



# A gelatin/PLA-b-PEG film of excellent gas barrier and mechanical properties

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## Abstract

A polylactic acid-polyethylene glycol block copolymer (PLA-b-PEG) was used as an additive to prepare gelatin/PLA-b-PEG blend films for the first time. The PEG molecule block enhanced the compatibility of the PLA molecule block with gelatin, which greatly improved the excellent mechanical and gas barrier properties of the gelatin film. The film contained 5 wt% PLA-b-PEG possessed the highest tensile strength and the highest elastic modulus. When the PLA-b-PEG content further increased to 20 wt%, the tensile strength, elastic modulus and elongation at the break of the blend film were all higher than pure gelatin film, suggesting that the gelatin/PLA-b-PEG blend film was pliable and tough. The blend film possessed not only excellent oxygen barrier property, but also a much-improved water barrier property. The degradation rate of the blend film was elongated controllably by regulating the content of the PLA-b-PEG copolymer. The blend film showed great potential in the application of food packaging.

**Keywords** Gelatin · PLA-b-PEG · Water barrier · Oxygen permeability · Mechanical property

## Introduction

Gelatin is a water soluble protein obtained by partial hydrolysis of collagen. It is widely used in the manufacture of gel desserts, capsules in the pharmaceutical industry and edible films in food industry due to their abundance, outstanding biological properties, well film-forming property and excellent oxygen and aroma barrier properties [1–4]. However, gelatin-based films are still encountering some problems which make them less competitive than petrochemical-based plastics, such as their poor barrier property toward water vapor due to their hydrophilic nature, poor mechanical properties and poor antioxidant activity [5–7]. Incorporating

hydrophobic substances could be an effective strategy to improve the water vapor barrier property of gelatin [8]. Combining gelatin with natural/synthetic polymers and nanoparticles has been used extensively to improve the mechanical properties of gelatin [9, 10].

Poly(lactic acid) (PLA) has been approved by the U.S. Food and Drug Administration (FDA) for its application in food-contact material. Comparing to gelatin, PLA has much better water vapor barrier property and mechanical property, but much poorer oxygen barrier property [11–14]. Thus, PLA and gelatin are two very complementary materials and their blends have great potential applications in the biomaterials and food packaging field. Martucci et al. prepared a PLA/gelatin/PLA sheet by a thermal compression method [4, 15]. Hosseini et al. prepared a PLA/gelatin/PLA three layers film by a solvent casting technique [5], and Lee et al. prepared a gelatin/PLA bilayer film by the same way [16]. These reports confirmed that a gelatin/PLA lamination could decrease the water permeability and enhance the mechanical properties of a gelatin film. In these works, a multistep processing is necessary for the preparation of multilayer products. These researches imply that a gelatin/PLA blend could be an excellent material for biological and food packaging fields. However, blending gelatin and PLA together is a challenge because it is well known that gelatin is highly hydrophilic, while PLA is highly hydrophobic.

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PEG is another polymer complementary for preparing gelatin blend. PEG is a hydrophilic material compatible with gelatin, which is different from PLA. PEG can be blended uniformly with gelatin as a plasticizer to improve the mechanical property of gelatin and extend storage time [17]. A research study shows that PEG of lower molecular weight has better plasticizing effect on gelatin, and the corresponding gelatin composites possess lower WVP and better visual properties [18]. Moreover, PEG can increase the cross-linking degree of gelatin and slow down the degradation of gelatin hydrogel [19, 20]. PEG-gelatin blend based hydrogel has been realized a potential candidate for mimicking extracellular matrix due to the above mentioned advantages [19, 21].

In our research, we prepared a kind of film for food packaging by combining gelatin with a PLA-b-PEG copolymer composed of a PLA molecule block and a PEG molecule block. This PLA-b-PEG copolymer had no film-forming property, which limited its application to the food packaging field [22–24]. The PEG block was supposed to improve the integrated properties of gelatin film as a plasticizer. What was more important was that the PEG block could improve the compatibility of the PLA molecule block with gelatin. Since PLA was a compensatory material to gelatin on mechanical and water barrier properties, blending the gelatin with and the PLA-b-PEG copolymer together could benefit for preparing a blend film combining the excellent properties of both gelatin and PLA.

## Materials and methods

### Raw materials

Gelatin (CP, Sinopharm Chemical Reagent Co. Ltd.  $M_w = 8000$ ), genipin (98 wt%, Sigma-Aldrich), PLA-b-PEG copolymer ( $M_w = 10,000$ , Daigang Technology Co. Ltd. Jinan, China) and PLA polymer ( $M_w = 10,000$ , Daigang Technology Co. Ltd. Jinan, China) were used directly without further purification. A PLA-b-PEG copolymer molecule was composed of two molecule blocks, a PLA block ( $M_w = 5000$ ) and a PEG block ( $M_w = 5000$ ). Deionized water was obtained from a Millipore water purification system. KBr for FT-IR was purchased from Sinopharm Chemical Reagent Co., Ltd. and used directly.

### Film preparation

A gelatin solution (10 wt%) was prepared by dissolving gelatin in water at 60 °C for 1 h. To determine the best addition amount of the PLA-b-PEG, different amount of the PLA-b-PEG was mixed with the gelatin solution while stirring at 60 °C for 2 h. Genipin was added into the gelatin solutions as crosslinker. The gelatin solutions were casted into open flat dies and dried at 60 °C for 24 h. Five gelatin blend films containing different

amount of PLA-b-PEG (0 wt%, 2 wt%, 5 wt%, 10 wt% and 20 wt%) and genipin (1 wt%) were prepared for investigation.

## Characterization of gelatin films

### Scanning electron microscopy (SEM)

A field emission scanning electron microscope (FE-SEM) (S-4800II, Japan) was used to characterize the surface and freeze-fractured cross-section morphology of the gelatin/PLA-b-PEG films. The samples were sputtered with Au before SEM observation.

### Film thickness

The film thickness was measured by a handheld micrometer, with a 0.001 mm accuracy. Five measurements were taken at random positions to check the reproducibility.

### Barrier properties and film transparency

The ultraviolet and visible light barrier properties of the films were measured according to ASTM method D 1746–92 with slight modification [25]. The measurement was carried out using an UV-Vis spectrophotometer (UV-3600, Shimadzu Co., Kyoto, Japan) at a wavelength range from 200 to 800 nm. All films were cut into a rectangular piece and placed directly in a UV-Vis spectrophotometer, using air as the reference. The opacity was calculated as follows:

$$\text{Opacity} = -\frac{\log T_{600}}{\chi}$$

Where  $T_{600}$  is fractional transmittance at 600 nm and  $\chi$  is the film thickness (mm).

