Science and Innovation
of Advanced Materials

The Materials Research
Society of Thailand

Research Article

In-situ Synthesis of Lignin/ZnO Composites from Black Liquor for UV-Resistant and Antioxidant Agents in Bioplastics

Kannika Pleejaroen[1], Doungporn Yiamsawas[2,*], Pakorn Opaprakasit[1,*]

[1] School of Integrate Science and Innovation, Sirindhorn International Institute of Technology (SIIT), Thammasat University, Pathum Thani 12121, Thailand
[2] National Nanotechnology Center, National Science and Technology Development Agency, Pathum Thani 12120, Thailand

* Corresponding author e-mail: pakorn@siit.tu.ac.th, doungporn@nanotec.or.th

Received: *May 17th, 2023* | ***Revised:*** *June 15th, 2023* | ***Accepted:*** *June 15th, 2023*

Abstract: An *in-situ* method has been developed to prepare lignin/ZnO composites from soda black liquor of oil palm empty fruit bunches. This method offers a new route to reduce the preparation steps and waste associated with the process. The effects of the lignin/zinc ratio on structures and properties of the obtained lignin/ZnO composites were investigated. The composites were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FE-SEM) with energy dispersive X-ray spectroscopy (EDX) analysis, Fourier transforms infrared (FTIR), and UV-Visible spectroscopy. The obtained lignin/ZnO composites were then employed as an additive in polylactic acid (PLA) films by solvent casting to enhance their UV-resistant and antioxidant properties. The PLA-based bio-composites exhibited excellent UV-resistant and antioxidant properties. The prepared lignin/ZnO composites, derived from the developed facile and low-cost process, eco-friendly, and sustainable methods may find useful applications, especially smart packaging and cosmetic applications.

Keywords: Lignin, Zinc oxide, Antioxidant, Ultraviolet-resistant, Bioplastic composites, PLA

1. Introduction

Biodegradable polymers have attracted tremendous scientific and industrial interest because of their environmentally and economically advantageous compostable properties. Polylactic acid (PLA) is a bio-based material used in various applications due to its excellent mechanical properties, biodegradability, and biocompatibility. However, the material has some disadvantages, especially low UV-resistant, and antioxidant properties, which limits its use in specific applications [1]. Zinc oxide (ZnO) has been widely employed in UV photodetectors due to its excellent electrical properties, simplicity of preparation, and low toxicity. In addition, ZnO is used as an additive for polymeric materials to enhance the polymer's antioxidant and UV-resistant activity [2,3]. However, ZnO has poor compatibility with polymers [4]. To overcome this problem, various compatibilizers are introduced. In this aspect, lignin can enhance not only compatibility with the polymeric matrix but also improve UV-resistant and antioxidant properties [4-6]. There are several techniques for preparing ZnO. A hydrothermal process is the most interesting technique due to its low cost and environmentally friendly approach. This method requires a precursor or template that is a substance to give hydroxyl ions (OH-), along with a mixture of zinc salt and an alkaline solution, to form ZnO at high temperatures [2,7].

---

* Presented at The 4th Materials Research Society of Thailand International Conference

Lignin is a complex three-dimensional structure in lignocellulosic materials. It is an extremely branching phenolic polymer consisting of three main monomers with controlled amounts of methoxy groups placed on aromatic rings (p-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units). Lignin can be used as a precursor to form ZnO due to its high hydroxyl content [6,8-10]. A significant amount of industrial lignin is obtained from black liquor byproducts of the pulping industries in the pretreatment process. Lignin is an attractive bioresource material related to its multi-functionality, which includes antioxidants and ultraviolet (UV)-absorbing properties. Lignin recovery from alkaline black liquor by CO_2 acidification is highly beneficial for resources and environmental sustainability because it is a valuable green process [8,9,11-14]. Some previous research [4,5,15-17] applied commercial lignin or recovered lignin as a template for lignin/ZnO composite preparation to improve the antioxidant and UV-resistant properties of polymers.

This research has developed an in-situ method to prepare lignin/ZnO composites from soda black liquor of oil palm empty fruit bunch. Lignin generates hydroxyl ions (OH-) in an alkaline condition, and later CO_2 acidification is applied to precipitate the lignin/ZnO composite. The resulting lignin/ZnO composites are then employed as an additive in polylactic acid (PLA) films by solvent casting. The materials have a high potential for antioxidant and UV-resistant composites.

2. Methodology

2.1 Materials

The black liquor in this research was obtained from a cellulose extraction process of oil palm empty fruit bunch with alkaline pretreatment (4% NaOH). Zinc acetate dihydrate and chloroform were purchased from Carlo Erba. Carbon dioxide (CO_2, 99.5%) was purchased from Praxair (Thailand). Polylactic acid (PLA-4043D) was obtained from NatureWorks.

