Fabrication of Lignin/Pbat Biodegradable Plastics Films via Reactive Extrusion and Their Thermal, Mechanical and Water Absorption Properties

Yanyan Dong , Weichang Gao , Zhenbao Luo , Heqing Cai , Aurore Richel , Jialei Liu , Yining Zhang , Zhichao Zhen , Wenqing He * , Qi Liu *

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Article

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Yanyan Dong [1], Weichang Gao [2], Zhenbao Luo [2], Heqing Cai [3], Aurore Richel [4], Jialei Liu [1], Yining Zhang [1], Zhichao Zhen [5], Wenqing He [1,*] and Qi Liu [1,*]

[1] Key Laboratory for Prevention and Control of Residual Pollution in Agricultural Film, Ministry of Agriculture and Rural Affairs, Institute of Environment and Sustainable Development in Agriculture, Chinese Academy of Agricultural Sciences, No.12 Zhongguancun South Street, Beijing 100081, China
[2] Guizhou Academy of Tobacco Science, Upland Flue-cured Tobacco Quality & Ecology Key Laboratory of China Tobacco, Guiyang, 550081, China
[3] Bijie Tobacco Company of Guizhou Province, Bijie, Guizhou 551700
[4] Laboratory of Biomass and Green Technologies - University of Liege, Gembloux 2 B-5030, Belgium
[5] Technical Institute of Physics and Chemistry, Chinese Academy of Sciences, Beijing, China
* Correspondence: hewenqing@caas.cn (W. He), liuqi@caas.cn (Q. Liu)

Abstract: Biodegradable and renewable plastic films have been regarded as promising alternative green materials to achieve the substitution polythene (PE)films to reduce plastic pollution. Poly (butylene adipate-co-terephthalate) (PBAT) is a kind of biodegradable polyester, which is widely used in the production of biodegradable mulching films. However, the high cost of PBAT limited it applications. Thus, lignin, one of the most abundant biomass resources was incorporated into PBAT matrix in the present work. A series of Lignin/PBAT biodegradable plastics films with different Lignin/PBAT weight ratios (0.00 %-5.00 %) were successfully fabricated using twin screw and twin roll extruders. The chemical compositions, morphologies, thermal stabilities, mechanical properties, and barrier properties of samples were characterized by XRD, FTIR, TG/DSC, mechanical testing machine, and WVTR, respectively. Results show that the corporation of lignin into PBAT matrix could lead to improved thermal stabilities, mechanical properties and barrier properties of films even after Xenon lamp aging process, especially when Lignin/PBAT weight ratio is 1.00 % in the present work. This work provides a very promising approach for fabrication of biodegradable plastics films with low cost, enhanced mechanical properties and barrier properties, the as-prepared samples may have potential applications in agricultural or food packaging materials.

Keywords: PBAT; Lignin; Biodegradable; film; fabrication; characterization

1. Introduction

Plastic pollution has always been a big problem plaguing the world! In 2015, the United Nations designated microplastic pollution as a new type of environmental pollution and listed it as a major global environmental problem along with global warming and ozone pollution. On March 2, 2022, many national leaders, ministers of environment and representatives of other departments from over 175 countries and territories adopted a landmark resolution at the resumed Fifth session of the United Nations Environment Assembly (UNEA-5.2), which aims to end plastic pollution, which involves the full life cycle of plastics, including plastics' production, design and disposal, as well as reduce the leakage and pollution of plastics in global ecosystems, including Marine environments. Most of the plastic pollution comes from the gradual decomposition of non-degradable plastics after abandonment, and the ecological environment pollution caused by non-degradable plastics, coupled with the increasing depletion of petroleum resources, makes bio-based materials attract more and more attentions in recent years.

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PBAT (polybutylene adipate/terephthalate) is a copolymer of butylene adipate and butylene terephthalate, which has the characteristics of PBA (polybutylene adipate) and PBT (polybutylene terephthalate). It is a kind of semi-crystalline polymer, showing a high elastic state under normal temperature conditions, and has good mechanical properties. It has high ductility, high elongation at break, and also has excellent biodegradability [1–3]. As a fully biodegradable polymer, PBAT can be fully degraded within a few weeks with the aid of enzymes naturally presents in fertile soil [4–6]. PBAT biodegradable plastics are mainly used in: packaging bags and packaging films; including pet feces bags, shopping bags, rolled garbage bags, electronic product bags, mulching films, food bags, etc [7–13]. Therefore, PBAT is regarded as an ideal material to replace traditional plastic polyethylene (PE) and has become a research hotspot in the field of biological materials [14–16]. However, the price of PBAT is very high, which is 3-5 times of PE, in addition, PBAT showed poor mechanical and thermomechanical properties [17,18], which limits the widely applications of PBAT films. To address these limitations, low-cost and biodegradable fillers, including organic fillers (starch, fibers, soybean meal, protein, rice flour, and lignin) and inorganic fillers (clays, layered silicate, and talcum powder), have been incorporated into the PBAT matrix to reduce the production cost and improve its properties, while maintaining its biodegradability [19–23].

