Self-Formation of Lignin Particles Through Melt-Extrusion for Active Biodegradable Food Packaging

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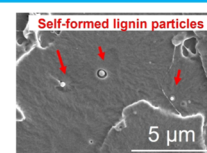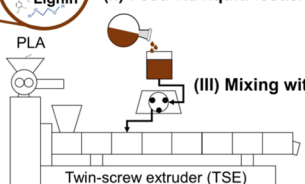ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: This study presents a method for the self-formation of lignin particles within a polylactic acid (PLA) matrix during melt-extrusion, eliminating the need for separation and drying steps typically associated with submicro-size lignin particles. This method effectively mitigates the problem of agglomeration often associated with the drying step. Softwood kraft lignin, guaiacyl lignin (GL-lignin), was dissolved in low-molecular-weight poly(ethylene glycol) (PEG) and was introduced into a twin-screw extruder using a liquid feeder. Lignin particles within a particle size range of 200−500 nm were observed in the extrudate of the PLA/PEG/GL-lignin composites. PLA/PEG/GL-lignin composite films were produced through blown film extrusion. These composite films demonstrated superior ultraviolet (UV)-barrier and antioxidant properties compared to neat PLA films, with optical and mechanical characteristics comparable to those of neat PLA. Moreover, migration values of the composite films in various food simulants were below regulatory limits, suggesting their potential for food packaging applications. This self-formation process offers a promising approach for utilizing lignin for PLA applications.

Self-formation lignin particles during melt-extrusion process
(I) Dissolution of lignin in PEG
(II) Feed via liquid feeder
(III) Mixing with molten PLA
Twin-screw extruder (TSE)
Self-formed lignin particles
5 μm

1. INTRODUCTION

The idea of a circular economy revolves around the goal of minimizing the negative environmental, social, and economic effects of waste materials. It encourages their revaluation, diminishes their creation, and offers direction for a more sustainable approach to their production.[1,2] The utilization of renewable resources, specifically lignocellulosic biomass from forestry and agricultural sectors, is now focused on promoting high-value-added materials instead of its previous primary use for generating renewable energy.[3−5] Lignocellulose is considered as a highly promising alternative to conventional carbon-containing sources for a wide range of applications.[6,7] Furthermore, it is abundantly available, renewable, entirely biodegradable,[7,8] and highly biocompatible.[9,10]

Lignin is the second most abundant component in lignocellulosic biomass after cellulose, and in fact, it is the most prevalent aromatic biopolymer on Earth.[11] Nonetheless, it remains an underutilized resource due to a limited understanding of its utilization and full potential, beyond its conventional use as a fuel source.[12] Annually, over 100 million tons of lignin was generated primarily from the pulp and paper industry.[13] However, a recent technoeconomic analysis of lignin has indicated that the use of lignin for energy recovery alone is not economically feasible. This is because only 40% of the generated lignin is burned to cover the internal energy demand of a biorefinery.[14,15] Therefore, it is imperative to

investigate alternative pathways for lignin utilization in order to maximize its valorization.

