Utilization of lignin extracted from Thai ago-waste as UV-blocking agent for BG-lignin/PLA composite films

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Abstract. The improving properties of poly(lactic acid), PLA, by utilizing natural resources attracted great intrigue to make such a green composite material that can be used as a commercial product in human life [1]. Lignin is one of biopolymer that can be used as bio-based filler and multifunctional bio-additive in a polymer composite. The most exciting properties of lignin that can be provided in a polymer composite is UV absorption and anti-oxidation [2]. In this current study, organosolv lignin extracted from sugarcane bagasse (BG-lignin) was utilized as multifunctional bio-additive in PLA for improving the UV absorption. The physicochemical and thermal properties of BG-lignin were determined using several techniques including SEM, GPC, quantitative ³¹P NMR, and DSC. BG-lignin at different loading contents (0.1, 0.2, 0.5, and 1 wt.%) was mixed with PLA via melt-extrusion. The attained compounds were converted to composite films via blown film extrusion. With the 0.5 wt.% loading content, the PLA composite films (0.5BG-lignin/PLA) absorbed almost all UV radiation which exhibits almost 70% blocking of UVB. The onset oxidation temperature of the PLA/0.5BG composite film increased by 34% as compared to that of the neat PLA film. Adding of BG-lignin enhanced tensile strength and Young’s modulus but did not favour to elongation at break.

1. Introduction

Ultraviolet (UV) radiation is high-energy-visible light with a wavelength from 200 to 400 nm and present in sunlight about 10% of total electromagnetic radiation; the long term of UV radiation exposure will cause photodegradation of polymeric materials [3]. Therefore, being an improvement of UV-shielding polymer composite is a desirable interest. Lignin is a polyphenolic compound and the second most abundant renewable biomaterial after cellulose. It is the main component of the plant cell wall to the cellulose and hemicellulose for mechanical support in their structure [4]. Lignin has an aromatic structure and many functional groups such as hydroxyls, methoxy, carbonyl, and carboxyl, etc. In the academic area, lignin has been recognized as the bio-multifunctional additive that can develop plastic composite properties, especially, antioxidant [2] and UV-shielding ability [5]. Sugarcane bagasse is one of the most agricultural waste in Thailand. It could also be one of the most promising resource for lignin
extraction. Utilization of lignin for high value-added applications is one of the great challenges, especially in the application for a biodegradable single-use plastics. Poly(lactic acid), PLA, has become an alternative choice to replacing petroleum-based plastics. However, poor UV absorption of PLA films might not be suitable for UV-sensitive products. Using of lignin as UV-absorber in PLA films sounds to be a promising choice to attain fully biodegradable PLA composite films.

The objective of this current work is to utilization of organosolv lignin extracted from sugarcane bagasse as multifunctional bio-additives for PLA films. BG-lignin/PLA composite films were prepared via ubiquitous melt-extrusion. Different contents of BG-lignin (0.1, 0.2, 0.5, and 1 wt.%) were incorporated into PLA. Properties of the obtained BG-lignin/PLA composite films including film color, mechanical properties, UV-blocking ability, and antioxidant activity were investigated in comparison with the neat PLA film.

2. Experimental
2.1. Materials
Organosolv sugarcane bagasse-lignin (BG-lignin) was kindly supported from the Biorefinery and Biological Technology Research Group (National Center for Genetic Engineering and Biotechnology (BIOTEC)). PLA (4043D) used in this study is a product of NatureWork LLC. Its number-average molecular weight ($M_n$) is 160,000 g/mol containing 94% L-lactic acid content and the melt flow rate is 6.0 g/10 minutes at 210°C.

2.2. Characterizations of BG-lignin
The morphology of BG-lignin was observed by field-emission scanning electron microscope (FE-SEM, model SU5000, Hitachi, Japan). The molecular weight distribution was thoroughly analyzed by gel permeation chromatography (GPC, Waters c2695 separation module, USA). Quantitative phosphorus-31 nuclear magnetic resonance spectroscopy, $^{31}$P NMR, (AV-500 Bruker Biospin, USA) were used for determining chemical characteristic. Protocol of $^{31}$P NMR solution preparation was followed steps reported in Nature protocol [7]. Glass transition temperature ($T_g$) of the BG-lignin was measured in a temperature scan at heating rate of 10°C/minute using differential scanning calorimetry (DSC-1, Mettler Toledo, Switzerland).