Lignin, which accounts for 15 %-30 % of all biomass, is one of the three main components (cellulose, hemicellulose, and lignin) of lignocellulosic biomass, and It exhibits high impact strength and good heat-resistance and very high char yield after decomposition which makes it a promising bio-based flame retardant additive. Lignin can improve the flowability and processing performance of the thermoplastic polymer matrices [24,25]. What's more, it has a lightweight and low cost which consequently reduces the cost and weight of final composites. Lignin featured with active groups such as hydroxyl groups, which can provide available sites to be chemically modified to meet various practical application needs, making lignin as a kind of desirable filler for the interaction between the polymer matrix and lignin [1,26,27]. Xiong et al (2020)., reported the successfully fabrication of biodegradable PBAT/lignin composites with high lignin contents by melt extrusion, which is expected to be used for preparing rubbish bags, packaging bags, and soil remediation film [1]. Botta et al (2022)., reported the fabrication of biocomposite PBAT/lignin blown films, the films displayed an increase of the elastic modulus and enhanced photo-stability when compared to neat PBAT films without affecting their elongation at break [26]. Wang et al (2020)., reported the fabrication of lignin-based (30-50 wt%) biodegradable composites with superior performances by incorporating lignin into the PBAT matrix, the work presents a green and feasible route to produce cost-efficient biodegradable materials with controlled mechanical and UV-shielding properties for packaging application [27]. According to the previous studies, it is not only modified lignin should be used for enhancing the performance of blend systems, but also additives should be used, such as coupling agents, plasticizers, and compatibilizers [1,28–30], the production process is very complex, high-cost, and is not environmentally friendly.

The study in the present work aims to fabricate Lignin/PBAT biodegradable plastics films with enhanced properties in a facial, cost-efficient, environmentally friendly way via reactive extrusion. In the present study, lignin was not modified before incorporated into the PBAT matrix, and no other additives were added into the system except talcum powder, which is a kind of common splitting agent in films production. X-ray diffraction Analysis, FT-IR spectroscopy, Scanning Electron Microscopy, Thermogravimetric Analysis, Differential Scanning Calorimetry were used to characterize and analyze the samples' chemical compositions, morphologies, and thermal stabilities. The barrier properties and mechanical properties were also evaluated in the study.

2. Materials and Methods

2.1. Materials

PBAT was purchased from JinhuiZhaolong High Technology Co., Ltd (Shanxi, China) with the trade name of Ecoworld®. It possessed a density of 1.26 g/cm^3, a melt index of 3–5 g/10 min (190 °C/2.16 kg), and an average melting temperature of 115°C. Lignin was obtained from Beijing Key

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Laboratory of Lignocellulosic Chemistry, Beijing Forestry University (Beijing, China). Talcum powder was purchased from Haicheng ShijingQiyang Co., Ltd (Liaoning, China).

2.2. Fabrication and Xenon lamp aging of Lignin/PBAT biodegradable plastics films

Lignin/PBAT biodegradable plastics films (LPs) were fabricated using twin screw and twin roll extruders. The twin screw extruder was first used to extrude Lignin/PBAT composites, and then the twin roll extruder was pressed into the film, where the twin roll was used to control the thickness of the film. PBAT were dried in a vacuum oven at 80 °C for 24 h before use. Then, PBAT was mixed with 2.00 wt% talcum powder and different lignin content (0.00, 0.50, 0.75, 1.00, 1.50, 2.50, and 5.00 wt%) in a plastic mixer. The compounds were prepared by melt-mixing in a twin-screw extruder (LTE-26-44, Labtech Engineering, Thailand) and then were prepared into pellets by a pelletizer cutting machine (LZ-120/vs, Labtech Engineering, Thailand). The temperature profiles were set from feed zone to die around 170 °C–185 °C. The feed speed and screw speed were 20 rpm and 100 rpm, respectively. The extruder was cooled in a water bath, pelletized, and dried at 60 ºC for 6 h. After that the PBAT films were prepared by blown film extruder (QY2200-1, Shandong Plastic Machinery Company, China) at 135 °C with Ecoflex® PBAT. The six resulting films were named as LP-0, LP-1, LP-2, LP-3, LP-4, LP-5,and LP-6.The blow-up ratio of the bubble was 3.5:1. This setting produced a bubble with an average thickness of 22.0±1.0 μm.

The Xenon lamp aging of Lignin/PBAT biodegradable plastics films were performed on a Xenon lamp aging test box (BGD 860, Guangzhou Biuged Laboratory Instrument Products Co., Ltd, China) with an inner test box temperature of 36.5 °C, and kept for 100 h. Then the samples were taken out for further analysis.

2.3. Characterization of Lignin/PBAT biodegradable plastics films

2.3.1. X-ray diffraction Analysis(XRD)

X-ray diffraction patterns of LPs were carried out by using a Rigaku D/Max 2200-PC diffractometer with Cu Kα radiation (λ= 0.15418 nm) and graphite monochromator at ambient temperature.

2.3.2. FT-IR spectroscopy(FTIR)

FT-IR spectroscopy for Lignin/PBAT plastic films were measured using a Micro-Attenuated Total Reflection Fourier Transform Infrared (Micro-ATR-FTIR) microscope (OPUS 7.5, Bruker, Germany). The FTIR spectrum of each sample was obtained at 4000–400 cm^{-1} with a resolution of 4 cm^{-1}.

2.3.3. Scanning Electron Microscopy(SEM)

The images of the surfaces of Lignin/PBAT plastic films were examined using a SEM (Hitachi S-4800, Hitachi High Technologies America, Inc., USA). Samples were cut into 4 mm wide, coated with gold by an ion sputter coater, and then observed under SEM at 15 kV.