### Water vapor permeability (WVP)

The water vapor permeability (WVP) was determined using a cup method [25]. Films were first fixed with paraffins onto the opening of weighing bottles with silica gel (0% RH) inside. Then the weighing bottles were placed in desiccators containing saturated NaCl solution (50% RH). The set was maintained in an electronically temperature-controlled incubator at 30 °C, and the bottles were weighed 1 h intervals over a 10 h period. The WVP was calculated as follows:

$$\text{WVP} = (\Delta m \times L) / (A \times t \times \Delta P)$$

Where  $\Delta m$  was the weight gain of the cup;  $L$  was the film thickness (mm);  $A$  was the film area ( $\text{m}^2$ );  $t$  was the elapsed time for the weight lost (h); and  $\Delta P$  was the partial vapor pressure difference between the two sides of the films.

## Oxygen permeability (OP)

The oxygen transmission rate (OTR) was determined using a gas permeability tester (Mocon 2/21, USA). The measurements were performed at 23 °C and 50% RH according to ASTM D 3985–05 (ASTM, 2005.). The sample area was 14 cm<sup>2</sup>, and the pressure of the oxygen was 1.5 bar. The OTR was normalized with respect to the pressure and material thickness, and converted to the oxygen permeance and oxygen permeability (OP), respectively.

## Moisture content and water solubility

The moisture content (MC) of the films was determined by calculating the mass loss of the samples (2 × 2 cm<sup>2</sup>) after drying in an oven at 105 °C for 24 h [26].

$$MC = (m_0 - m_1) / m_0$$

Water solubility (WS) was measured following the MC test. The dried films were immersed in 15 ml distilled water and placed in a shaker water bath at 25 °C and 60 °C. Then the films were dried at 105 °C for 24 h to calculate the WS of the films using the following equation [27]:

$$WS = (m_1 - m_2) / m_1 \times 100\%$$

In this case,  $m_1$  was the weight of the dried film,  $m_0$  was the weight of the film,  $m_2$  was the weight of the film after absorbing water.

## Hydrophilicity of the film

Hydrophilicity of the films was evaluated by measuring the contact angles of water droplets on the films with an OCA20-type contact angle analyzer (data physics Co, Ltd., Germany). Water droplets (5.0 μL) were dropped carefully onto the surface of the film [28], and the contact angles were measured in 10 s. Five measurements were taken at random positions to check the reproducibility.

## Degradation in water

The degradation of the films in water was determined by placing the samples in 15 ml distilled water in a shaker water bath at 25 °C for different time to calculate the mass loss of the samples.

## Mechanical properties

The mechanical properties of the films including tensile strength (TS), elongation at break (EAB) and elastic modulus (EM) were measured with a Universal Tensile Machine (INSTRON 3300, USA,) following the ASTM Standard Test Method D882–91. The samples were mounted between

the grips with an initial separation of 6.0 cm, and the cross-head speed was set at 1 mm/s.

The blend films were put in a close box with a humidifier. The blend films of different moisture content were obtained in a humid environment. The mechanical properties of the blend films were measured right after the films were taken out of the box.

## Ft-IR

The structural interaction of gelatin based films was characterized using a Tensor 27 FTIR-ATR spectrometer. The scans were carried out in a spectral range varying from 500 cm<sup>-1</sup> to 4000 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

## Thermogravimetric analysis (TGA)

The TGA tests were performed on a Pyris 1 TGA thermogravimeter (Pyris 1 TGA, USA). After being dried in a vacuum oven at 40 °C for 48 h, samples of 10 mg were sealed in an aluminum pan. TGA was performed at a rate of 10 °C/min from 30 °C to 600 °C in a nitrogen atmosphere.

## Statistical analysis

Data were presented as means ± standard deviation with  $n = 5$ , and a probability value of  $P < 0.05$  was considered significant.

## Results and discussion

### Ft-IR

The FT-IR spectra of the films (Fig. 1) showed the characteristic peaks of gelatin/PLA-b-PEG blend films. The wide peak