2.2 Methods

Preparation of lignin/ZnO composites

Zinc acetate dihydrate was dissolved in 300 mL oil palm empty fruit bunch soda black liquor in a Teflon vessel with a magnetic stirrer at 75 °C for 2 h. The Teflon vessel was then installed in a semi-batch reactor with a temperature of 120 °C for 24 h. After that, 5 bars of carbon dioxide (CO_2) were fed into the reactor for 30 min to precipitate lignin/ZnO products. The suspension of composites was centrifuged at 9,500 rpm for 15 min and washed with deionized water to remove impurities. The products were dried in a vacuum oven at 40 °C overnight and aged in an oven at 200 °C for 24 h to obtain a final product. The mass ratio of lignin to zinc was varied at 1:1(1LZ), 1:3(3LZ), and 1:5(5LZ) to investigate the effect of the feed ratio on the formation of the lignin/zinc oxide composites.

Preparation of lignin/zinc oxide/polylactic acid composites

A solution casting was applied to prepare the PLA-based composites. PLA (1.0 g) was dissolved in 10 mL of chloroform ($CHCl_3$) and stirred at room temperature for 2 h. At the same time, the lignin/ZnO composite (0.1 g) was dispersed in $CHCl_3$ using stepped microtip sonication (2 mm) in an ice bath with an amplitude of 30% for 2 min. Then the polymer solution and the lignin/ZnO composite suspension were stirred for 1 h at room temperature. The mixture was then cast on a glass Petri dish and dried at room temperature for 72 h.

Characterization of lignin/ZnO composites

Hunter Lab spectrophotometer (MiniScan EZ) analyzed the composite sample's color with CIE L*a*b* color space. The X-ray diffraction (XRD) patterns of samples were recorded on a D8 Advance instrument (Bruker-Axis, Ltd.) using a Cu tube with 1.5418 Å at 40 kV and 40 mA. The samples were scanned from 20° to 80° (2θ) at a rate of 4°/min. The morphology and composition of the samples were studied through a field emission scanning electron microscope (FE-SEM) with energy dispersive X-ray spectroscopy (EDX) analysis (Versa 3D) at 5 kV. The chemical structures and functional groups of the samples were analyzed by Fourier transform infrared (FTIR) spectroscopy on a Thermo

Scientific, Nicolet iS50, in an attenuated total reflection (ATR) mode. The spectra were recorded in a range of 4,000–400 cm^{-1}, with 32 scans, at a resolution of 4 cm^{-1}.

Ultraviolet-resistant property of PLA-based composite films

A UV–Visible spectrophotometer (LABDA 650, PerkinElmer) was applied to examine the UV transmittance of the film samples from 200-800 nm using a film holder.

Antioxidant property of PLA-based composite films

A 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical scavenging assay was used to determine the antioxidant properties of neat PLA and the PLA composite films [5]. Small pieces of the film (0.1 g) were shaken vigorously in 2 mL of absolute methanol and maintained for 24 h. After that, 1 mL of the methanol solution was taken to mix with 1 mL of 0.2 mM DPPH. The solution was kept at room temperature in the dark for 60 min. The absorbance of the solution was measured at 517 nm on a UV-Visible spectrophotometer (GENESYS 180). A mixed solution of methanol and DPPH from neat PLA film is represented as a control. The DPPH radical scavenging activity (RSA) was evaluated according to Equation 1.

$$\mathrm{RSA}(\%) = \frac{\mathrm{A_{control}} - \mathrm{A_{sample}}}{\mathrm{A_{control}}} \times 100 \tag{1}$$

Where $\mathbf{A_{sample}}$ is the absorbance of the sample, and $\mathbf{A_{control}}$ is the absorbance of the control.

3. Results and discussion

The physical properties of the prepared lignin/ZnO composites

The visual images of lignin and lignin/ZnO composites are compared in Figure 1. The composite's color was slightly brown. This was whitened as the zinc content increased. The visual color of obtained products was also investigated by HunterLab spectrophotometer (MiniScan EZ) with CIE L*a*b* color space. Table 1 shows the darkness to brightness (L: 0-100), greenness to redness (-a* to +a*), and blueness to yellowness (-b* to +b*) of the obtained products. The L* value refers to brightness. According to the visual images and CIE L*a*b* color space results, it is likely that the formation of ZnO may also increase when zinc content increases. This can be attributed to the higher availability of zinc atoms for reactions with oxygen, enhancing the probability of zinc atoms encountering oxygen and subsequently forming ZnO. Therefore, the higher the zinc content, the greater the possibility of ZnO formation through the reaction between zinc and oxygen.

Figure 1 Visual images of lignin and lignin/ZnO composites obtained at different lignin-to-zinc ratios.