2.3.4. Thermogravimetric Analysis(TGA)

TG analysis was carried out using a TGA/DSC thermogravimetric analyzer (Mettler Toledo Corporation, Switzerland) within a temperature range from room temperature to 800 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

2.3.5. Differential Scanning Calorimetry (DSC)

The DSC measurements for all the LPs were carried out on a TA DSC Q200 calorimeter (TA instruments) under nitrogen atmosphere, with typical heating/cooling rate of 10 °C/min. A total of 5–10 mg sample was weighed and placed in a crucible under a nitrogen atmosphere. A three-step procedure of heating/cooling/heating ramps was adopted. The temperature program was set as

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follows: Samples were heated from room temperature to 200 °C at 10 °C/min and kept at a constant temperature for 3 min to eliminate the thermal history. Then, subsequent cooling was performed from 200 °C to room temperature at 10 °C/min. In the second heating run, the sample was heated from room temperature to 200 °C at 10 °C/min again to obtain the second heating curve. The glass transition temperature (Tg) and melting temperature (Tm) were obtained on the second heating run, while the melt crystalization enthalpy (ΔH_c) was collected on the cooling run.

2.3.6. Water Vapor Permeability Testing (WVTR)

To determine the moisture permeability of the films, WVTR were determined by a water vapor transmission rate tester (W3/060 PERME, Labthink, China) according to ASTM E96/E96M-2014 [31]. The samples were cut with a sampler with an area of 33.2 cm^2. Samples were sealed on top of the permeation cells with appropriate amount of ultra-pure water. The cells were set in the sample chamber of the water vapor transmission tester. The pressure of the output pressure gauge is 4–5 Mpa, and the pressure of the automatic drying filter is 0.3–0.35 Mpa by adjusting the air source of the system. The temperature and relative humidity of the tester were set to 38 ℃ and 90% RH. All measurements were repeated three times.

2.3.7. Mechanical Property Testing

A universal testing machine (XLW, Labthink, China) was usedto determine the tensile and tear properties of the PLs. Tensile properties were determined according to the ASTM D882-2018 method [32]. Films were cut into 10 mm wide strips and at least 80 mm long. The grip separation and crosshead speed were 50 mm and 500 mm/min, respectively. At least five specimens were tested for each sample. The tear properties of films were determined according to the ASTM D1004-2013 method [33]. The samples were cut into the shape of a mold. The strain rate was 200 mm/min. At least five specimens were tested for each sample. The thicknesses of five replicates of each sample were measured with a micrometer (C1200, Mahr Millimar, Germany) with an accuracy of ± 0.1 μm according to the ASTM D6988-2013 method [34].

3. Results and Discussion

3.1. XRD analysis

The LPs were fabricated with different Lignin/PBAT weight ratios, the width and compositions of LPs films were summarized in Table 1. The corresponding XRD patterns of LPs films were collected in the present work. As were shown in Figure 1, all samples of LPs films showed similar characteristic X-ray diffraction peaks, indicating that all the samples had the same compositions, the specific contents in the samples were further confirmed by FTIR analysis.

Table.1 The contents of different samples

Sample	thickness (μm)	Lignin (g)	Talcum Powder (g)	PBAT (g)
LP-0	24.9	0	20	1000
LP-1	22.4	5	20	1000
LP-2	22.1	7.5	20	1000
LP-3	22.6	10	20	1000
LP-4	21.9	15	20	1000
LP-5	22.6	25	20	1000
LP-6	22.2	50	20	1000

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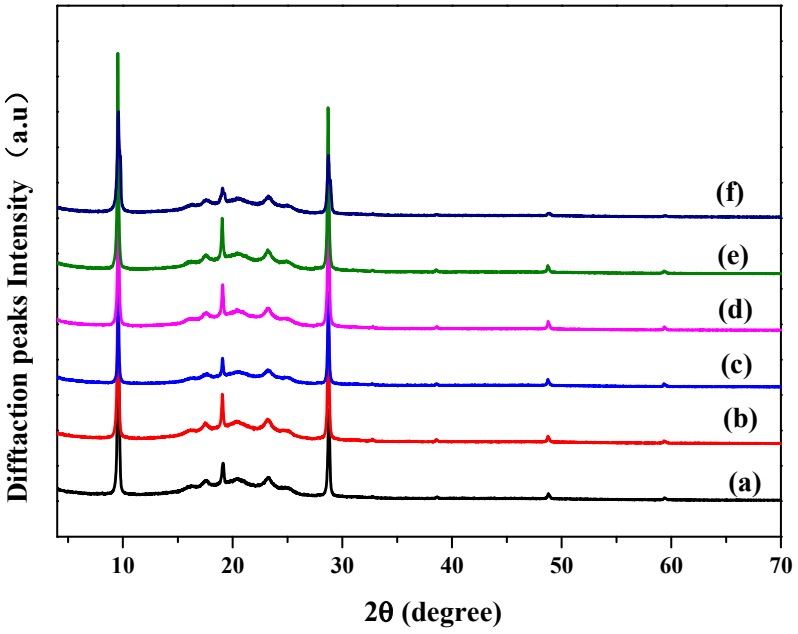

Figure 1. XRD patterns of samples fabricated with different Lignin/PBAT weight ratios: (a) 0.50%, (b) 0.75%, (c) 1.00%, (d) 1.50%, (e) 2.50% and (f) 5.00%.

3.2. FTIR analysis

The FTIR spectra of several LPs were collected as shown in Figure 2. All the samples of LPs showed similar absorption peaks near 2930–2950 cm^{-1}, which correspond to the stretching vibration peak of aliphatic C–H stretching; the absorption peak at approximately 1713 cm^{-1} should be assigned as the stretching vibration of C=O in PBAT; the absorption peak from 1270cm^{-1} and 1010 cm^{-1} were all stretching absorptions of C–O–C in PBAT, and the absorption peaks near 729 cm^{-1} represent the bending vibration absorption of C–H of the benzene ring. The peak at 1118 and 1027 cm^{-1} are indicative of the in-plane deformation of aromatic C-H from syringyl (S) and guaiacyl (G) structures, respectively. The FTIR results indicated that the LPs were successfully fabricated in the present work.