The current lignin valorizations are related to its chemical structure[14,16,17] possessing polyphenolic rings providing hydrophobic characteristics and sites that can be used for the synthesis of aromatic chemicals. Lignin offers numerous unique features, such as high stiffness,[18] high thermal stability,[19] superb ultraviolet (UV) absorption,[20,21] and ability to inhibit oxidation reactions and biological attacks.[22,23] Lignin has emerged as a viable alternative to petrochemicals in the development of new materials or chemicals due to the low price, biodegradability, and nontoxicity. The incorporation of lignin in polymers, particularly in biopolymers, can introduce active functional attributes while retaining the benefits of being biobased and biodegradable.[21,24−26] For example, Domínguez-Robles et al.[27] introduced technical softwood Kraft lignin (BioPiva 100) from UPM (Helsinki, Finland) into poly-(butylene succinate) (PBS) using melt extrusion processes. The resulting PBS/lignin composites exhibited radical
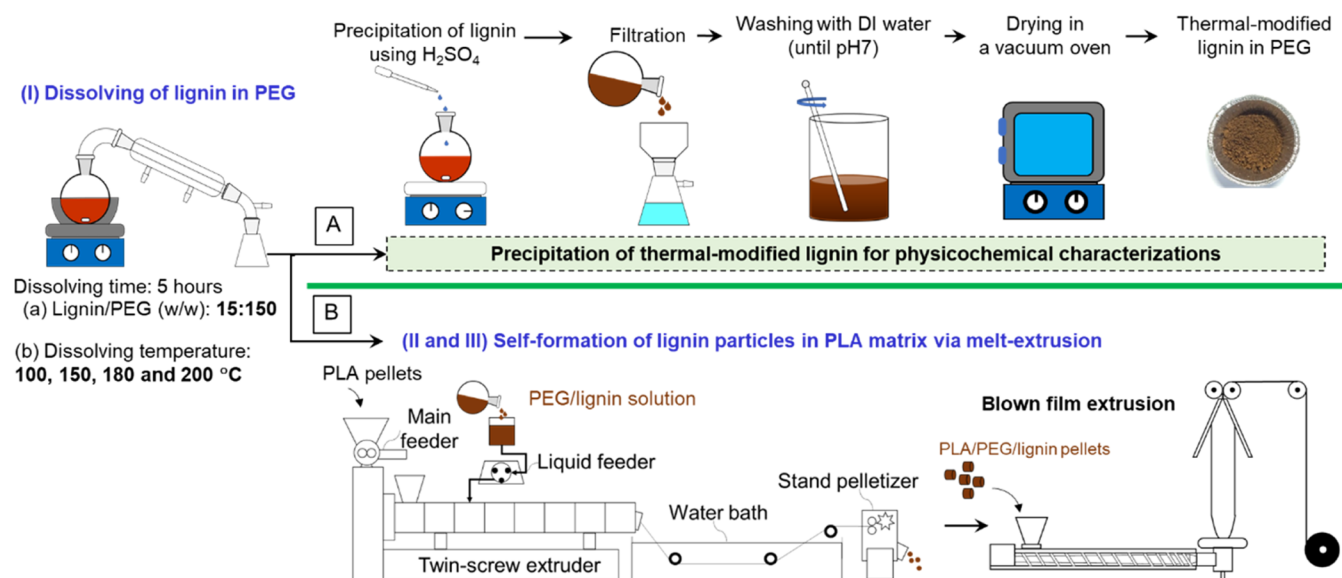
Figure 1. Schematic illustration: (a) precipitation of PEG-modified lignin for physicochemical characterizations and (b) a procedure to produce PLA/self-formed lignin composite films.

scavenging capabilities and resistance to the adhesion of common nosocomial pathogens. However, it was observed that the mechanical properties, including tensile, flexural, and impact strength, significantly decreased. This reduction in mechanical properties is a common trend observed in other polymers[20,26,−] when incorporating large technical lignin particle[31,32] caused by their low surface area, tendency to agglomerate, and poor interaction with the host polymers. To address this issue, researchers have explored chemical modifications of lignin to enhance its compatibility with host polymers.[33,34] Moreover, it is noted that the use of large lignin particles was found to be unsuitable for flexible packaging requiring film thicknesses in the range of 10−60 μm.[35,36]

Emerging use of lignin nanoparticles in food packaging can promote synergistic effects among active compounds, such as antibacterial[37−39] and antioxidant properties[40] arising from surface phenolic groups, and offer high thermal stability and UV protection.[41−43] This improvement is attributed to their high surface-area-to-volume ratio, which enables more effective physical and chemical interactions, thus making them highly suitable for various applications. Various techniques have been documented for the fabrication of lignin nanoparticles, including methods such as dialysis, solvent exchange, nano-precipitation, homogenization, ultrasonic cavitation, etc.[14,44] Lignin nanoparticles, initially dispersed in liquid media, undergo a drying process before being incorporated into polymers via economic melt extrusion. However, this drying process often results in significant agglomeration, posing a challenge when these particles are used in polymer nano-composites. Furthermore, de Assis et al.[45] conducted a study evaluating the manufacturing costs of nanoparticles. Their research identified that lignin, utilities, and depreciation were the major cost contributors. Notably, the estimated manu-facturing costs are approximately 600−1170 USD per metric ton.

In this study, we propose a novel method for the spontaneous formation of lignin particles within a PLA matrix, bypassing the need for a drying process and mitigating agglomeration issues. The method involves three main stages: (i) dissolving lignin in low-molecular-weight poly(ethylene glycol) (PEG), where the effects of dissolution temperature on physicochemical and thermal properties were investigated; (ii) feeding the lignin solution through a twin-screw extruder via a liquid feeder; and (iii) mixing with molten PLA using twin screw extrusion. PLA composite films were fabricated via blown film extrusion. Morphology of self-formed lignin particles in the PLA matrix was observed, and optical and tensile properties of the PLA/self-formed lignin composite films were measured. Furthermore, UV-barrier and antiox-idation abilities and overall migration were evaluated. Our work aims to shed light on the feasibility and potential advantages of this method for incorporating lignin into PLA matrix materials, particularly in the context of food packaging applications.

2. MATERIALS AND METHODS

2.1. Materials. BioPiva100, a type of softwood kraft lignin (GL-lignin) that is enriched in guaiacyl monomers, was acquired from UPM Biochemicals in Finland. NatureWork LLC provided the biodegradable poly(lactic acid) (PLA), commercially available, with a weight-average molecular weight (M_w) of 160,000 g/mol. This PLA composition is primarily composed of 94% L-lactic acid. Chemipan in Thailand supplied poly(ethylene glycol) (PEG) with a M_w of 400 g/mol.