Table 1 The color of lignin and lignin/ZnO composites using a color spectrophotometer with CIE L*a*b* color space

Sample	Lignin-to-zinc ratio	L*	a*	b*
Lignin		75.58	2.94	18.19
1LZ	1:1	71.18	6.46	17.02
3LZ	1:3	80.76	4.82	15.02
5LZ	1:5	86.35	2.63	9.21

Effect of lignin/zinc ratio on structures of the prepared lignin/ZnO composites

The crystal structure of the obtained products was investigated using XRD, as shown in Figure 2. The diffraction peaks closely correlate with those of wurtzite hexagonal ZnO. (ICDD 00-065-0726). The diffraction peaks at 2θ = 31.8, 34.4, 36.3, 47.5, 56.6, 62.9, 66.5, 68.0, and 69.1° can be indexed to (100), (002), (101), (102), (110), (103), (200), (112), and (201) crystal planes of ZnO, respectively. The intensity of the (101) peak is the strongest, while the (002) peak is stronger than that of (100), indicating that ZnO has strong preferential growth along the c-axial [16]. The intensity of the peaks increased when the content of zinc salt increased, reflecting higher content of ZnO.

Moreover, the Scherrer formula (Equation 2) was used to estimate the crystallite sizes (D) from the high-intensity diffraction peaks of (101) planes, as summarized in Table 2. The crystallite size of the prepared lignin/ZnO composites is smaller than 10 nm.

$$D = \frac{\kappa\lambda}{\beta\cos\theta} \qquad (2)$$

Where κ is the shape factor (0.9), λ is X-ray wavelength (0.15405 nm), θ is Bragg's angle (radian), and β is the full width at half-maximum height (FWHM).

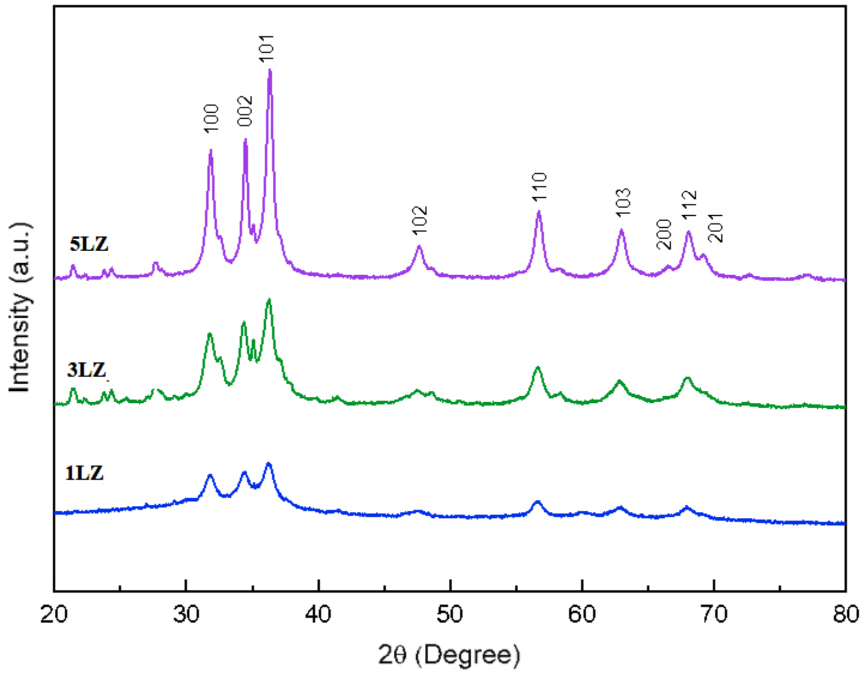


Figure 2 XRD patterns of the lignin/ZnO composites with different lignin to zinc ratios.

Table 2 The crystallite size (nm) of lignin/zinc oxide composites

Sample	Lignin-to-zinc ratio	*hkl*	2θ (degree)	FWHM (degree)	Crystallite size (nm)
1LZ	1:1	(101)	36.2	1.1	7.7
3LZ	1:3	(101)	36.3	1.8	4.8
5LZ	1:5	(101)	36.3	0.9	9.9

The morphology of the obtained products was analyzed by FE-SEM, as shown in Figure 3. All three samples derived from different lignin-to-zinc ratios exhibited non-uniform shapes and agglomerated. An EDX analysis was used to confirm the composition of the obtained products, as demonstrated in Figure 4.