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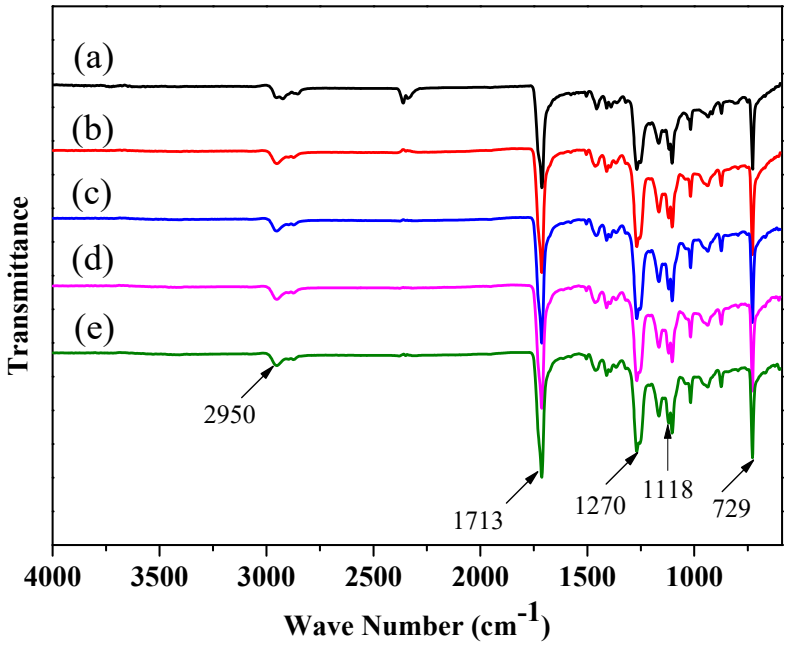

Figure. 2 FTIR analysis of samples fabricated with different Lignin/PBAT weight ratios: (a) 0.00%, (b) 0.50%, (c) 1.00%, (d) 2.50% and (f) 5.00%.

3.3. Morphology

Scanning electron microscope (SEM) was used to characterize the micro-structures and morphology of the as-fabricated LPs samples. Figure 3 presented the SEM images of LPs samples with different Lignin/PBAT weight ratios. As were presented in Figure 3, the LPs samples fabricated with different Lignin/PBAT weight ratios displayed different morphologies. Compared with pure PBAT plastic films, the existence of lignin in PBAT plastic films make the LPs films show rough surfaces, with increasing lignin ratios, the surfaces of LPs films became more rough. As was shown in Figure 5a, when Lignin/PBAT weight ratio in LPs films was 0.50 %, there were several small bumps appeared on the surface of LP-1 (Figure 3a); when Lignin/PBAT weight ratio in LPs films increased to 0.75%, there were more bumps appeared on the surface of LP-2, some of the bumps were even very big (Figure 3b); when Lignin/PBAT weight ratio in LPs films increased to 1.00 %, there were many small bumps, but no obvious big bumps observed on the surface of LP-3 (Figure 3c). It is worth mentioning that when Lignin/PBAT weight ratios in LPs films increased to 1.25 % or higher, the surfaces of LPs films became more and more rough, the bumps became bigger with increasing Lignin/PBAT weight ratios (Figure 3d and 3e). As was shown in Figure 3f, there were no obvious smooth areas observed obviously in LP-6. According to the SEM results, it could conclude that Lignin/PBAT weight ratios have significant effects on the surface morphologies of LPs films, 1.00 % is an ideal Lignin/PBAT weight ratio for the dispersion of lignin in PBAT matrix among all the samples in the present work.