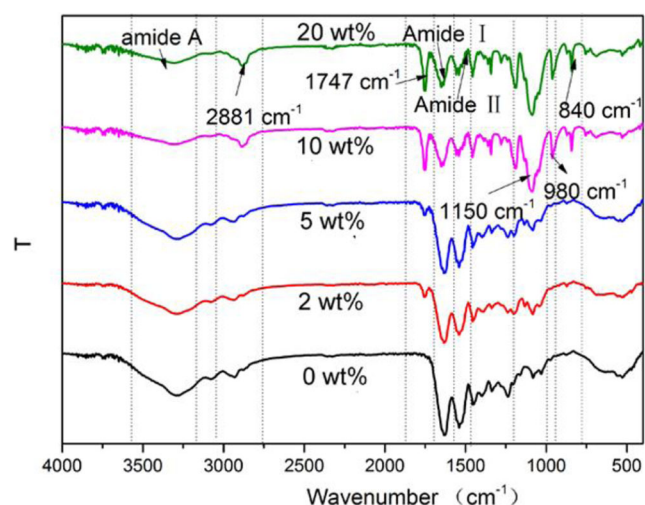
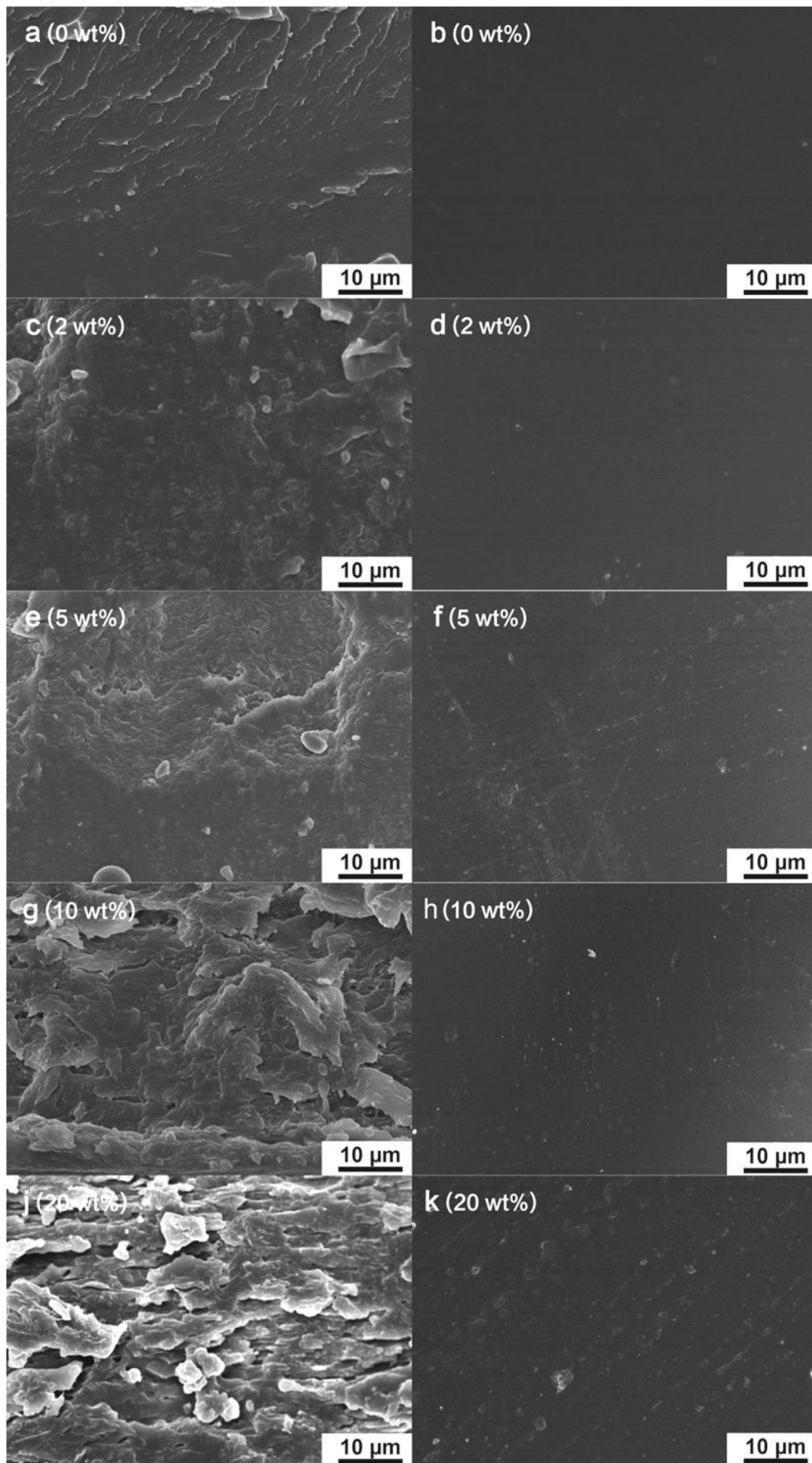


Fig. 1 The FT-IR spectra of PLA-b-PEG/gelatin blend films





◀ **Fig. 2** SEM images of the cross-sections (left column) and the surfaces (right column) of gelatin films with the different addition of PLA-b-PEG

between 3600 and 3100  $\text{cm}^{-1}$  was attributed to the mix of O-H and N-H groups forming huge amount of hydrogen bonds. This peak became weaker and weaker following the addition of the PLA-b-PEG copolymer, suggesting that the hydrogen bonds became less. The peak at 1640  $\text{cm}^{-1}$  (amide I) was attributed to C=O stretch; the peak at 1540  $\text{cm}^{-1}$  (amide II) was attributed to the N-H bending and C-H stretch coupled with N-H in-plane bending vibrations [5, 29]. With the addition of PLA-b-PEG, the PLA-b-PEG-related stretching modes were represented by the peaks at 2881  $\text{cm}^{-1}$  (asymmetric  $-\text{OCH}_3$  stretching), 1747  $\text{cm}^{-1}$  (C=O stretching), 1150  $\text{cm}^{-1}$  and 920  $\text{cm}^{-1}$  (C=O non-plane swing) and 840  $\text{cm}^{-1}$  (C- $\text{CH}_3$  out of plane swing) [30, 31]. The more addition of the PLA-b-PEG, the stronger these peaks became. The incorporation of the PLA-b-PEG had no significant influence on the chemical composition of the gelatin films.

### SEM observation

The mechanical and gas barrier properties could be affected by the microstructure of the films. The SEM micrographs of the surface and freeze-fractured cross-section of the gelatin films incorporated without and with the PLA-b-PEG were shown in Fig. 2. It was observed that the surface and cross-section of the pure gelatin film were homogeneous and smooth with almost no defects. When the PLA-b-PEG content was increased to 2 wt% or 5 wt%, the surface of the gelatin/PLA-b-PEG films was still smooth, but the cross-section became rough. When the PLA-b-PEG content was higher than 5 wt% (10 wt% and 20 wt%), the film surface became rough because the PLA molecule blocks started to agglomerate together and phase separation take place. The phase separation was more obvious in the cross-sections of the gelatin/PLA-b-PEG films containing PLA-b-PEG of 10 wt% and 20 wt%, and a typical fibrous morphology was observed, as shown by Fig. 2e, g. Similar phase separation occurred when starch was blended with gelatin [32, 33]. Fibrous regions were observed in the cross-sections of the gelatin/starch films, confirming the polymer phase separation, too. These fibrous zones could be gelatin association domains where helical chain conformation and association (triple helix) occurred, as observed by some other researchers [34]. The holes in the fibrous region could decrease the TS of the films and oxygen barrier property as defects. A good effect of the holes on the properties of the blend films could be that they afforded space for deformation of macromolecule chains under stress and enhance the EAB of the blend film. The obvious phase

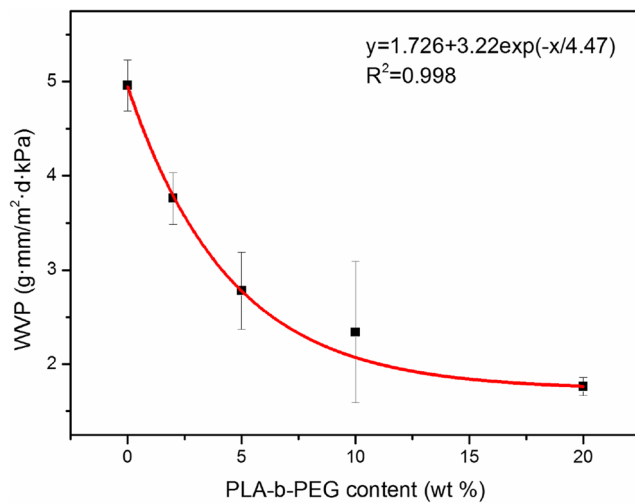
separation implied that further enhancing the content of the PLA-b-PEG could be not necessary.