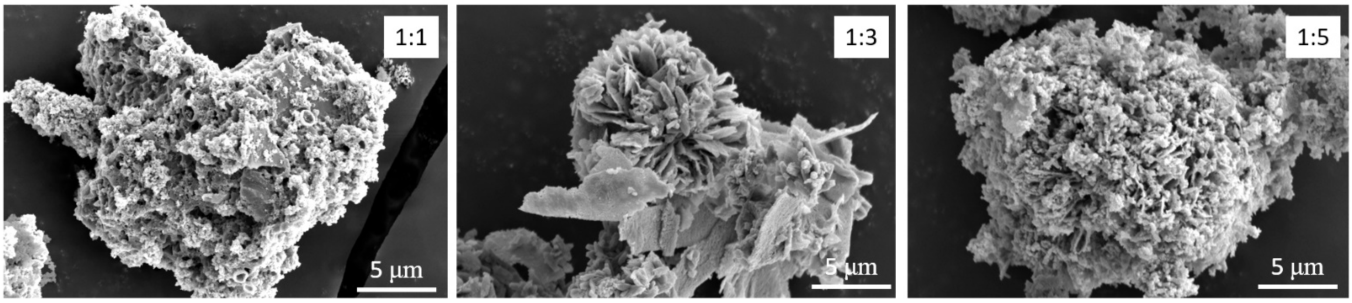
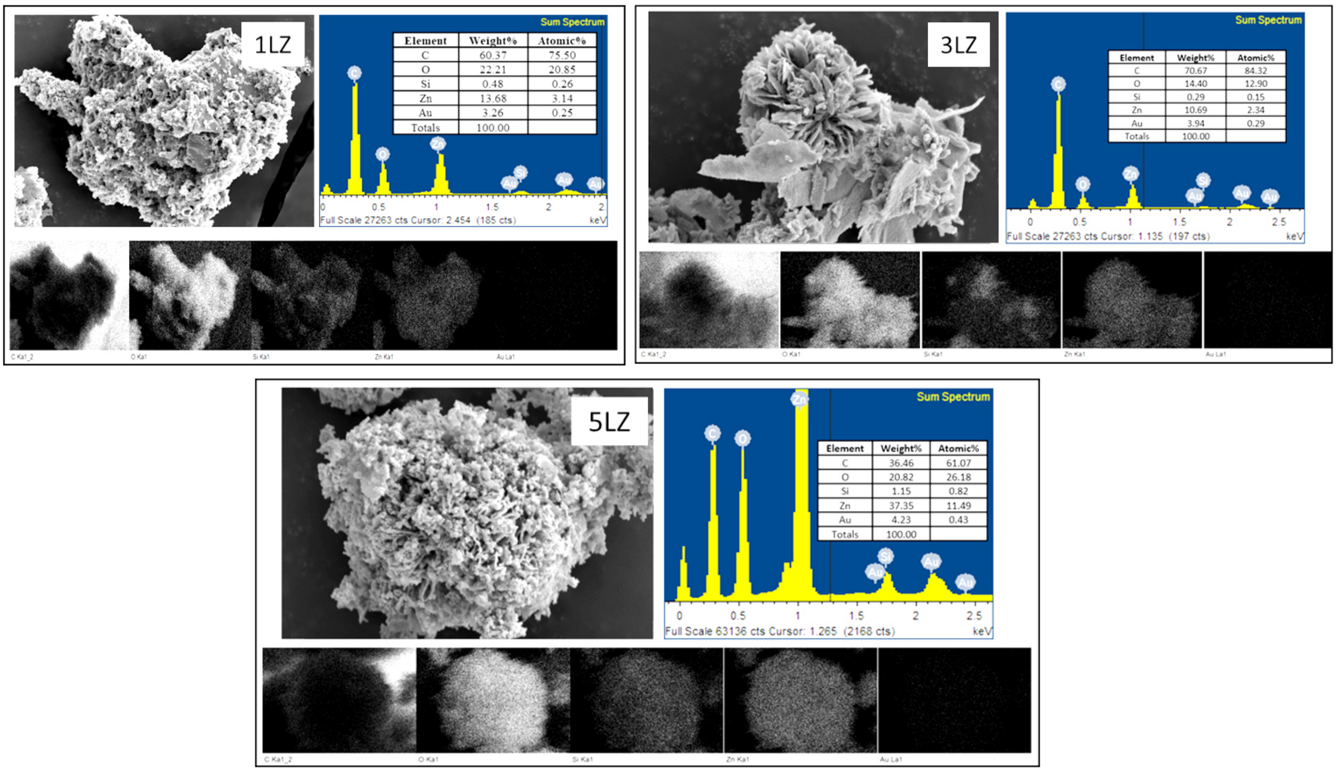


Figure 3 SEM images of the obtained products with lignin to zinc ratio of 1LZ (1:1), 3LZ (1:3), and 5LZ (1:5).



1LZ

Element	Weight%	Atomic%
C	60.37	75.50
O	22.21	20.85
Si	0.48	0.26
Zn	13.68	3.14
Au	3.26	0.25
Totals	100.00	

3LZ

Element	Weight%	Atomic%
C	70.67	84.32
O	14.40	12.90
Si	0.29	0.15
Zn	10.69	2.34
Au	3.94	0.29
Totals	100.00	

5LZ

Element	Weight%	Atomic%
C	36.46	61.07
O	20.82	26.18
Si	1.15	0.82
Zn	37.35	11.49
Au	4.23	0.43
Totals	100.00	

Figure 4 EDX profiles and element compositions of the obtained products with lignin-to-zinc ratios of 1LZ (1:1), 3LZ (1:3), and 5LZ (1:5).

Zinc (Zn), oxygen (O), and carbon (C) are major elements in the lignin/ZnO products. The carbon (C) element is attributed to the lignin structure. Zn, O, and C elements were distributed throughout the composite, confirming the formation of lignin/ZnO composites. However, Si was also observed in the obtained products. This is likely from the impurity in the black liquor derived from oil palm empty fruit bunches [18].