2.2. Preparation of Lignin Solution and Character-izations. Preparation of lignin solution and production of PLA/self-formed lignin composite films are illustrated in Figure 1. As-received lignin (GL-lignin) was subjected to a vacuum drying process in an 80 °C oven for a duration of 12 h in order to eliminate any remaining moisture. To investigate the effects of temperature on the physicochemical and thermal characteristics of PEG-modified lignin, the predried lignin was dissolved in PEG at a consistent weight ratio of 15:150, while dissolving temperatures were varied (100, 150, 180, and 200 °C). The mixture was agitated using a magnetic stirrer and at the desired dissolving temperature for a duration of 5 h. In order to investigate the physicochemical and thermal proper-ties of the resultant lignins, PEG-modified lignins, a pH2-sulfuric acid was slowly added to the lignin/PEG solution (see Figure 1(a)). The acid-precipitated lignin was filtrated through
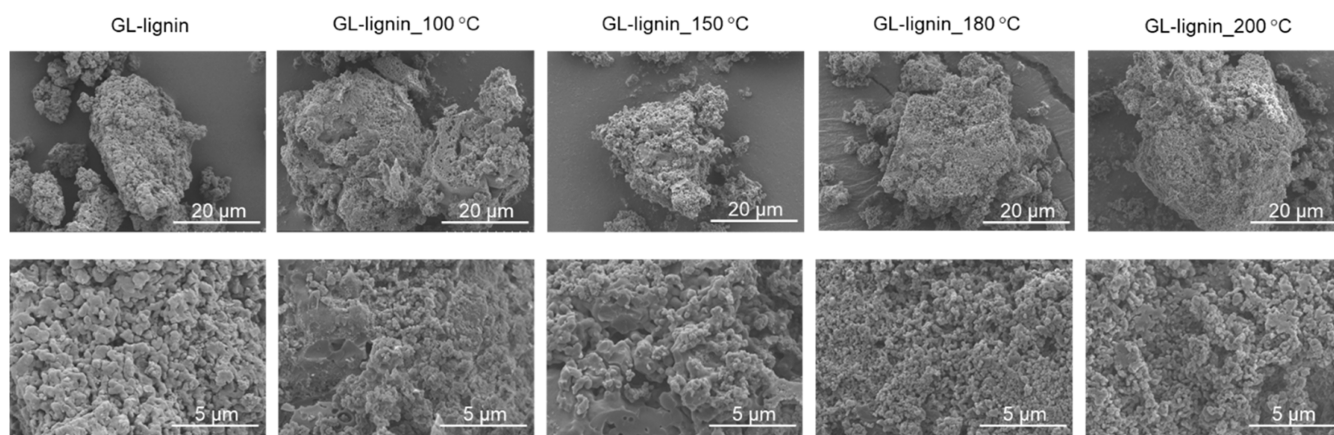
Figure 2. SEM micrographs of GL-lignin and its derivative lignins dissolved in PEG at different temperatures.

a glass filter with a pore size of 1 μm and then subjected to multiple washes with deionized water until the pH reached 7. The obtained PEG-modified lignin samples were dried and stored in an airtight vial until they were required for characterizations.

The molecular weight distribution of lignin samples was assessed using gel permeation chromatography (GPC) with a Waters e2695 separation module from the USA. Calibration was performed using polystyrene standards. Phosphorus-31 nuclear magnetic resonance spectroscopy (^{31}P NMR) (AV-500 Bruker Biospin) was carried out to identify and change the chemical compositions of PEG-modified lignins. For ^{31}P NMR analysis, modifications of hydroxyl groups within the lignin sample were achieved through a phosphitylation reaction, following the procedure outlined in a nature protocol.[46] To determine the glass transition temperatures (T_g) of the PEG-modified lignin samples, a differential scanning calorimeter (Mettler Toledo: DSC1, Switzerland) was employed. The T_g value was reported at the middle temperature and calculated as the average between the onset and end-set T_gs.

2.3. Preparation of PLA/Self-Formed Lignin Composite Films and Characterizations. Figure 1(b) shows a procedure to produce PLA/self-formed lignin composite films. PLA pellets underwent drying at 80 °C for 6 h within a dehumidifier oven and were subsequently introduced into a twin-screw extruder (Labtech, Germany) with a screw diameter of 25 mm and an L/D ratio of 32. Lignin/PEG solutions were prepared at different dissolving temperatures (100, 150, 180, and 200 °C) at lignin/PEG weight ratios of 15:150 and a stirring duration of 5 h. The attained lignin/PEG solution was fed via a controllable liquid feeder (Watson Marlow, 300 Series, U.K.); after that, the solution was blended with the molten PLA. The resulting compound contained a controlled PEG content at 5 wt % and lignin at 0.5% w/w. This dosage is recommended from our previous works.[43,47] The temperature profile for the extrusion process was set as follows: 140−180 °C, with a die temperature maintained at 180 °C. The rotating screw speed of the extruder was confabulated at 110 rpm. The extrudates of PLA/self-formed lignin were conveyed through a water bath and subsequently pelletized into 3 mm pellets. A single-screw extruder equipped with a blown film die (34 mm inner diameter and 0.5 mm die gap) was employed for the production of PLA/self-formed lignin composite films. The screw speed and take-up speed were

maintained at 60 rpm and 3.7 m/min, respectively, to produce films with a width of 13 cm and a thickness of 35 μm.