### Water vapor permeability

WVP was measured to evaluate the water vapor barrier property of the films. The WVP value of a food packaging film should be as low as possible to avoid or decrease the moisture transfer between the food and the surrounding atmosphere and keep food fresh [35]. However, the WVP value of a pure gelatin film was very high ( $4.96 \pm 0.27 \text{ g}\cdot\text{mm}/\text{m}^2\cdot\text{d}\cdot\text{kPa}$ ) because of its hydrophilic property. The WVP of the films decreased significantly following the increase of the PLA-b-PEG content (Fig. 3). When the content of the PLA-b-PEG reached 20 wt%, the value of WVP reduced almost 64.5% to  $1.76 \pm 0.10 \text{ g}\cdot\text{mm}/\text{m}^2\cdot\text{d}\cdot\text{kPa}$ . The decrease was remarkable even when only 2 wt% PLA-b-PEG was added into the blend and the value of WVP reduced 24.2% to  $3.76 \pm 0.27 \text{ g}\cdot\text{mm}/\text{m}^2\cdot\text{d}\cdot\text{kPa}$ . The decrease of WVP was attributed to both of the PLA and PEG molecule blocks. It was reported that the WVP of a gelatin film decreased when PEG was used as a plasticizer, because the hydrophilic property of PEG was lower than that of gelatin [18]. PLA possessed excellent water vapor barrier property because of its hydrophobic property [5, 6]. A pure PLA film in this research only possessed a WVP of  $0.3 \text{ g}\cdot\text{mm}/\text{m}^2\cdot\text{d}\cdot\text{Bar}$ . The hydrophilic PEG blocks of the PLA-b-PEG could favor the PLA molecule blocks to disperse uniformly in gelatin and hinder water vapor permeation. However, the dependence of the WVP on the PLA-b-PEG content was not linear but could be fit to be a curve (Fig. 3). The decrease of WVP was not remarkable when the PLA-b-PEG content was enhanced from 10 wt% to 20 wt% (Fig. 3). The porous fibrous region emerged in phase separation process could promote water vapor permeation and counteract the hydrophobic effect of the PLA-b-PEG molecules.

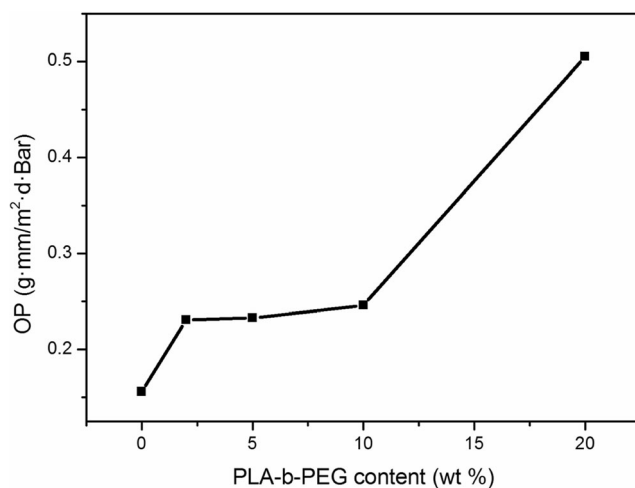
### Oxygen permeability

A barrier to oxygen in a packaging system was very important for food preservation, since oxygen could cause lipid oxidation and food spoilage. The gelatin films possessed excellent oxygen barrier property because they were hydrophilic material possessing huge amount of O-H and N-H groups. These groups could form hydrogen bonds, which could hinder oxygen permeation [11, 16]. On the contrary, PLA was a hydrophobic material possessed much higher OP ( $38 \text{ g}\cdot\text{mm}/\text{m}^2\cdot\text{d}\cdot\text{Bar}$  in this research) than gelatin film [16]. Addition of PLA could lower the oxygen barrier property of the blend films because PLA could break the hydrogen bonds formed between the gelatin molecules. Fortunately, the OP of the gelatin/PLA-b-PEG blend films did not increase significantly

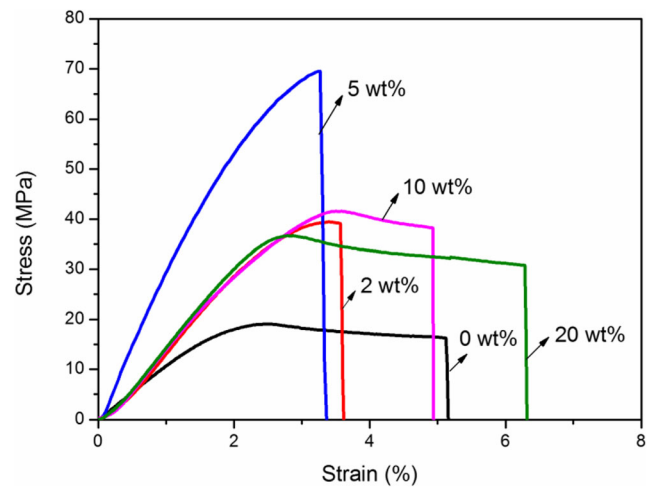


**Fig. 3** The water vapor permeability of the PLA-b-PEG/gelatin blend films decreased following the increase of the PLA-b-PEG content ( $\text{g}\cdot\text{mm}/\text{m}^2\cdot\text{d}\cdot\text{Bar}$ )

comparing to a pure PLA film when the PLA-b-PEG content was lower than 20 wt%, as shown in Fig. 4. The reason could be that PEG molecule blocks improved the dispersion of the PLA molecule blocks in the gelatin matrix and hindered the formation of PLA phase. Gelatin dominated the properties of the blend film as a continuous phase and PLA affected the properties of the blend film as a dispersed phase, as confirmed by the SEM images (Fig. 2). The OP of the blend film increased significantly when the PLA-b-PEG content was enhanced to 20 wt%, comparing to the samples containing less PLA-b-PEG. The reason could be that phase separation became more evidence and the continuous phase of gelatin was damaged following the increase of the PLA molecule block content. Many holes emerged inside the film (Fig. 2e, g), which could increase OP and decrease oxygen barrier property of the film as defects. Thus, further enhancing the PLA-b-PEG content was not suggested