The chemical structures and functional groups of the lignin/ZnO products were analyzed by FTIR spectroscopy, as shown in Figure 5. A broad band at 400-600 cm^{-1} indicates the stretching vibration of Zn-O-Zn and O-Zn-O. Lignin is a complex three-dimensional structure composed of three main monomers with different numbers of methoxy groups substituted on aromatic rings and linked by C-O-C ethers or C-C bonds. A broad band at around 3300-3400 cm^{-1} is related to the -OH stretching mode, associated with phenolic and aliphatic -OH groups in the lignin structure. The absorption band at 1640, 1575, 970, 880, and 778 cm^{-1} are assigned to aromatic skeletal, aromatic ring vibration, =CH out of plane deformation modes (C–H wagging of C=C of coniferyl aldehyde and alcohol), C–H out-of-plane deformation (one H, aromatic ring), and ring bend of G-rings, respectively [4,17,19,20]. The band at 970 cm^{-1} was weaker when the lignin-to-zinc ratio decreased. By increasing the zinc ions in the system, there is a potential for them to interact with the hydroxyl groups in the lignin structure. This interaction can affect the vibrational characteristics of the lignin, leading to changes in the C-H out-of-plane deformation. The interaction between zinc and the hydroxyl groups may restrict the movement of the hydrogen atom, resulting in a reduction in the observed deformation. This confirms that the formation of ZnO increases when zinc salt content increases.

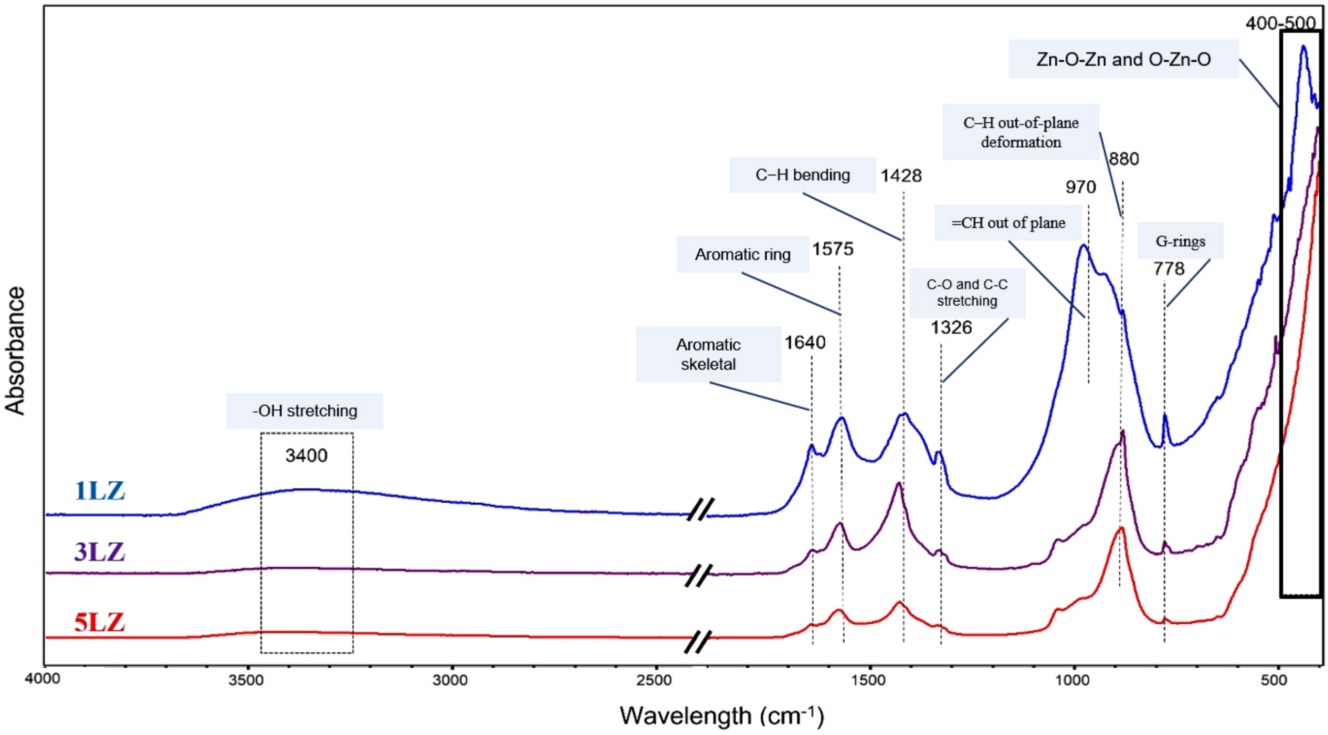


Figure 5 FTIR spectra of the obtained composite products with lignin-to-zinc ratios of 1LZ (1:1), 3LZ (1:3), and 5LZ (1:5).