2.3. Preparation of BG-lignin/PLA composite films
Pre-dried PLA pellets were premixed with the 2 wt.% of BG-lignin powders prior to load to a feeder of the single-screw extruder (Thermo-Haake Rheomix OS, Germany) equipped with 3-mm rod die. Temperature profile was set as 170, 180, 185°C and die temperature was 180°C. Rotating speed was 45 rpm. The extrudates were extruded through a water bath and was then pelletized into 3-mm pellets. Attained 2 wt.% BG-lignin/PLA pellets were diluted to the desired loading contents (0.1, 0.2, 0.5, and 1 wt.%) by adding of pristine PLA. BG-lignin/PLA composite films were manufactured using the same single-screw extruder equipped with blown film (34-mm inner diameter and 1-mm die gap). Screw speed was kept at 60 rpm to fabricate film with the width and thickness of 13 cm and 35 µm, respectively.

2.4. Characterizations of BG-lignin/PLA composite films
Properties of the obtained neat PLA film and its composite films with BG-lignin/PLA were conducted. Color of the films was determined by datacolor spectrophotometer (datacolor 650, Pakistan). Mechanical properties including tensile strength, Young’s modulus and elongation at break were performed using a universal testing machine (Instron 4502 series, USA) by following ASTM D882 at the cross-head speed of 400 mm/10 minute. Light transmittance of all the films was measured using a UV spectrometer (UV-3600Plus, Japan) ranges from 200-800 nm. The oxidative induction temperature (OIT$_{temp}$) was measured by using DSC under oxygen atmosphere, a DSC protocol as described in literature [8].
3. Results and discussion

SEM images of BG-lignin are presented in Figure 1. BG-lignin particles seem to be constructed by the accumulation of small lignin particles (see Figure 1a). The surface and shape of BG-lignin particles were evaluated at high magnification of 20,000x (see Figure 1b). BG-lignin were irregular in their shape, which varied diameter from sub-micrometer to a few microns. Molecular weight (Mₘ) and polydispersity index (PDI) of BG-lignin were evaluated by the GPC technique using the polystyrene as a standard polymer. Mₘ and the PDI of BG-lignin are 1,638 g/mol and 1.62, respectively. The phenolic hydroxy group was considered as an essential functional group due to the UV-absorption of its active group, which was investigated by ³¹P NMR, BG-lignin exhibits high content of phenolic to aliphatic hydroxyl groups, which is 1.82 mmol/g. The content of the phenolic hydroxyl group could be correlated to the active functions of lignin including UV-shielding and antioxidant [2]. Tₘ of BG-lignin was detected at 135°C.

![SEM images of BG-lignin particles at (a) 2,000x and (b) 20,000x.](image)

Clear neat PLA film and brownish BG-lignin/PLA composite films were observed. Chromatic coordinate was employed to determine the effect of BG-lignin on PLA film color and transparency. The neat PLA film exhibited L*, a*, b* at 90.41, -0.52, and 11.51, respectively. All these values were used as the reference for testing on the BG-lignin/PLA composite films containing different contents of BG-lignin. The neat PLA film exhibited the highest L* value, while that of the BG-lignin/PLA composite films decreased with an increase of the BG-lignin contents. Color change represented in ΔL, Δa, Δb was calculated based on the neat PLA film. At the highest loading contents of 1.0 wt.% (1.0BG-lignin/PLA), the values of ΔL, Δa, Δb became -4.69, 1.48 and 7.50, respectively. This could be implied that the composite film became darker and the color turned to brownish.