Morphology of self-formed lignin particles in the PLA matrix was observed using field-emission scanning electron microscopy (FE-SEM). PLA/self-formed lignin composite samples were submerged fractured in liquid nitrogen to prepare cryofracture surface. Haze and clarity were measured by using a Hazemeter (BYK-Gardner Haze Gard Plus, BYK-Gardner GmbH, Geretsried, Germany), flowing ASTM D1003. UV and visible light transmittance of all prepared films were measured using a UV spectrometer (PerkinElmer Lambda 950) with a scanning range of 200−800 nm. Tensile properties were examined using a Shimadzu EZ-Test (EZ-LX) series texture analyzer machine following the ASTM D882 standard. The composite films were cut as rectangular strips with dimensions of 15 mm width and 50 mm gauge length, and the tensile tests were conducted at a cross-head speed of 50 mm/min.

Antioxidant performance of PLA composite films with self-formed lignin was examined using the 2,2-diphenyl-1-picrylhydrazyl (DPPH) free radical scavenging method. The measurements were conducted following the steps reported by Crouvisier-Urion et al. and Valencia et al.[25,48] Film samples with 100 mg (100 cm^2) were immersed in 10 mL of DPPH solution in ethanol (50 mg/L) contained in a UV-shielded vial. The mixture was stirred and left at room temperature in darkness for durations of 24 h. To determine the DPPH scavenging activity, the absorbance of DPPH at 517 nm was quantified using an ultraviolet−visible (UV−vis) spectrophotometer (PerkinElmer Lambda model 950) and ethanol was used as the experimental blank. The reduction in radical scavenging activity (RSA) in % was calculated as shown in eq 1[23,49]

$$\text{free radical scavenging activity (RSA, \%)} = \frac{(A_{\text{DPPH}} - A_{\text{sample}})}{A_{\text{DPPH}}} \times 100 \qquad (1)$$

where A_{DPPH} is the absorbance of the free radical DPPH solution and A_{sample} is the absorbance measured for the free radical DPPH solution obtaining from the composite film sample.

The overall migration of lignin from composite films into food simulant was assessed following the guidelines outlined in Commission Regulation EU No 10/2011.[50] The composite

films were cut into rectangular strips, collectively covering an area of 1 dm², and the precise weight of each specimen was recorded. These film samples were fully immersed in 100 mL of food simulants: simulant A (ethanol/water (1:9, v/v)), B (3%w/v acetic acid), C (ethanol/water (2:8, v/v)), D1 (ethanol/water (1:1, v/v)), and D2 (n-heptane). These food simulants represent aqueous food (pH > 4.5), acidic food (pH ≤ 4.5), alcoholic food (up to 20% v/v), dairy product, and fatty food, respectively. After being incubated for a period of 10 days at 40 °C, the film specimens were removed from the food simulants. The food simulant was then evaporated at 105 °C until a constant weight was achieved. The nonvolatile residues remaining were carefully weighed using a four decimal place analytical balance (BOECO BAS 31 Plus, Germany) with an accuracy of ±0.1 mg. This process was conducted in triplicate for each composite film, and the average overall migration in milligrams per kilogram was computed and reported.

The data were analyzed using one-way analysis of variance (ANOVA) with Minitab19.2020.1 (64-bit) (Minitab Inc.). Data were compared using Tukey's test at a significant difference p-value of 0.05 (95% confidence interval).

3. RESULTS AND DISCUSSION

3.1. Physicochemical and Thermal Properties of PEG-Modified Lignins Prepared at Different Dissolution Temperatures.

PEG-modified lignin was precipitated from the PEG/lignin solution to investigate its physicochemical and thermal properties, presenting in dark-brown powders. Figure 2 shows SEM images of GL-lignin and its derivative lignins dissolved in PEG at distinct temperatures: 100 °C (GL-lignin_100 °C), 150 °C (GL-lignin_150 °C), 180 °C (GL-lignin_180 °C), and 200 °C (GL-lignin_200 °C). These particles exhibited irregular shapes and sizes ranging from a few micrometers to 50 μm, highlighting their heterogeneous nature formed during the acid precipitation process. However, their microscale dimensions and agglomeration issues make them unsuitable for polymer filler applications in flexible films with thicknesses ranging from 10 to 60 μm.[35,36]