UV-resistant properties of lignin/ZnO/PLA composites

The visual images (Figure 6(a)) and optical microscope images (Figure 6(b-d)) of lignin/ZnO/PLA composite films at 20x magnification are compared. Lignin/ZnO composite was dispersed in the PLA matrix, reflected by dark particle domains. The films were opaque when the content of zinc oxide in composites increased. UV-Vis spectra of the resulting composite films are shown in Figure 6(e). The transmittance of all films in the UV region (230-400 nm) showed a considerable drop from 60-70% to lower than 10% compared to neat PLA, reflecting the high UV-resistant efficiency of the lignin/ZnO composites. ZnO is a wide-bandgap material known for its exceptional UV-resistant properties. PLA-5LZ film had the best UV protection effect. However, a slight decrease in the transmittance in the visible region (400-800 nm) was also observed in all samples, likely due to the absorption from the lignin structures, due to the presence of phenolic groups in its structure. Adding the lignin/ZnO composite in the PLA matrix enhances the UV-protection effect of the PLA-based composite films, providing high anti-UV aging performance [4,6,21].

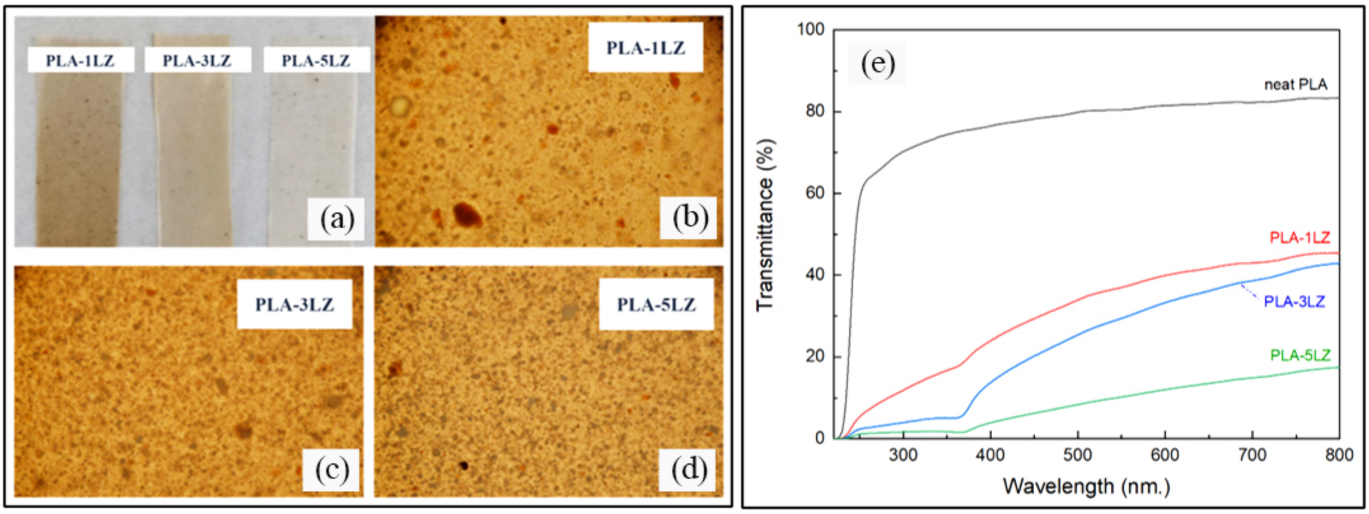


Figure 6 Visual images (a), optical microscope images (b-d) of lignin/ZnO/PLA composites film in 20x magnification and UV light transmittance curves (e) of lignin/ZnO/PLA composite films.

Antioxidant properties of lignin/ZnO/PLA composites

The antioxidant properties of the PLA-based composite films are evaluated as radical scavenging activity (RSA), as summarized in Table 3. DPPH is a stable radical in methanol that exhibits deep violet solution and absorbs wavelengths of 517 nm. Lignin can trap free radicals by forming phenoxy radicals, as demonstrated by the color change of the DPPH solution to plate yellow. In addition, ZnO exhibits antioxidant activity by transferring free electrons from the oxygen atoms to free radicals at the nitrogen atom of DPPH molecules [5,22]. The changing color of the DPPH solution for lignin/ZnO/PLA composites compared with neat PLA is presented in Figure 7(a). UV-Vis absorbance of the corresponding solutions at 517 nm is compared in Figure 7b. The content of lignin in the composites positively influences the RSA response of the composite films. Although both lignin and ZnO exhibited antioxidant properties, the results indicated that the composite films with high lignin contents had higher antioxidant activity than those with higher ZnO contents.