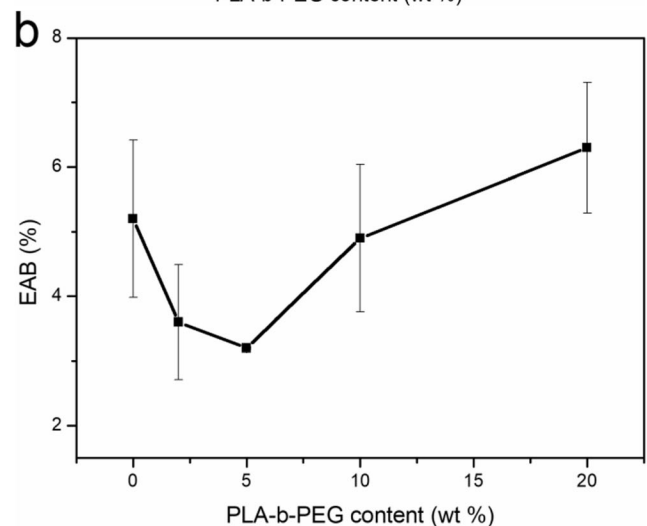
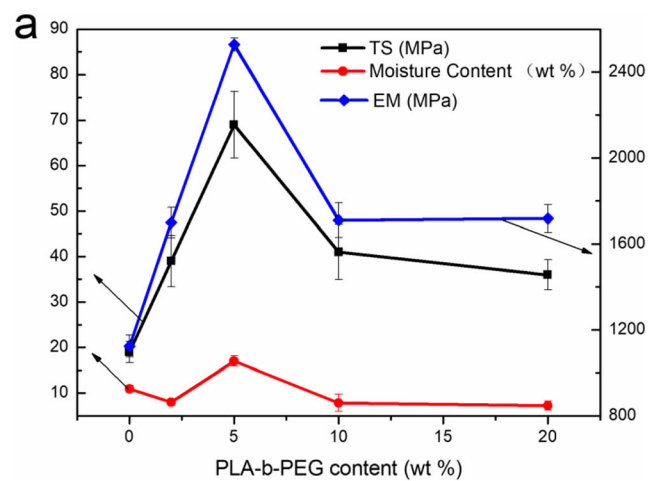


**Fig. 4** The oxygen permeability of the PLA-b-PEG/gelatin blend films increased following the increase of the PLA-b-PEG content



**Fig. 5** The tensile stress–strain curves confirmed the enhancement of the mechanical properties of the PLA-b-PEG to the gelatin blend films

in order to obtain a gelatin film of excellent oxygen barrier property.



**Fig. 6** The PLA-b-PEG/gelatin blend films showed complicated mechanical properties following the increase of the PLA-b-PEG content

### The mechanical properties

Enhancing the mechanical properties of a gelatin film, a tender material in tradition, was important, because films used for food packaging must be strong enough to keep the properties and the integrity of food in transport, application and handling process. The mechanical properties of different films were shown in Figs. 5 and 6. Adding a little amount of PLA-b-PEG could improve the mechanical properties of the gelatin film greatly. The TS came from 19 MPa to 39 MPa for a 105.3% increase and the EM came from 1124 MPa to 1699 MPa for a 51.2% increase when the PLA-b-PEG content was enhanced from 0 wt% to 2 wt% (Fig. 6a). When the addition amount of the PLA-b-PEG was 5 wt%, the films attained the greatest TS ( $83 \pm 5.43$  MPa, increased 336.8%) and EM ( $3196 \pm 40.50$  MPa, increased 184.3%). The reason could be that PEG was an effective plasticizer of gelatin [17, 18] and PLA possessed much better mechanical properties than gelatin [5]. The load endured by the gelatin could transfer effectively from the gelatin to the PLA molecule block by the PEG molecule block which had strong intermolecular hydrophilic interaction and hydrogen bonds with gelatin. Although the TS and EM of the blend films start to decrease when the PLA-b-PEG content was higher than 5 wt%, the TS and EM of the blend film containing 20 wt% PLA-b-PEG were still much higher than those of the pure gelatin film. The decrease of the TS and EM following the increase of the PLA-b-PEG content could be caused by the destruction of the gelatin continuous phase and phase separation which led to emergence of a lot of defects (the holes in the fibrous region observed by SEM) inside the blend film. Moreover, the load endured by the gelatin could not transfer to the PLA molecule blocks effectively because most of the PLA-b-PEG molecules could

Fig. 7 The tensile stress–strain curves of the PLA-b-PEG/gelatin blend films with different moisture content

