Effect of PBAT on Property of PLA/PHB Film Used for Fruits and Vegetables

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Abstract: A blend of poly(lactic acid) (PLA) (70% by weight) and poly(3-hydroxybutyrate) (PHB) (30% by weight) with a solubilizing agent (PBAT) at four different concentrations (5%, 10%, 15% and 20% by weight per 100 parts of the blends) were investigated by FTIR, SEM, mechanical testing, water vapor permeability test and biodegradation studies. SEM showed that PBAT can improve the compatibility between PLA and PHB. The film show a great Oxygen transmission rate and Water vapor permeability property when the content of PBAT is 10%.

1 Introduction

In recent years, sustainability, environmental concerns and green chemistry have played a big role in guiding the development of the next generation of materials, products and processes. The persistence of plastics in the environment, dwindling petroleum resources, shortage of landfill space and the concerns over emissions of toxic gases during incineration have fuelled efforts to develop biodegradable polymers from renewable resources[1]. The high social demand for sustainable biomaterials in the production of consumer goods has lead to increased attention in “green” technologies, in particular by developing environmentally friendly packaging systems [2, 3]. The proposal of new structures coupling adequate functionalities and sustainability is one of the current challenges in the research for new packaging materials. Important efforts have been recently devoted to obtain high performance bio-based materials, including polymer matrices, nanostructures and additives, fully derived from renewable resources [4, 5].

Poly(lactic acid) (PLA) is a linear thermoplastic polyester derived from the fermentation of renewable agricultural crops, such as starch, cellulose and other polysaccharides [6]. Moreover, it is compostable disappearing completely in less than one month [7, 8] and it is currently the most used biobased and biodegradable polymer for short-term applications. However, the main drawbacks of PLA are that it shows lower thermal and mechanical performance with respect of their petrochemical counterparts. Poly (3-hydroxybutyrate) (PHB), an aliphatic polyesters, synthesized by microorganisms, with high crystallinity and high melting point, is often used as components for blending with PLA, and leads to materials with interesting physical, thermal, and mechanical properties compared to neat PLA. This paper focuses on the effect of on oxygen and water vapor permeability of PLA/PHB film through using PBAT as a solubilizing agent, in order to find the best amount of additives, and explore

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the controlled conditions of fruits and vegetables film properties.

2 Materials and methods

2.1 Materials

The PLA (4032D, NatureWorks Co. LLC, USA) had an average molecular weight of 52,000 g·mol^{-1}, a polydispersity (M_w/M_n) of 1.9 and a high optical purity with 98% L-lactide content. The poly(3-hydroxybutyrate) (PHB under the trade name EM10080) was purchased from Shenzhen Ecomann Biotechnology Co., Ltd. The poly(butylene adipate-co-terephthalate) (PBAT ecoflex® F Blend C1200) was obtained from BASF.

2.2 Preparation of the blends

The materials were pre-treated by drying at 60℃for 24h to eliminate possible absorbed water on the surface of the particles. Compositions containing 70% PLA and 30% PHB in weight were mixed, respectively designated PBAT at four different concentrations (5%, 10%, 15% and 20% by weight per 100 parts of the blends). All the formulations were melt-compounded in a single screw extruder. The mixture was granulated after melt blending extrusion within the torque rheometer (RM-200A, Harbin HARP electrical technology Co., Ltd). The melt compounding temperature at different zones was independently controlled in order to achieve a temperature profile in the range of 170~190℃. The screw speed was set at 25RPM.

2.3 Morphological characterization by scanning electron microscopy (SEM)

Blend materials were fractured in liquid nitrogen to observe the interior of the unstressed composite. A sample was dropped directly into liquid nitrogen and fractured with a pre-chilled razor blade held in a vice-grip. The fractured pieces were picked out of the liquid nitrogen using pre-chilled forceps and placed in a desiccator to thaw and reduce the condensation of water on the surface of the material. All specimens were coated with gold-palladium for 45s. Specimens were viewed in a Hitachi S4700 field emission scanning electron microscope (Hitachi HTA, Japan) at 2 kV.

2.4 Mechanical property

An electronic universal material testing machine was used to measure mechanical property of films. And the referring standard of measurement was GB/T13022-91—Plastics-Determination of tensile properties of films. The reported values were the average of at least 5 measurements.

2.5 Fourier transformed infrared spectroscopy (FTIR)

Infrared spectroscopy analysis (FT-IR) was performed at room temperature in transmission and reflection modes by using a VECTOR 22 spectrometer at a wavenumber range 4000-400 cm^{-1}.