Table 3 DPPH radical scavenging activity of lignin/ZnO/PLA composites films

Sample	Lignin-to-zinc ratio	Radical scavenging activity, RSA (%)
Neat PLA	-	-
PLA-1LZ	1:1	24.60
PLA-3LZ	1:3	11.07
PLA-5LZ	1:5	4.37

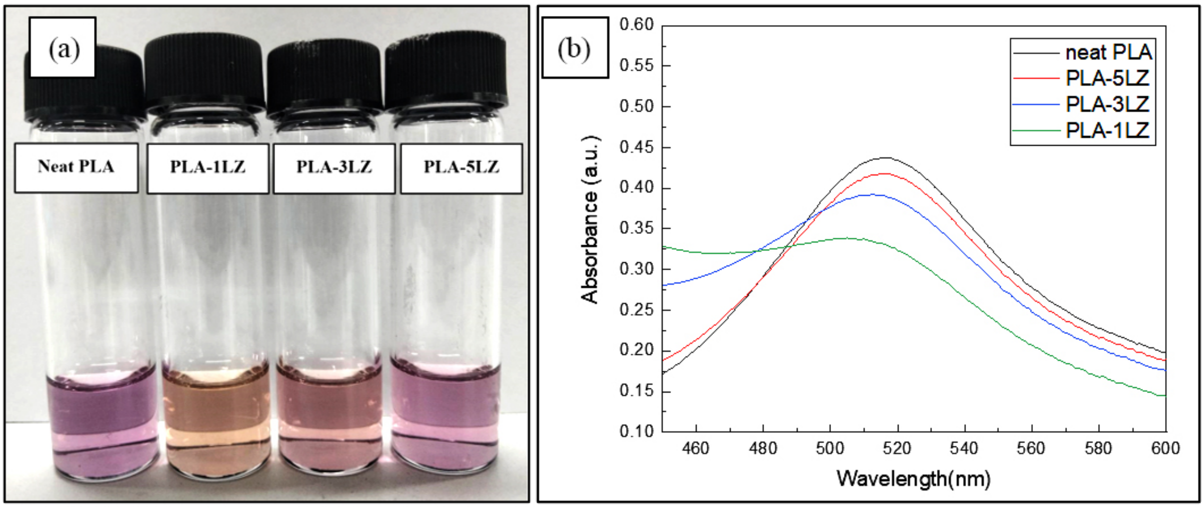


Figure 7 Measurements of antioxidant activity by monitoring the color change of DPPH solutions for lignin/ZnO/PLA composites compared with neat PLA (a) and UV-Vis spectra at 517 nm (b).

4. Conclusion

Lignin/ZnO composite was successfully synthesized by an *in-situ* hydrothermal method. Zinc salt was added directly into oil palm empty fruit bunch soda black liquor, which contains lignin as a precursor. The effect of the lignin-to-zinc ratio on the structures and properties of the lignin/ZnO composites was investigated. The increase of zinc salt content resulted in higher content of ZnO in the composites, reflected by the whitened color of the resulting composites. This is also confirmed by XRD and FTIR results. This technique produced non-uniform and agglomerated lignin/ZnO composites. The lignin/ZnO composite was then used as an additive to improve UV resistance and antioxidant characteristics of PLA biopolymer. The transmittance of the composite films in the UV region decreased considerably compared to neat PLA film. Increasing ZnO content in the polymer composites improved the UV protection effect, while increasing lignin content led to higher values of antioxidant activity. The sample of PLA-3LZ exhibits optimized enhancement of UV-resistance and antioxidant properties, effectively improving both desirable characteristics. The preparation process of lignin/ZnO composite in this study is an efficient approach that extends the range of potential applications for lignin, a renewable and abundant resource derived from black liquor. The resulting lignin/ZnO composites have a high potential for various applications, particularly in smart packaging and cosmetics.

Acknowledgment

This work was supported by the Functional Advanced Materials Engineering Research Center (CoE FAME), Thammasat University, and the Nano Agricultural Chemistry and Processing Research Team, Unit Lab of the National Nanotechnology Center (NANOTEC), National Science and Technology Development Agency (NSTDA). Ms. Kannika Pleejaroen thanks the TAIST-Tokyo Tech scholarship, National Science and Technology Development Agency (NSTDA), and Sirindhorn International Institute of Technology (SIIT), Thammasat University.

References

[1] F. Wu, M. Misra, A. K. Mohanty, Challenges and new opportunities on barrier performance of biodegradable polymers for sustainable packaging, *Prog. Polym. Sci.* **117** (2021) 101395.

[2] A. Kołodziejczak-Radzimska, T. Jesionowski, Zinc oxide–from synthesis to application: A review, *Materials* **7** (2014) 2833-2881.

[3] B. Kumar, K. Smita, L. Cumbal, A. Debut, Green approach for fabrication and applications of zinc oxide nanoparticles, *Bioinorg. Chem. Appl.* **2014** (2014) 523869.

[4] H. Wang, W. Lin, X. Qiu, F. Fu, R. Zhong, W. Liu, D. Yang, In situ synthesis of flowerlike lignin/ZnO composite with excellent UV-absorption properties and its application in polyurethane, *ACS Sustain. Chem. Eng.* **6** (2018) 3696-3705.