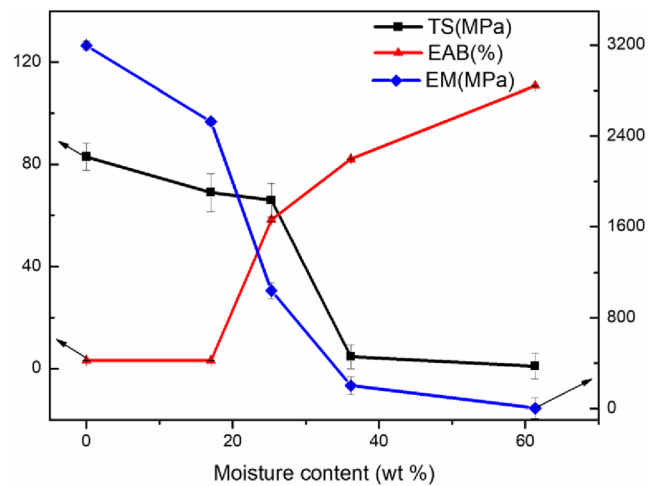
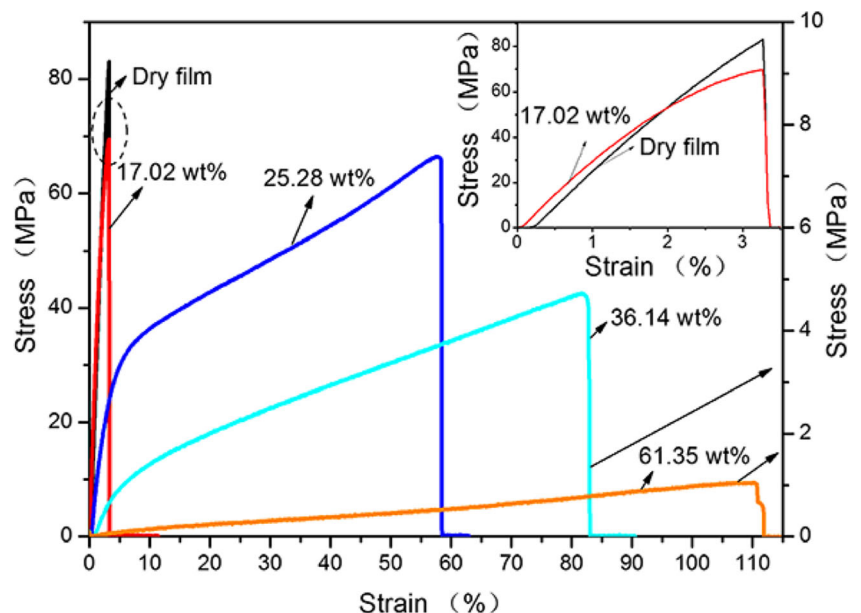
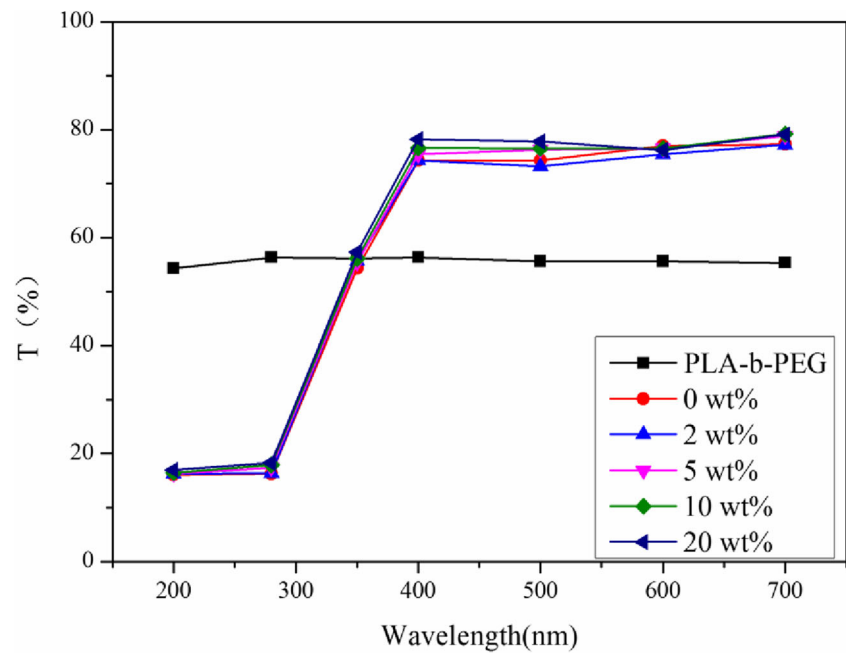


Fig. 8 The mechanical properties of the PLA-b-PEG/gelatin blend film with different moisture content

not form strong intermolecular interaction with the gelatin when the gelatin and PLA phases separated. An interesting phenomenon was that the EAB of the blend films decreased when the PLA-b-PEG content increased from 0 wt% to 5 wt%, but increased when the PLA-b-PEG content increased from 5 wt% to 20 wt% (Fig. 6b). The EAB of the blend film containing PLA-b-PEG of 20 wt% reached 6.3%, which was even higher than that of the pure gelatin film (5.2%). The reason could be that the phase separation caused many holes in the films (Fig. 2e, g), which afforded space for deformation of the gelatin and the PLA-b-PEG under stress and led to the recovery of the EAB.

The mechanical properties of the gelatin/PLA-b-PEG blend films were sensitive with environmental humidity because they could absorb lots of water from air. The absorbed water could exist in four states: 1) it could bind to the triple

**Fig. 9** The light transmission of the PLA-b-PEG/gelatin blend films following with the increase of the PLA-b-PEG content



helix through hydrogen bonds; 2) it could bind directly to the protein and was called structural water; 3) it could cover the triple helix and form polymolecular layer; 4) it could exist as free water [36–38]. In this case, the blend film containing PLA-b-PEG of 5 wt% was chosen to test the effect of moisture content on mechanical properties (Figs. 7 and 8). A dry film showed typical mechanical properties of glassy state with a TS of  $83 \pm 5.43$  MPa and a EM of  $3196 \pm 40.50$  MPa. When the moisture content reached 17.02 wt%, the blend film showed a brittle behavior with weak plastic deformation. The TS of the blend film decreased to  $69 \pm 7.37$  MPa and the EM decreased to  $2528 \pm 30.50$  MPa. When the moisture content further increased to 25.28 wt% and 36.14 wt%, the blend film showed evident plastic behavior. The TS and EM decreased significantly and the EAB increased significantly. The reason could be that a part of the absorbed water in the blend film bound to the triple helix through hydrogen bonds and other water could exist as structural water and polymolecular layer water. The structural water and polymolecular layer water could favor the movement of gelatin molecules and PEG molecular blocks. When the moisture content increased to 61.35 wt%, most of the absorbed water could exist as free water and the mechanical properties of the blend film were too poor to use.

**Table 1** The light transmission of the PLA-b-PEG/gelatin blend films following with the increase of the PLA-b-PEG content

Sample	PLA-b-PEG	0 wt%	2 wt%	5 wt%	10 wt%	20 wt%
Opacity	4.58	1.54	1.60	1.60	1.59	1.56

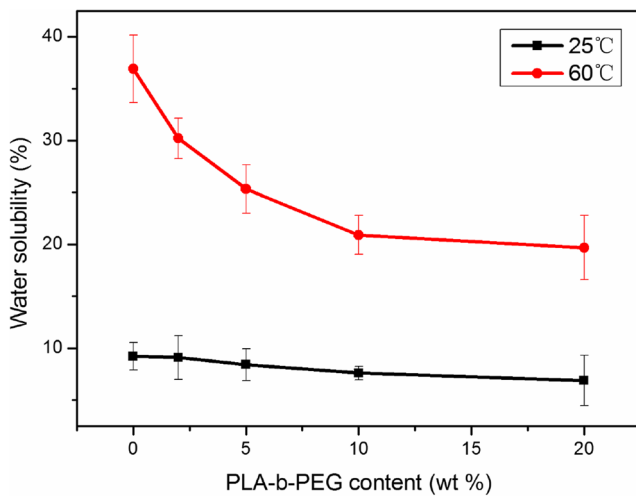
### Barrier properties and film transparency