In Figure 3(a), the molecular weight distribution of lignin samples dissolved in PEG is presented alongside that of GL-lignin for comparison. GL-lignin exhibited a broad, normally distributed molecular weight profile with a higher molecular weight shoulder. Weight-average molecular weight (M_w) and number-average molecular weight (Mn) were determined using polystyrene calibration, resulting in values of 6000 and 2700 g/mol, respectively. The polydispersity index (PDI) was calculated to be 2.22 for GL-lignin. Notably, significant changes were observed as the molecular weight distribution shifted from unimodal to bimodal after lignin dissolution in PEG. Within this bimodal distribution, the lower molecular weight segment shifted toward smaller weights compared to GL-lignin, suggesting the impact of the dissolution process on lignin fragmentation. Conversely, the higher molecular weight portion of the bimodal distribution expanded toward larger weights, indicating potential lignin polymerization, possibly influenced by the elevated dissolution temperature effects.

The Mw values for the PEG-modified lignin samples dissolved at different temperatures (100, 150, 180, and 200 °C) were 6240, 8357, 8255, and 8179 g/mol, respectively. Correspondingly, the PDI values for these samples were 2.43, 2.82, 2.69, and 2.65, respectively. Both the M_w and PDI values of PEG-modified lignins exceeded those of GL-lignin, indicating a significant influence of temperature on lignin
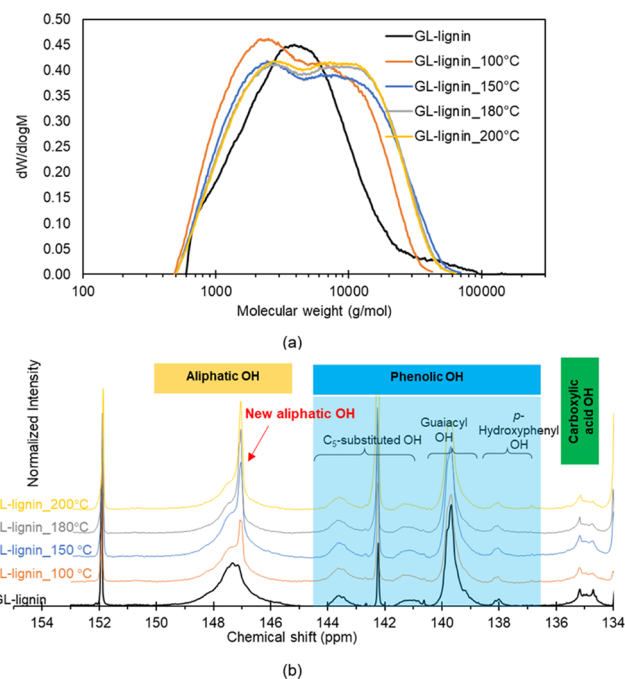

Figure 3. (a) Molecular weight distribution and (b) ³¹P NMR spectra of GL-lignin and its derivative PEG-modified lignins dissolved in PEG at different temperatures.

behavior in PEG. Higher dissolution temperatures correlated with higher M_w values, suggesting an increased likelihood of polymerization. The associated PDI values further underscored a wider range of molecular weights, highlighting increased molecular variation as the dissolution temperature increased.

In Figure 3(b), the ³¹P NMR spectra reveal a new aliphatic signal emerging at around 147 ppm in the aliphatic hydroxyl region of lignins after they are dissolved in PEG. This new aliphatic hydroxyl is responsible for creating intermonomeric connections between lignin and PEG through α-PEG-β-O-4.[51,52] The intensity of this signal increases with higher dissolution temperatures. Additionally, the peak at 142.3 ppm, representing the linkage of 4-O-5,[46] increased with increased dissolution temperature. Table S.1 provides data on the hydroxyl content of GL-lignin and its PEG-modified derivatives, obtained by quantitative ³¹P NMR using an internal standard, endo-N-hydroxy-5-norbornene-2,3-dicarbox-imide (NHND). Dissolution of lignin in PEG leads to a noticeable rise in aliphatic and condensed-phenolic (C₅-substituted) hydroxyl contents, which demonstrated an upward trend with rising dissolution temperatures. The increase in the aliphatic content and C₅-substituted hydroxyl content corresponds to the creation of α-PEG-β-O-4 and 4-O-5, respectively, aligning well with the higher molecular weight indicated by GPC analysis.