[5] E. Lizundia, I. Armentano, F. Luzi, F. Bertoglio, E. Restivo, L. Visai, L. Torre, D. Puglia, Synergic effect of nanolignin and metal oxide nanoparticles into poly(l-lactide) bionanocomposites: Material properties, antioxidant activity, and antibacterial performance, *ACS Appl. Bio Mater.* **3** (2020) 5263-5274.

[6] S. Imlimthan, P. Figueiredo, H. A. Santos, M. Sarparanta, Chapter 1 - Introduction to lignocellulosic materials, In Lignin-Based Materials for Biomedical Applications, Elsevier (2021).

[7] D. E. Kwabena, W. B. Siong, S. F. Chin, Y. Kuan, Kok, M. F. Maligan, Zinc oxide nanoparticles synthesis methods and its effect on morphology: A review, *Biointerface Res. Appl. Chem.* **12** (2021) 4261-4292.

[8] X. Erdocia, F. Hernández-Ramos, A. Morales, N. Izaguirre, P. L. de Hoyos-Martínez, J. Labidi, Chapter 3 - Lignin extraction and isolation methods, In Lignin-Based Materials for Biomedical Applications, Elsevier (2021).

[9] S. Hidayati, W. Satyajaya, A. Fudholi, Lignin isolation from black liquor from oil palm empty fruit bunch using acid, *J. Mater. Res. Technol.* **9** (2020) 11382-11391.

[10] M. Behr, M. E. Jaziri, M. Baucher, Chapter 2 - Lignin: An innovative, complex, and highly flexible plant material/ component, In Lignin-Based Materials for Biomedical Applications, Elsevier (2021).

[11] R. C. A. Ela, L. Spahn, N. Safaie, R. C. Ferrier Jr., R. G. Ong, Understanding the effect of precipitation process variables on hardwood lignin characteristics and recovery from black liquor, *ACS Sustainable Chem. Eng.* **8** (2020) 13997-14005.

[12] M. Nagy, M. Kosa, H. Theliander, A. J. Ragauskas, Characterization of CO_2 precipitated Kraft lignin to promote its utilization, *Green Chem.* **12** (2010) 31-34.

[13] J. Velez, M. C. Thies, Liquid lignin from the SLRPTM process: The effect of processing conditions and black-liquor properties, *J. Wood Chem. Technol.* **36** (2016) 27-41.

[14] W. Zhu, H. Theliander, Precipitation of lignin from softwood black liquor: An investigation of the equilibrium and molecular properties of lignin, *BioRes.* **10** (2015) 1696-1714.

[15] F. Luzi, I. Tortorella, A. D. Michele, F. Dominici, C. Argentati, F. Morena, L. Torre, D. Puglia, S. Martino, Novel nanocomposite PLA films with lignin/zinc oxide hybrids: Design, characterization, interaction with mesenchymal stem cells, *Nanomaterials* **10** (2020) 2176.

[16] K. M. Samb-Joshi, Y. A. Sethi, A. A. Ambalkar, H. B. Sonawane, S. P. Rasale, R. P. Panmand, R. Patil, B. B. Kale, M. G. Chaskar, Lignin-mediated biosynthesis of ZnO and TiO_2 nanocomposites for enhanced antimicrobial activity, *J. Compos. Sci.* **3** (2019) 90.

[17] H. Wang, X. Qiu, W. Liu, F. Fu, D. Yang, A novel lignin/ZnO hybrid nanocomposite with excellent UV-absorption ability and its application in transparent polyurethane coating, *Ind. Eng. Chem. Res.* **56** (2017) 11133-11141.

[18] K. N. Law, W. M. W. Daud, A. Ghazali, Morphological and chemical nature of fiber strands of oil palm empty-fruit-bunch (OPEFB), *Bioresources* **2** (2007) 351-362.

[19] B. S. Gupta, B. P. Jelle, T. Gao, Wood facade materials ageing analysis by FTIR spectroscopy, *Proceedings of the Institution of Civil Engineers - Construction Materials* **168** (2015) 219-231.

[20] P. Bock, P. Nousiainen, T. Elder, M. Blaukopf, H. Amer, R. Zirbs, A. Potthast, N. Gierlinger, Infrared and Raman spectra of lignin substructures: Dibenzodioxocin, *J. Raman Spectrosc.* **51** (2020) 422-431.

[21] A. Anžlovar, A. Kržan, E. Žagar, Degradation of PLA/ZnO and PHBV/ZnO composites prepared by melt processing, *Arab. J. Chem.* **11** (2018) 343-352.

[22] C. A. Marin-Flores, O. Rodríguez-Nava, M. García-Hernández, R. Ruiz-Guerrero, F. Juárez-López, A. d. J. Morales-Ramírez, Free-radical scavenging activity properties of ZnO sub-micron particles: Size effect and kinetics, *J. Mater. Res. Technol.* **13** (2021) 1665-1675.