A food packaging film was required to protect food from the effects of light, especially UV radiation. The results of spectroscopic scanning of all samples at wavelength range from 200 to 800 nm were shown in Fig. 9 and Table 1. Gelatin based films were generally known to have excellent UV barrier properties due to the presence of high content of aromatic amino acids which could absorb UV light [39]. The gelatin film as a control was transparent with a high transmittance value in the visible light range (higher than 75%), and had a good UV barrier property showing low transmittance value in the UV range (200–280 nm). The gelatin/PLA-b-PEG blend films showed similar transmittance spectra as that of the pure gelatin film, suggesting that the PLA-b-PEG dispersed uniformly in the gelatin continuous phase, which was consistent with other results discussed above. The results confirmed that phase separation occurred in the blend films containing 10 wt% and 20 wt% PLA-b-PEG did not affect the light transmission and UV barrier properties, though the pure PLA-b-PEG showed low UV barrier property (Fig. 9 and Table 1).

**Table 2** The hydrophilicity of the gelatin blend films containing different amount of PLA-b-PEG

PLA-b-PEG content	Thickness (nm)	Water contact angle(°)
0 wt%	$0.101 \pm 0.004$	$47.5 \pm 2.347$
2 wt%	$0.098 \pm 0.012$	$60.0 \pm 2.487$
5 wt%	$0.103 \pm 0.008$	$75.1 \pm 3.776$
10 wt%	$0.095 \pm 0.004$	$88.4 \pm 6.932$
20 wt%	$0.105 \pm 0.010$	$91.6 \pm 4.331$





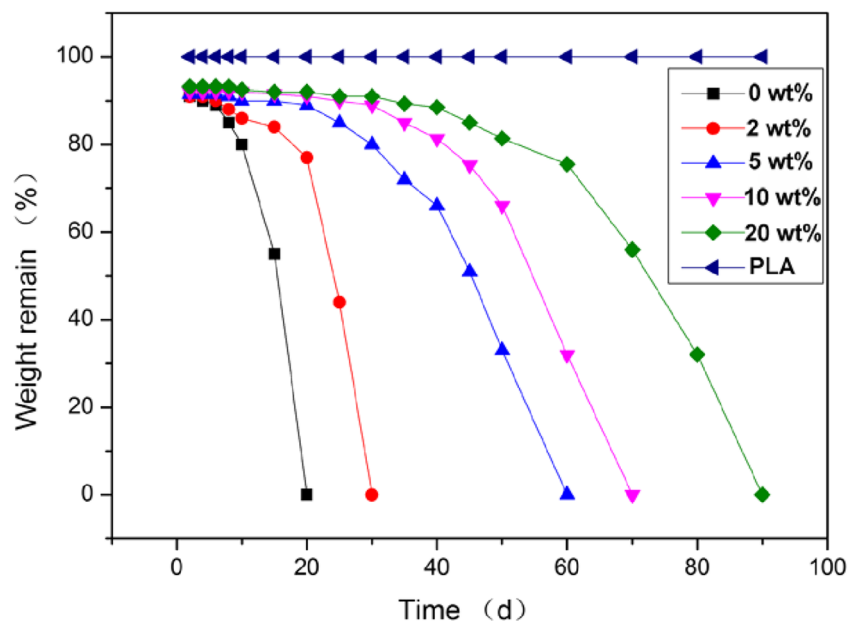
**Fig. 10** The water solubility of the PLA-b-PEG/gelatin blend films decreased following the increase of the PLA-b-PEG content

This result implied that the gelatin/PLA-b-PEG blend film could protect food from UV radiation as well as a pure gelatin film.

**Hydrophilicity and water solubility of the films**

The hydrophilicity of the films was characterized by a water contact angle ( $\theta$ ) test. As shown in Table 2, the initial contact angle of the control sample (0 wt% of PLA-b-PEG addition) was confirmed fairly low due to the excellent hydrophilicity of gelatin. Following the addition of PLA-b-PEG, the contact angles increased significantly, suggesting that the hydrophilicity of the films decreased due to the increase of the hydrophobic PLA block content in the blend films.

**Fig. 11** Degradation rate of the PLA-b-PEG/gelatin blend was slowed down controllably following the increase of the PLA-b-PEG content



The water solubility of all films decreased too, following the addition of the PLA-b-PEG (Fig. 10). The water solubility measurement at 25 °C indicated that the blend films contained a similar amount of water as those films measured by the moisture content test. This result suggested that the films could not absorb more water from water or wet fresh food at 25 °C than from an atmosphere under storage condition. When the water solubility test was carried out at 60 °C, it was confirmed that all the films absorbed more water than those at 25 °C. The reason was that the gelatin became more water soluble and could dissolve very well in water at 60 °C. However, the gelatin films were not dissolved in the water solubility test because they were crosslinked well by genipin, and the water content decreased following the increase of the PLA-b-PEG content due to the hydrophobic property of PLA. The decrease of the water solubility was not remarkable when the PLA-b-PEG content was improved from 5 wt% to 20 wt% (Fig. 10). The reason could be that phase separation enhanced the surface area of the blend films and promoted dissolution of the samples in water, which counteract the hydrophobic effect of the PLA-b-PEG molecules. The decrease of the hydrophilicity, moisture content and water solubility following the increase of the PLA-b-PEG content could be beneficial to protect fresh food from losing water when the film was used for food packaging.

