Anti-bacterial PLA films were prepared by extrusion blow molding. Elongation at break, water vapor permeability and Oxygen permeability of modified PLA files were greatly improved. The antibacterial rate to Escherichia coli, Staphylococcus aureus and Mildew were exceeded 95%. T_g, T_m and the thermal weight loss temperature of modified PLA is lower than those of pure PLA due to the introduction plasticizers. Modified PLA has a lower apparent shear viscosity and thermal stability in comparison with pure PLA. The PLA films melt behaved like a pseudoplastic non-Newtonian fluid and exhibited adequately shear-thinning behavior.

5.Acknowledgements

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