2.6 Oxygen transmission rate (OTR) and Water vapor permeability

The OTR was measured by using a GDP-C oxygen permeation analyzer (Brugger, Germany) at room temperature. 12cm×12cm films were prepared referring to GB/T 1038-2000‘Plastics-Film and sheeting-Determination of gas transmission Differential-pressure method’. WVTR of film sample was determined gravimetrically at 38℃ and 90% RH conditions using water vapor transmission measuring cups in accordance with the GB/T 1037-88 ‘Test method for water vapor transmission of plastic film and sheet-Cup method' standard method with a modification. Circle sample was sheared about 65 mm in diameter, and then put above the desiccant in moisture vapor transmission cup, fixed by sealing wax.

2.7 Soil burial test

Biodegradation studies under real soil burial conditions were carried out within the campus of Tianjin University of Science & Technology, Tianjin, China. The soil biodegradation test lasted for two months. The film samples were cut into 3cm×4cm pieces and all the samples were buried 10-20cm under the soil. Every ten day a sample was retrieved, and the corresponding film samples were cleaned and dried at room temperature. The film weight before and after soil biodegradation test was recorded accordingly. Then calculate the weight loss rate.

3 Results and discussion

3.1 Mechanical properties

The films intended for food packaging applications are subjected to elongation during the packaging procedure, being important their elastic modulus and elongation characteristics. Tensile strength and elongation at break properties of different films are represented in Table 1. The film of PLA/PHB without PBAT has a very high tensile strength and a low elongation at break. Because the composite film contain 70% of PLA which is a glossy polymer. The blends of PLA/PHB with PBAT showed different behavior. The tensile strength was significantly reduced by addition of PBAT, but the elongation at break increased in value. PLA/PHB without PBAT had a higher Young's modulus (YM) than that for other material blend with PBAT. The introduction of PBAT into the system provoked a significant reduction in Young modulus and tensile strength.

Table 1. Effect of PBAT content on mechanical properties of film

Code	Young's modulus (MPa)	Tensile Strength (MPa)	Elongation at break (%)
0	2374.94	36.36	318.42
5%	2235.05	32.40	339.04
10%	2126.48	31.68	369.51
15%	2155.19	28.98	372.03
20%	2071.43	25.61	382.49

3.2 Water vapor permeability (WVP) and Oxygen transmission rate (OTR)

The oxygen transmission permeability and water vapor permeability were studied and the obtained results are shown in Figure 1. The WVP of PLA/PHB without PBAT was 9.52×10^{-15} g·cm/cm^2·s·Pa. The WVP of PLA/PHB film increased by blending with PBAT. The value of WVP is increased quickly with the addition of PBAT first and then become steady. It is well known that plasticizers addition increases the free volume in PLA matrix and as a result a reduction in the oxygen barrier properties is produced. The oxygen transmission permeability of films increased with increase in PBAT content.