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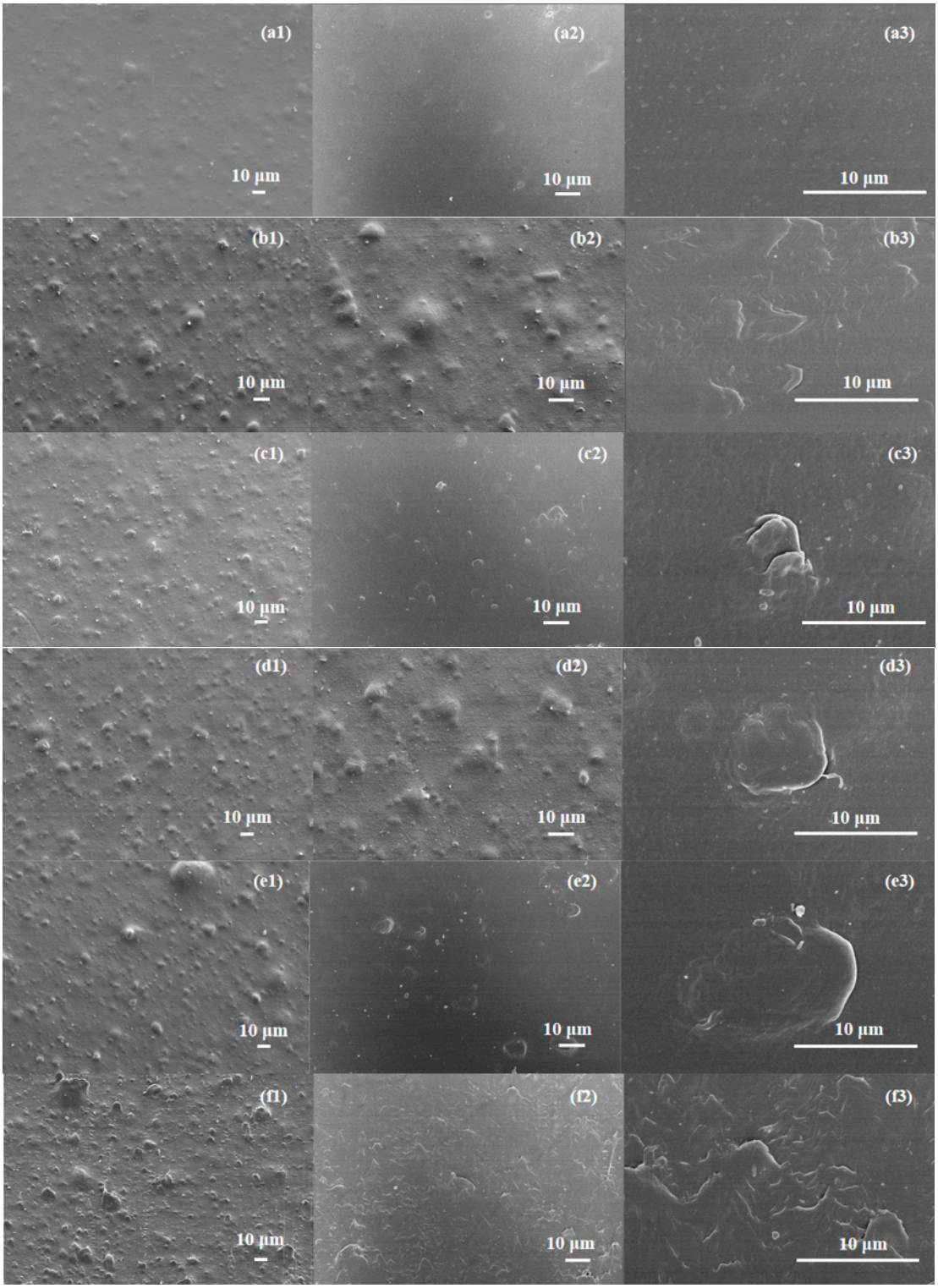

Figure 3. SEM images of samples fabricated with different Lignin/PBAT weight ratios: (a) 0.50%, (b) 0.75%, (c) 1.00%, (d) 1.50%, (e) 2.50% and (f) 5.00%.

3.3. Thermal analysis

The crystallization temperatures (T_c) and the crystallization enthalpy (ΔH_c) were determined from the cooling ramp. The melting temperatures (T_m) and corresponding melting enthalpy (ΔH_m) were obtained from the second heating circle. Temperature at the maximum degradation rate (T_{max}), determined by the first derivative thermogravimetric (DTG) curves

The thermal stabilities of LPs films were evaluated by TG and DTG, the results are shown in Figure 4, and the corresponding T_{max} are summarized in Table 2. It can be seen that all the LPs films

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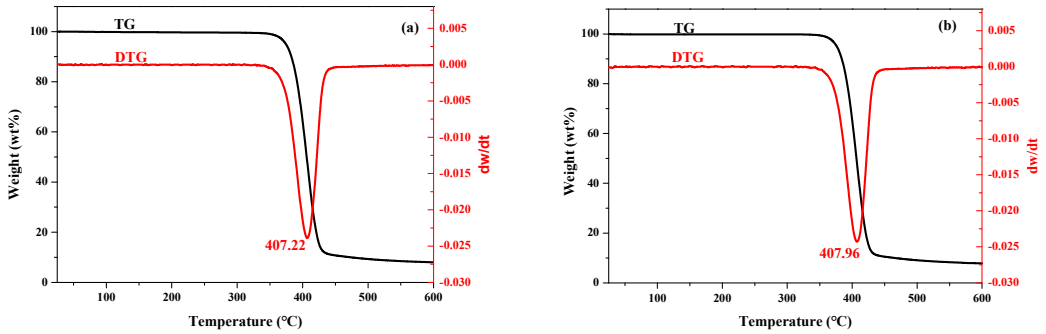
underwent a one-step degradation process (DTG curves). As is summarized in Table 2, the pure PBAT plastic film (LP-0) started to decompose at around 369.0 °C and showed a major weight loss at around 400.0 °C. After lignin was added into PBAT matrix, the corresponding T_{max} of LP-1, LP-2, LP-3, LP-4, LP-5, LP-6 were 407.2, 407.9, 407.2, 406.4, 406.9 and 405.9 °C, respectively. Based on the results, the LPs films fabricated in the present work showed increased thermal stability compared to the neat PABT. It can be concluded that the addition of lignin has positive effect on the thermal stabilities of LPs films, but when Lignin/PBAT weight ratios in LPs films increased to 1.25 % or higher, a slight decrease occurred on T_{max}, which were decreased from 407.9 °C to 406.4 °C.

Table 2. TGA and DSC Results of PLs films.

Samples	TG	DSC			
	T_{max} (°C)	T_c (°C)	ΔH_c (J·g^{-1})	T_m (°C)	ΔH_m (J·g^{-1})
LP-0	400.0	79.9	14.7	120.9	15.2
LP-1	407.2	91.7	11.4	123.8	11.5
LP-2	407.9	92.1	10.9	125.6	12.1
LP-3	407.2	92.6	10.9	123.9	11.6
LP-4	406.4	91.7	10.6	123.6	10.2
LP-5	406.9	91.8	10.6	127.8	13.9
LP-6	405.9	91.1	10.3	125.4	9.5