Mechanical properties of the neat PLA film and its BG-lignin composite film were measured and compile in Table 1. Tensile strength and Young’s modulus of the BG-lignin/PLA composite films increased as compared to the values of the neat PLA film. This increasing trend reveal to the high stiffness aromatic structure of lignin, and it possible due to the good interfacial adhesion between BG-lignin and PLA matrix [5]. The highest tensile strength at 65.0±2.0 MPa was found when the BG-lignin was 0.1 wt.%. The highest Young’s modulus at 2.0±0.3 GPa was detected on the composite film containing 0.2 wt.% BG-lignin. Further increasing of BG-lignin, tensile strength and Young’s modulus were decreased.
Therefore, the neat PLA satisfied lignin achieve sugarcane bagasse in 4.

An antioxidant activity is considered as the results noticed this indicates poor UV transmittance wavelength UV as shown this shows an improvement of UV absorption. It is due to the phenolic hydroxyl groups of the BG-lignin. Increasing of BG-lignin effected directly to increase the UV absorption, while the transparency was satisfied [2]. However, loading content of BG-lignin resulted in film color as more brownish was noticed. Composite film with 0.5 wt.% BG-lignin (0.5BG-lignin/PLA) is expected as a suitable film which exhibits almost 70% blocking of UVB (315-280 nm).

As the results shown in Table 1, antioxidant activity for the neat PLA and its composite films was considered using OIT\textsubscript{temp}. The OIT\textsubscript{temp} of each film was evaluated on the onset temperature of exothermal characteristic. An antioxidant activity (%) was calculated based on the neat PLA film. Additional BG-lignin can enhance significantly on the OIT\textsubscript{temp} and the anti-oxidation activity. This can be explained by the phenolic hydroxy groups in lignin acting as free radical scavenger that can promote anti-oxidation activity of the composite films.

| Samples               | Tensile strength at break (MPa) | Young’s modulus (GPa) | Elongation at break (%) | OIT\textsubscript{temp} (ºC) | Anti-oxidation ability (%) |
|-----------------------|---------------------------------|-----------------------|--------------------------|-----------------------------|-----------------------------|
| Neat PLA              | 54.5±4.5                        | 1.3±0.4               | 5.0±0.3                  | 215                         | 0                           |
| 0.1BG-lignin/PLA      | 65.0±2.0                        | 1.7±0.1               | 4.8±0.6                  | 247                         | 15                          |
| 0.2BG-lignin/PLA      | 63.9±2.0                        | 2.0±0.3               | 4.4±0.1                  | 271                         | 25                          |
| 0.5BG-lignin/PLA      | 62.7±2.2                        | 1.7±0.1               | 4.5±0.2                  | 289                         | 34                          |
| 1.0BG-lignin/PLA      | 56.6±1.4                        | 1.5±0.3               | 5.0±0.6                  | 299                         | 38                          |

UV-visible spectra of the neat PLA and BG-lignin/PLA composite films were plotted as a function of wavelength as shown in Figure 2. The neat PLA film exhibits a nearly transparent character at 90% transmittance in visible region (400-800 nm). High 90% transmittance was still detected in UV region, this indicates poor UV absorption of PLA film. Adding small amount of BG-lignin, the composite films show an improvement of UV absorption. It is due to the phenolic hydroxyl groups of the BG-lignin.

4. Conclusions

In this current work, we have demonstrated the utilization of lignin extracted from Thai ago-waste, sugarcane bagasse, as multifunctional bio-additive in PLA film. BG-lignin/PLA composite films achieve excellent in UV-shielding ability and anti-oxidation. The composite film with 0.5 wt.% BG-lignin (0.5BG-lignin/PLA) exhibits almost 70% blocking of UVB while film transparency and color are satisfied. The OIT\textsubscript{temp} of the 0.5BG-lignin/PLA film become to 289ºC which is 74ºC higher than that of the neat PLA. Mechanical properties of the composite films were kept in the acceptable criteria. Therefore, BG-lignin can be an alternative bio-additive providing multifunctional for PLA films.
Acknowledgement

Authors appreciate the funding support from MTEC, NSTDA, Thailand (project no.2052415). The grant from Program Management Unit Competitiveness (PMUC) “Lignin valorization for production of biochemicals and biomaterials in biorefinery”.

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