The total phenolic content in lignin plays a crucial role in influencing its UV-barrier, antioxidant, and antimicrobial properties. GL-lignin has a total phenolic content of 2.42 g/mol, which comprises guaiacyl (G-unit) and p-hydroxyphenyl (H-unit) components. Interestingly, the total phenolic content of the resulting PEG-modified lignins falls within a similar range, ranging from 2.40 to 2.50 g/mol. This implies that dissolving lignin in PEG within the temperature range 100−200 °C does not significantly impact the phenolic content.
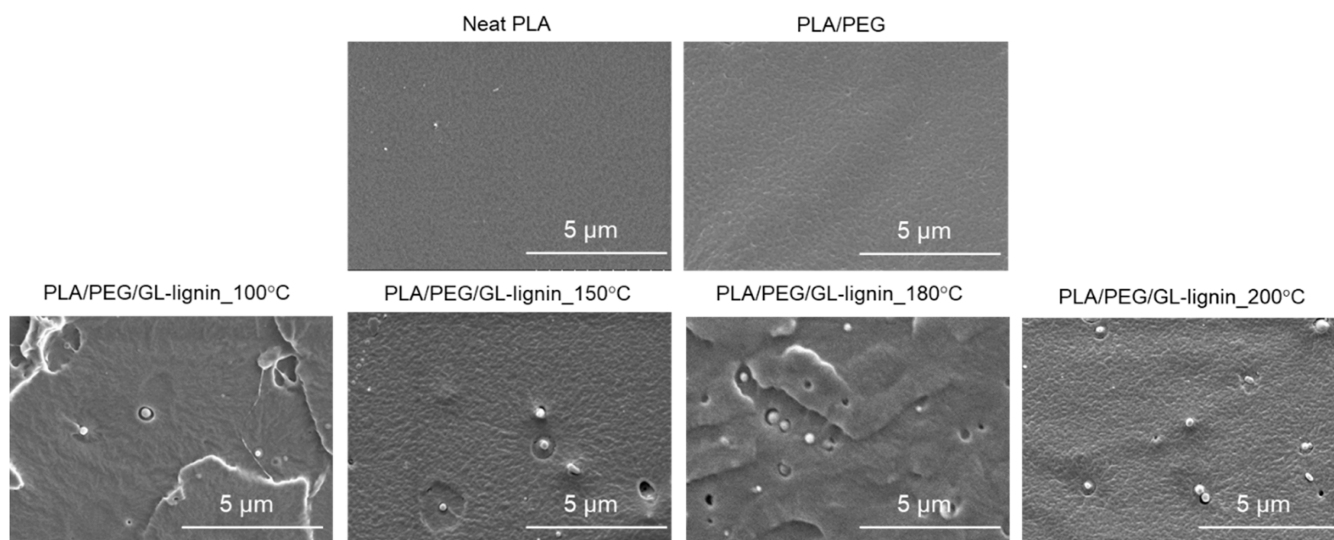
Figure 4. SEM micrographs of extruded PLA without incorporation of lignin (neat PLA and PLA/PEG) and its composites with GL-lignin.
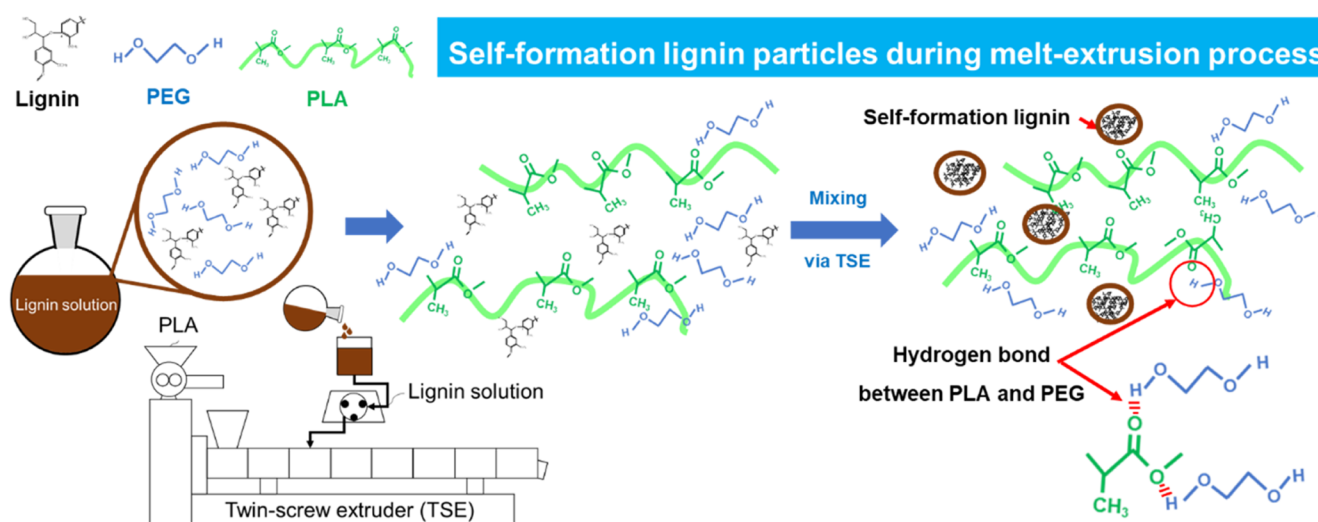

Figure 5. Schematic illustration showing the self-formation lignin particles in poly(lactic acid) via a twin screw extruder.