The DSC analysis were also carried out to investigate the crystallization temperature T_c, and crystallization enthalpy (ΔH_c), melting temperature T_m, and melting enthalpy (ΔH_m) of LPs films. The thermograms of cooling and second heating run of LPs films are shown in Figure 5, the calorimetric parameters and related data are summarized in Table 2. With the incorporation of lignin in PBAT matrixes, T_c and T_m of PLs films shifted gradually to higher temperatures with higher Lignin/PBAT ratio, from 79.9 °C (T_c, LP-0) up to 92.6 °C (T_c, LP-3) , and from 120.9 °C (T_m, LP-0) up to 125.6 °C (T_m, LP-2). While ΔH_c and ΔH_m of PLs films shifted gradually to lower energy with higher Lignin/PBAT ratio, from 14.7 J·g^{-1} (ΔH_c, LP-0) down to 10.3 J·g^{-1} (ΔH_c, LP-6) , and from 15.2 J·g^{-1} (ΔH_m, LP-0) down to 9.5 J·g^{-1} (ΔH_m, LP-6). Particularly for LPs films, the increase of T_c and T_m could be attributed to the excellent thermal stability of lignin, as well as the interaction between lignin and PBAT to constrain the polymer chain mobility.



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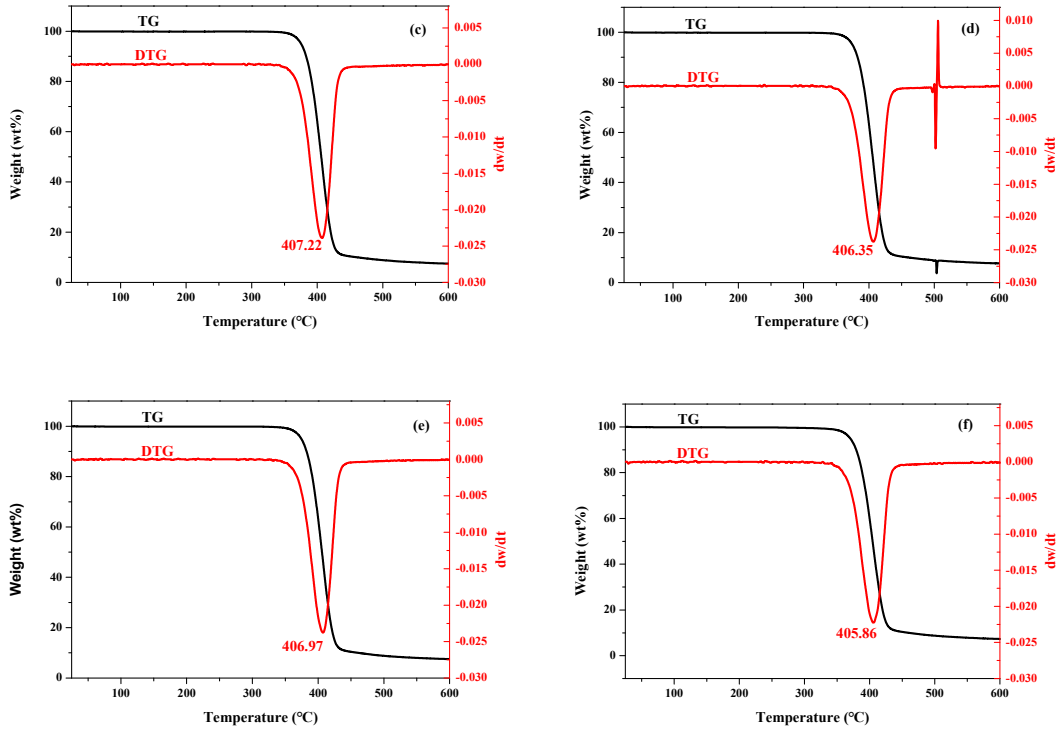
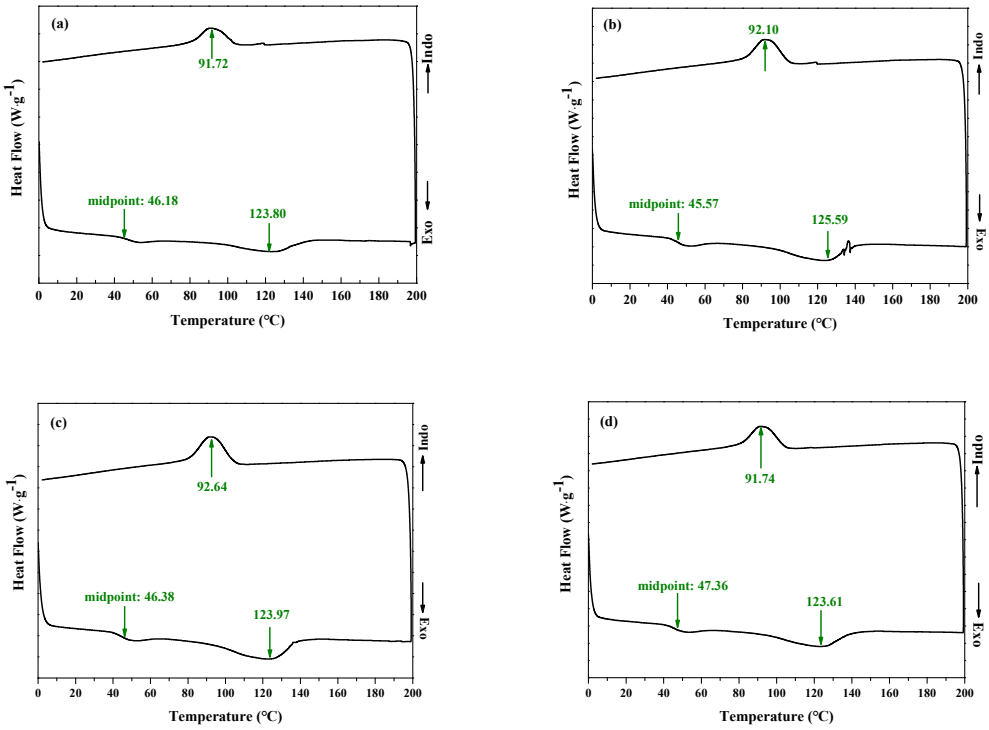


Figure 4. TG and DTG curves of samples fabricated with different Lignin/PBAT weight ratios: (a) 0.50%, (b) 0.75%, (c) 1.00%, (d) 1.50%, (e) 2.50% and (f) 5.00%.