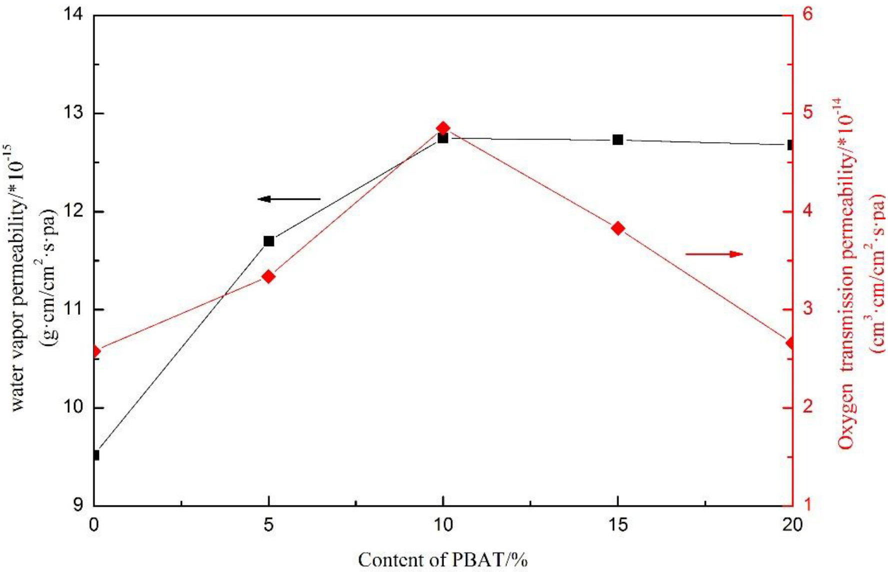

Figure 1. Effect of PBAT on oxygen and water vapor permeability of film

3.3 FT-IR analysis

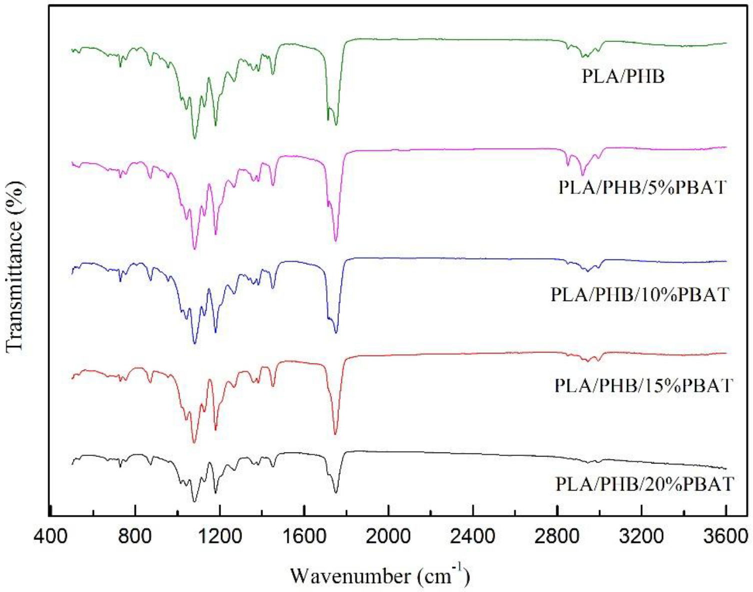

Figure 2. FT-IR spectra of PLA/PHB and PLA/PHB/PBAT samples in 400cm^{-1}~3600cm^{-1}.

FTIR spectra of PLA/PHB and PLA/PHB/PBAT films are shown in Figure 2 with an offset comparison. In the PLA film, the peak at the wavenumber of 3502 cm^{-1} represents CH_3 stretching vibration. The peaks at 2995 and 2945 cm^{-1} clearly are associated with the antisymmetric and symmetric stretching vibrations of CH_3 of saturated hydrocarbons, respectively [9]. At 1085 cm^{-1} a band associated with the –O–C– asymmetric mode of PLA appears [10]. Meanwhile, at 1180 cm^{-1} a band associated with the –C–O– bond stretching in the –CH–O– group of PLA appears [11]. There is a band at 1278 cm^{-1} assigned to the crystalline –C–O–C stretching of PHB and At 1360 cm^{-1} the CH deformation and asymmetric bands appear. The typical asymmetric stretching of the carbonyl group (–C=O) in neat PLA mat is centered at 1752 cm^{-1} and it is attributed to the amorphous carbonyl vibration [10]. It is possible to observe a small shoulder near 1740 cm^{-1} related with the amorphous state of PHB, showing that the PHB presents mainly crystalline structure with minor amorphous component [12]. In the PLA/PHB/PBAT blend films, peaks with low intensity which revealed the stretching vibration of C–O at 1718 cm^{-1}, the symmetric stretching vibration of C–O at 1271 cm^{-1}, and the bending vibration absorption of CH- plane of the benzene ring at 729 cm^{-1} of PBAT were found in addition to the peaks of PLA. The peaks positions of PBAT and PLA did not change after blending, which indicates that there was no chemical interaction between these two polymers [13].

3.4 Morphological properties

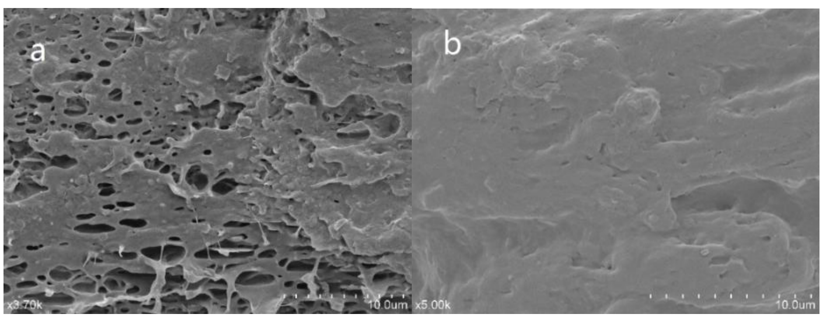

Figure 3. SEM images of PLA/PHB (a) and PLA/PHB/PBAT (b)

The initial particle size, the polymer elasticity, the dispersed phase percentage and the draw ratio are the main factors affecting the morphology formed during drawing. The morphologies of the fracture surfaces were investigated by SEM, as shown in Fig.3. The PLA/PHB film without PBAT presents an irregular fracture surface due to the crystalline structure of PHB in blends. There is almost no hole at the fracture surface in Fig. b, in which the PBAT fill in it.