The DSC thermogram obtained from the second heating scan of GL-lignin and its PEG-modified lignin dissolved at different temperatures is presented in Figure S.1. The amorphous nature of lignin is evident through the detection of a distinct step in the baseline, signifying the presence of a T_g. Interestingly, T_g consistently decreases with higher dissolution temperatures. For instance, GL-lignin_100, GL-lignin_150, GL-lignin_180, and GL-lignin_200 °C exhibit T_g values of 144.1, 130.4, 103.9, and 101.2 °C, respectively. This reduction in T_g suggests structural changes in lignin due to an increased proportion of α-PEG-β-4. A similar finding has been reported,[53] acid-catalyzed poly(ethylene glycol) (PEG, 400 g/mol) solvolysis of Japanese cedar wood was conducted at 140 °C for 90 min. The HSQC analysis indicated the conversion of α−OH-β−O−4 units abundant in the lignin extracted from Japan cedar to α−PEG-β−O−4 linkage during solvolysis using PEG. Furthermore, the higher portion of α−PEG-β−O−4 linkage resulted in a decrease in T_g of the PEG-modified lignin.[53] Additionally, a similar finding was reported by Zhang et al.,[54] where the soda lignin was blended with PEG (400 g/mol) at various weight ratios (lignin to PEG: 1:2, 1:3, and 1:4) at 175 °C with continuous mechanical stirring for 2 h.

Analysis of the ^{13}C NMR spectra revealed that the PEG moiety was grafted onto the lignin structure with methylene carbons bonded to the α carbon on the lignin side chain through ether linkages. The T_g of the pristine lignin (129 °C) decreased with an increase in the PEG weight ratio. Specifically, the T_g of the PEG-modified lignin was 110 °C when the weight ratio of lignin to PEG was 1:4.

3.2. Characterizations of PLA/Self-Formed Lignin Composite Films. Control film samples, comprising neat PLA and PLA with 5 wt % of PEG (PLA/PEG), were fabricated using conventional blown film extrusion. The prepared PLA/PEG/lignin composite films underwent characterizations, and their properties were assessed in comparison to the control film samples.

3.2.1. Effects of Dissolution Temperatures of Lignin in PEG. Lignin dissolution in PEG was conducted at various temperatures (100, 150, 180, and 200 °C) before blending with PLA. The purpose of this was to investigate how the dissolution temperature affects the properties of the PLA/PEG/lignin composite films. The final composition of PLA/PEG/lignin was adjusted to PEG content at 5 wt % and lignin at 0.5% w/w. The resulting composite films, derived from

lignin dissolution at 100, 150, 180, and 200 °C, were labeled as PLA/PEG/GL-lignin_100, PLA/PEG/GL-lignin_150, PLA/PEG/GL-lignin_180, and PLA/PEG/GL-lignin_200 °C, respectively. SEM micrographs of the extruded samples are presented in Figure 4. Neat PLA and the PLA/PEG exhibited a notably smooth surface, while a remarkable observation was made with all the PLA/PEG/lignin composite samples, as they displayed spherical lignin with an average particle size of 200−500 nm. The morphology of the observed spherical lignins was notably different from their original lignins, as shown in Figure 2. The majority of lignin particles observed in SEM micrographs exhibit a spherical shape, while a few show signs of attachment to one another. These results suggest the presence of an inherent self-assembly phenomenon governing the formation of lignin particles during the extrusion process.

The self-formation mechanism is postulated and is illustrated in Figure 5. Initially, lignin undergoes complete dissolution within the low-molecular-weight PEG. Then, when the lignin solution is mixed with PLA using the melt extrusion technique, lignin spontaneously undergoes self-formation due to its immiscibility with PLA, and this formation might be assisted by shear force generated during the melt-extrusion process. In contrast, PEG is miscible with PLA and acts as a plasticizer, improving the toughness of the PLA matrix. This process results in the unique morphology observed in PLA composites.