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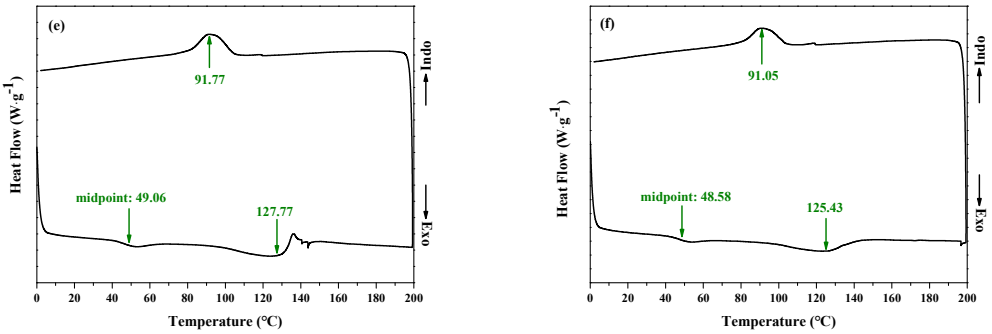

Figure 5. DSC cooling and heating curves of samples fabricated with different Lignin/PBAT weight ratios: (a) 0.50%, (b) 0.75%, (c) 1.00%, (d) 1.50%, (e) 2.50% and (f) 5.00%.

3.4. Water absorption properties

PBAT, a kind of biodegradable polyesters, is moisture sensitive. Water vapor barrier property is an important factor when it is applied in agricultural mulching film. The WVTR values of PLs films with different Lignin/PBAT weight ratios before and after Xenon lamp aging process are presented in Figure 6. As is presented in Figure 6, The WVTR values of all samples were below 500 g/m²·day. What's more, both the new neat PBAT plastic film and new Lignin/PBAT plastics films showed higher WVTR values than that after Xenon lamp aging process except LP-6. According to the above results, it can be concluded that the incorporation of lignin in PBAT matrixes is helpful to increase their barrier property, which may be due to the chemical and physical interactions between lignin and PBAT, although the detail mechanism was not yet clear, we will give more efforts on this area in the following research work in the near future.

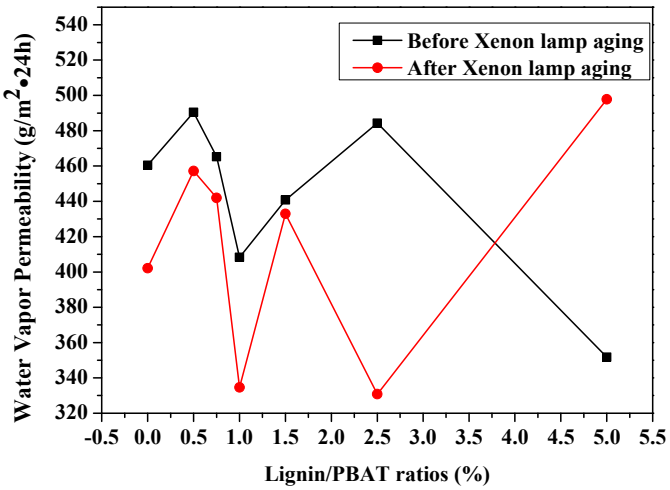

Figure 6. Water vapor permeability of samples fabricated with different Lignin/PBAT weight ratios before and after Xenon lamp aging.

3.5. Mechanical analysis

The mechanical properties of LPs films were also evaluated in the present work, and the results were presented in Figure 7 and summarized in Table 3. Figure 7a and b showed the tensile stress of PLs films with different Lignin/PBAT weight ratios before and after Xenon lamp aging process in vertical and horizontal, respectively. Both the new neat PBAT plastic film and new Lignin/PBAT plastics films showed higher vertical tensile strength than that after Xenon lamp aging process except

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LP-4, and all the LPs films showed higher horizontal tensile strength than that after Xenon lamp aging process. Among all the samples, LP-3 displayed the highest tensile strength of 28.4 Mpa in vertical and 19.8 Mpa in horizontal, respectively. Figure 7c and d showed the corresponding tensile strain of PLs films in vertical and horizontal, respectively. Among all the samples, LP-3 displayed the highest tensile strain of 485.7 % in vertical and 511.3 % in horizontal, respectively. Figure 7e and f showed the corresponding right-angled tearing load of PLs films, similarly, LP-3 displayed the highest right-angled tearing load of 2.6 N in vertical and 4.1 N in horizontal among all the samples, respectively. Based on the above results, one can conclude that 1.00 % is an ideal Lignin/PBAT weight ratio for increasing the mechanical properties of LPs films in the present work, which is similar with SEM results in Figure 3.