**Degradation in water**

The degradation rate of the films in water was important for evaluating the environmental stability of the blend films. If the rate was too fast, the films could not protect food well and the shelf-life of the food product could be short; on the contrary, the films might take some environmental problems. As shown

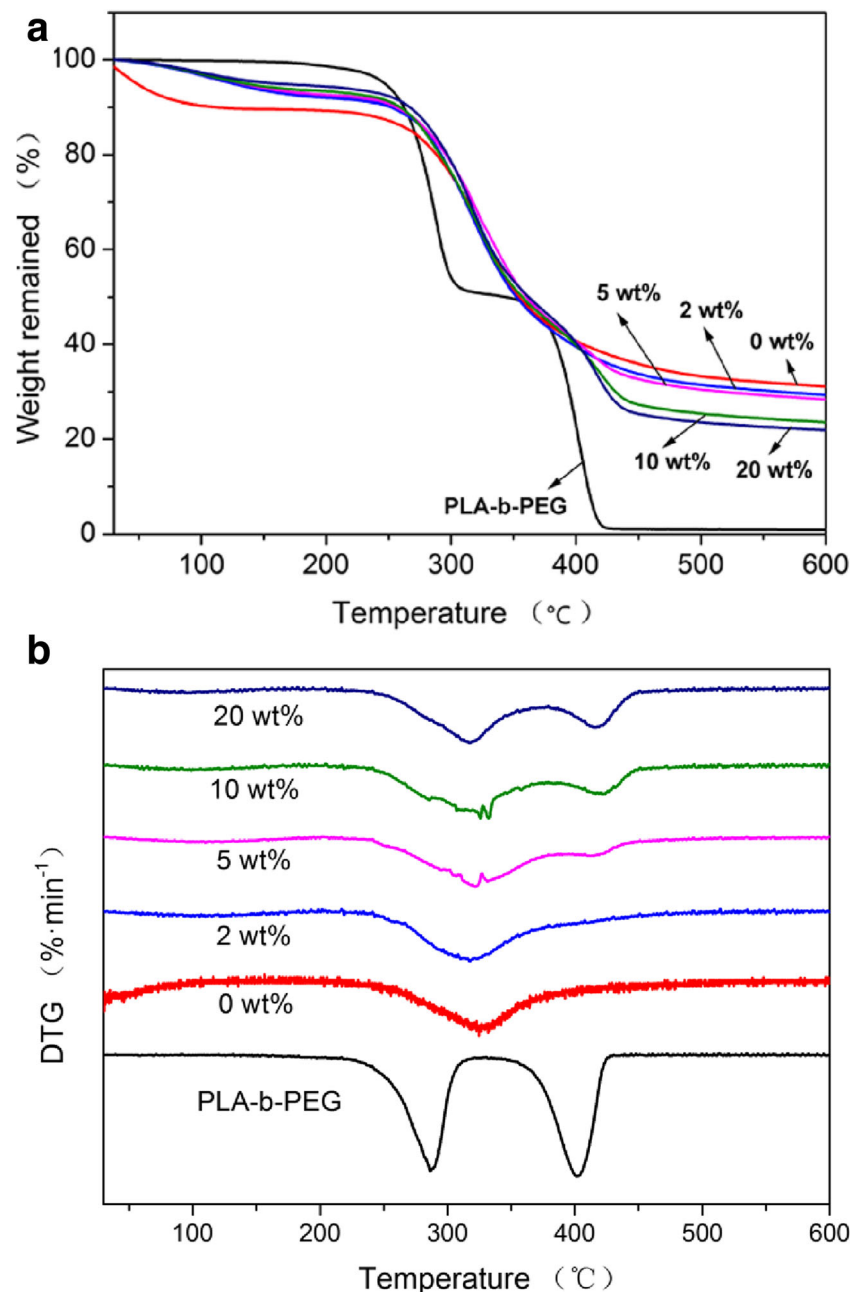
in Fig. 11, a gelatin film degraded quickly in water because a gelatin was composed of hydrophilic and tender proteins, and the gelatin film was very thin with a thickness of around 0.100 mm (Table 2). The degradation rate decreased significantly following the addition of PLA-b-PEG, suggesting that the degradation rate of the gelatin/PLA-b-PEG blending films was controllable. A pure gelatin film in water degraded completely in 20 d. The film containing 5 wt% of PLA-b-PEG degraded much slower than a pure gelatin film and a film containing 2 wt% of PLA-b-PEG. Phase separation could lead to formation of hydrophobic PLA phase and break hydrophilic gelatin continuous phase, which decreased the degradation rate of the blend films. When 20 wt% of PLA-b-PEG

was added, the film in water degraded about 10% in 40 d. This blend film was stable enough for packing a wet and fresh food product. The controllable degradation rate in water was also meaningful for extending the application of the gelatin/PLA-b-PEG blend.

### TGA and DTG

The thermal stability of the gelatin/PLA-b-PEG films was tested by TGA and DTG, as illustrated in Fig. 12. The TGA thermogram of the PLA-b-PEG showed two main stages of weight loss (Fig. 12a). The first stage weight loss ( $\Delta_{pw1} = 48.9$  wt%) at 306 °C could be associated with the PEG

**Fig. 12** a TGA thermograms confirmed that the thermal stability of the PLA-b-PEG/gelatin blend films was improved; b The result of DTG was consistent with that of TGA



degradation [40], and the second stage weight loss ( $\Delta_{pw2} = 50.1$  wt%) at 371 °C could be associated with the degradation of PLA [41]. Also, the TGA thermogram of the gelatin showed two main stages of weight loss. The first stage weight loss ( $\Delta_{gw1} = 11.0$  wt%) started at 30 °C could be associated with the loss of free and bound water adsorbed in the film [32], and the second stage weight loss ( $\Delta_{gw2} = 46$  wt%) at 236 °C was associated with the degradation of gelatin.

When the addition of the PLA-b-PEG was at a low amount (2 wt% and 5 wt%), the TGA thermogram was similar to that of the gelatin. When the addition of the PLA-b-PEG became higher, the thermogram became the mixture of gelatin and the PLA-b-PEG thermograms. Following the addition of the PLA-b-PEG, the degradation temperature of the film became higher (from 237 to 260 °C), suggesting that the PLA-b-PEG could improve the thermal stability of the blend film. DTG characterization confirmed the result of TGA (Fig. 12b).

## Conclusions

In summary, adding the PLA-b-PEG copolymer into the gelatin instead of a PLA material could overcome the challenge of blending a hydrophobic PLA and a hydrophilic gelatin together. The PEG blocks improved the compatibility of the PLA molecule block with the gelatin, which was critical for combing the gelatin and the PLA to prepare a film with excellent gas barrier and mechanical properties. The degradation rate of the gelatin/PLA-b-PEG blend film was elongated controllably by regulating the content of the PLA-b-PEG copolymer, suggesting that a gelatin/PLA-b-PEG blend could be used in application field requiring certain material stability, such as food packaging or biological scaffold. Besides, since the PLA-b-PEG could be mixed with the gelatin as a general additive, this gelatin/PLA-b-PEG blend film could be produced by a one-step process, just as simple as producing a pure gelatin film.

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