3.5 Biodegradation testing

From the weight loss data in Table 2, all of the samples have lost certain amount of weight after the soil biodegradation test. For instance, after the first ten days, the PLA/PHB film lose the weight of 0.8%, while the weight of others were 1.08%, 1.14%, 1.06% and 2.14%, respectively. The weight loss of PLA/PHB blends with PBAT are all higher than that of PLA/PHB, which indicate that PBAT can increase the degradation rate. Also, the degradation rate is relate to the content of PBAT in blends.

Table 2. Film weight loss after the soil burial test

Entries	Weight loss rate (wt%)					
	10d	20d	30d	40d	50d	60d
0	0.8	1.24	2.86	4.15	5.96	7.35
5	1.08	2.47	4.01	6.58	7.35	9.66
10	1.14	2.45	4.46	6.59	7.86	9.97
15	1.06	2.68	4.85	6.89	7.83	10.56
20	2.14	3.26	5.65	7.74	8.96	11.53

4 Conclusions

The current study investigated the PBAT effect on the morphology, mechanical properties, as well as on the WVP and OTR properties, of PLA//PHB/PBAT blends in the form of blown films. Mechanical properties test showed that PLA/PHB blends with PBAT could increase elongation at break and introduction of PBAT into the system provoked a significant reduction in Young modulus and tensile strength. SEM results showed that PBAT can improve the compatibility between PLA and PHB. The soil biodegradation test proved that the weight loss increased with the content of PBAT increasing.

References

1. Mohamed A., Abdelwahab, Allison Flynn, et al. Thermal, mechanical and morphological characterization of plasticized PLA/PHB blends [J]. Polymer Degradation and Stability, 2012, 97: 1822-1828.
2. Murali M. Reddy, Singaravelu Vivekanandhan, Manjusri Misra, et al. Biobased plastics and bionanocomposites: current status and future opportunities [J]. Progress in Polymer Science, 2013, 38 (10): 1653-1689.
3. Perlette N. Takala, Stephane Salmieri, Afia Boumail, et al. Antimicrobial effect and physicochemical properties of bioactive trilayer polycaprolactone/methylcellulose-based films on the growth of foodborne pathogens and total microbiota in fresh broccoli [J]. Journal of Food Engineering, 2013, 116 (3): 648-655.
4. Arrieta, M. P., Peltzer, M. A., López, J., et al. Functional properties of sodium and calcium caseinate antimicrobial active films containing carvacrol [J]. Journal of Food Engineering, 2014, 121: 94-101.
5. Arrieta, M. P., Samper, M. D., López, J., et al. Combined effect of poly (hydroxybutyrate) and plasticizers on polylactic acid properties for film intended for food packaging [J]. Journal of Polymers and the Environment, 2014, 22 (4): 460-470.
6. M.P. Arrieta, J. López, D. López, et al. Biodegradable electrospun bionanocomposite fibers based on plasticized PLA–PHB blends reinforced with cellulose nanocrystals [J]. Industrial Crops and Products, 2016, 93: 290-301.
7. Arrieta, M.P., López, J., Rayón, E., et al. Disintegrability under composting conditions of plasticized PLA-PHB blends [J]. polymer degradation and stability, 2014, 108: 307-318.
8. Dolores, S.M., Patricia, A.M., Santiago, F., et al. Influence of biodegradable materials in the recycled polystyrene [J]. Journal of Applied Polymer Science, 2014, 131.
9. Al-Itry, Racha, Lamnawar, Khalid, Maazouz, Abderrahim. Rheological, morphological, and interfacial properties of compatibilized PLA/PBAT blends [J]. Rheologica Acta, 2014, 53 (7): 501-517.
10. R. Auras, B. Harte, S. Selke. An overview of polylactides as packaging materials [J]. Macromolecular Bioscience, 2004, 4 (9): 835-864.
11. E. Fortunati, D. Puglia, C. Santulli, et al. Biodegradation of Phormium tenax/poly(lactic acid) composites [J]. Journal of Applied Polymer Science, 2012, 125 (2): E562-E572.
12. T. Furukawa, H. Sato, R. Murakami, et al. Structure, dispersibility, and crystallinity of poly(hydroxybutyrate)/poly(L-lacticacid) blends studied by FT-IR microspectroscopy and differential scanning calorimetry[J]. Macromolecules, 2005, 38 (15): 6445-6454.
13. Long-Feng Wang, Jong-Whan Rhim, Seok-In Hong. Preparation of poly(lactide)/poly(butylene adipate-co-terephthalate) blend films using a solvent casting method and their food packaging application [J]. LWT-Food Science and Technology2016, 68: 454-461.