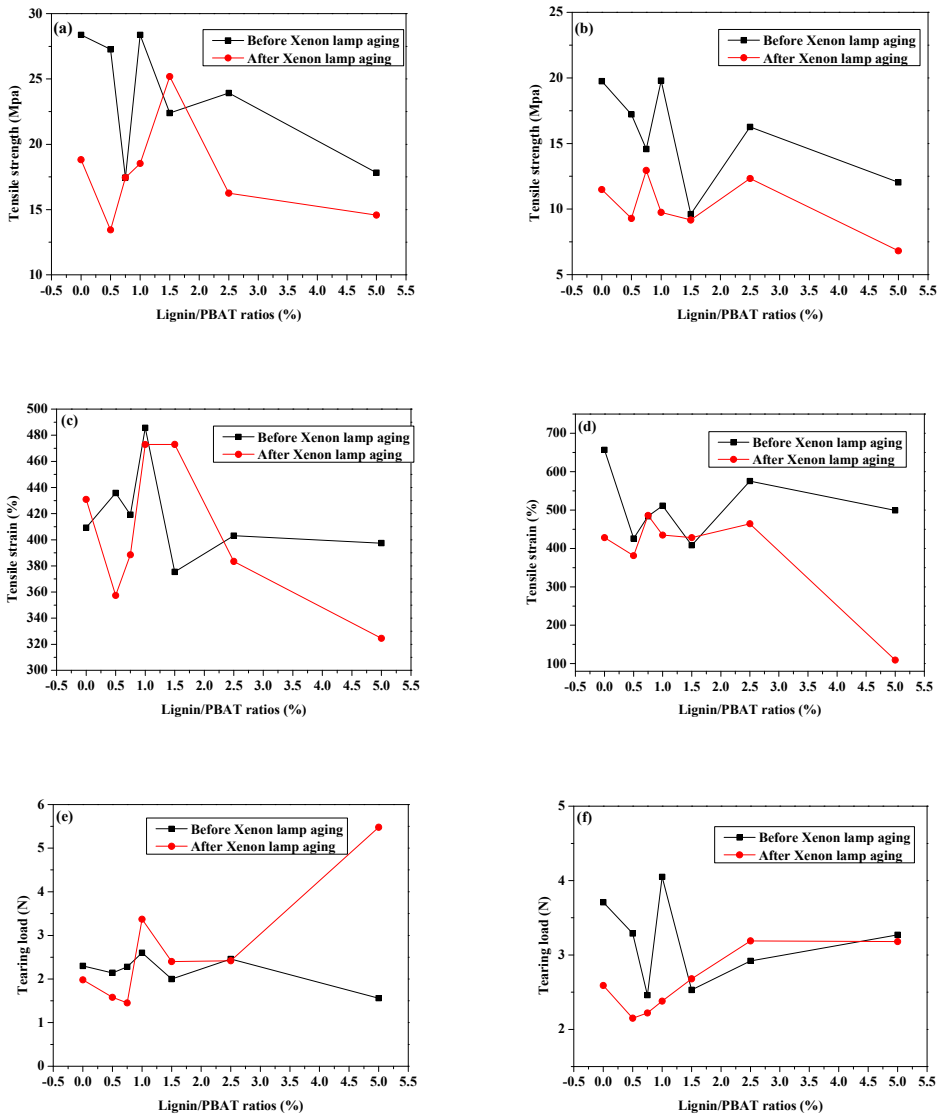

Figure 7. Tensile strength (a and b), tensile strain (a and b), and tearing load (e and f) of samples fabricated with different Lignin/PBAT weight ratios in vertical (a, c, e) and horizontal (b, d, f), respectively.

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Table. 3 Mechanical Results of PLs films

Sample	tensile strength (Mpa)				tensile strain (%)				right-angled tearing load (N)			
	vertical		horizontal		vertical		horizontal		vertical		horizontal	
	before	after	before	after	before	after	before	after	before	after	before	after
LP-0	28.4	18.8	19.8	11.5	409.2	430.9	656.8	428.4	2.3	1.9	3.7	2.6
LP-1	27.3	13.4	17.2	9.3	435.8	357.4	426.0	381.2	2.2	1.6	3.3	2.2
LP-2	17.5	17.5	14.6	13.0	419.2	388.5	484.0	486.1	2.3	1.5	2.5	2.2
LP-3	28.4	18.5	19.8	9.8	485.7	472.9	511.3	434.8	2.6	3.4	4.1	2.4
LP-4	22.4	25.2	9.6	9.2	375.4	473.0	408.2	428.4	2.0	2.4	2.5	2.7
LP-5	23.9	16.3	16.3	12.3	403.1	383.5	575.5	464.4	2.5	2.4	2.9	3.2
LP-6	17.8	14.6	12.0	6.8	397.4	324.6	499.1	109.3	1.6	5.5	3.3	3.2

4. Conclusions

In the present work, Lignin/PABT biodegradable plastic films were successfully fabricated with different Lignin/PABT weight ratios using twin screw and twin roll extruders. Successful incorporation of lignin in PBAT matrix was confirmed with the results from XRD, FTIR, and SEM. The incorporation of lignin in PBAT matrix was proved to possess increased thermal stability than the neat PBAT biodegradable plastic film. SEM results demonstrated the uniform distribution and dispersion of lignin throughout the PBAT matrix when Lignin/PBAT weight ratio reached 1.00 %, mechanical analysis demonstrated that the Lignin/PABT biodegradable plastic film had the highest tensile strength, tensile strain and right-angled tearing load values when Lignin/PBAT weight ratio reached 1.00 %, water vapor permeability testing results demonstrated that the Lignin/PABT biodegradable plastic film had the best barrier property even after Xenon lamp aging process among all the samples. This study provides a new window to obtain novel low-cost biodegradable plastic films with excellent mechanical and barrier property, as well as increases the potential of the Lignin/PABT biodegradable plastic film in packaging or agricultural applications.

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