In Figure 6, it is evident that the UV transmission of PLA/PEG/GL-lignin composite films is significantly reduced
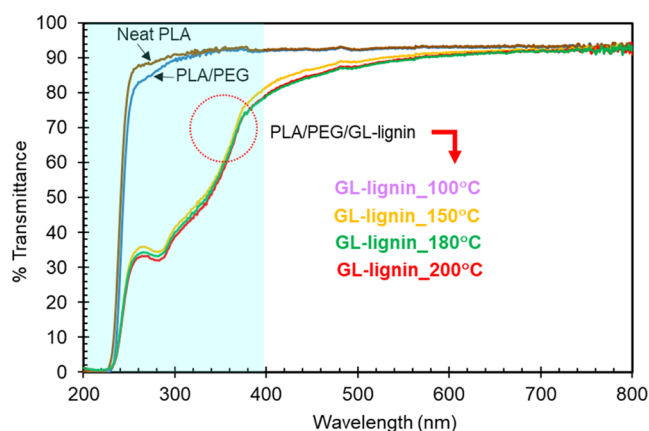

Figure 6. Overlaid UV−visible spectra of PLA/lignin composite films at various dissolution temperatures of 100, 150, 180, and 200 °C, compared to neat PLA and PLA/PEG films.

compared to that of films without lignin incorporation. Both Neat PLA and PLA/PEG films showed limited UV-barrier, with UV transmission approaching 90%. In contrast, PLA composite films containing self-formed lignin particles (at 0.5% w/w) exhibited UV-barrier properties, without noticeable variations linked to different dissolution temperatures. The UV-barrier properties of the composite films can be attributed to the presence of chromophoric groups in lignin.[55]

3.2.2. Application of PLA/Self-Formed Lignin Composite Films for Active Packaging. UV light is widely recognized as a contributing factor to the degradation of food quality due to processes such as photolysis and photooxidation. In the context of this study, composite films composed of PLA and self-formed lignin offer a sustainable and viable alternative for products sensitive to UV light. This includes items such as

vitamins, chlorophyll, and common food colorants typically found in oils and fats. To evaluate their potential for food packaging applications, the study focused on two composite film variants: PLA/PEG/GL-lignin_100 and PLA/PEG/GL-lignin_180 °C. These composite films incorporated self-formed lignin, each with distinct glass transition temperatures (T_g) of 144.1 and 103.9 °C, respectively. Comparative analyses were carried out using pristine films (neat PLA and PLA/PEG) in addition to the selected PLA/self-formed lignin composite films.

A low haze value is a desirable property for food packaging films, as it contributes to improved transparency. The haze and clarity of the PLA/self-formed lignin composite films as well as the plain films (neat PLA and PLA/PEG) are summarized in Table S.2. Neat PLA and PLA/PEG exhibited excellent optical properties with low haze (2%) and high film clarity (98%), consistent with the results reported in the literature.[56,57] The PLA/self-formed lignin composite films had slightly higher haze values, but their clarity remained at approximately 97%. Specifically, the haze of the composite films with lignin dissolved at 100 °C (PLA/PEG/GL-lignin_100 °C) was 13.7%. Increasing the dissolution temperature of lignin to 180 °C did not significantly affect the haze value. The presence of self-formed lignin particles, which constitute a heterogeneous phase in the PLA matrix,[58] leads to an increase in the haze value due to the scattering of light at wide angles (over 2.5° from normal). According to the ASTM D1003 definition, the haze value of the PLA/self-formed lignin composite films is not considered as a diffusing film (a haze value >30%). This aligns well with the UV results presented in Figure 6, where the transmittance of all of the PLA/self-formed lignin composite films is over 80%, meeting the criteria for transparent films.[59]

The tensile properties of composite films containing self-formed lignin particles were assessed, including tensile strength, Young's modulus, and elongation at break, in both the machine direction (MD) and transverse direction (TD). The results are presented in Table S.2. Neat PLA films displayed a tensile strength of 57.3 ± 5.1 MPa, Young's modulus of 2.8 ± 0.2 GPa, and an elongation at break of 3.5 ± 0.8% in the MD, while in the TD, the values were 47.2 ± 4.2 MPa, 2.5 ± 0.1 GPa, and 3.2 ± 0.1%, respectively. These results indicate that the material exhibits higher tensile strength and Young's modulus in the MD compared to the TD, suggesting an anisotropic characteristic of the films produced via blown film extrusion. The addition of 5 wt % PEG to PLA (PLA/PEG) did not significantly alter these mechanical properties. Moreover, the mechanical properties of PLA/self-formed lignin composite films were comparable to those of neat PLA and PLA/PEG. This suggests that the PLA/self-formed lignin composite films demonstrated in this study could serve as a viable alternative to neat PLA in various applications without compromising the mechanical performance. Additionally, these composite films exhibit superior UV-barrier properties. Further characterizations, including the antioxidation ability and overall migration, were investigated for potential food packaging applications.

The antioxidant performance of PLA/self-formed lignin composite films was assessed in comparison to that of plain films without lignin incorporation (neat PLA and PLA/PEG). The DPPH scavenging assay was employed, and the calculated RSA was reported to evaluate the antioxidant activity of the films. Figure 7(a) illustrates the absorbance of a stock solution of DPPH in ethanol (50 mg/L) overlaid with the absorbances
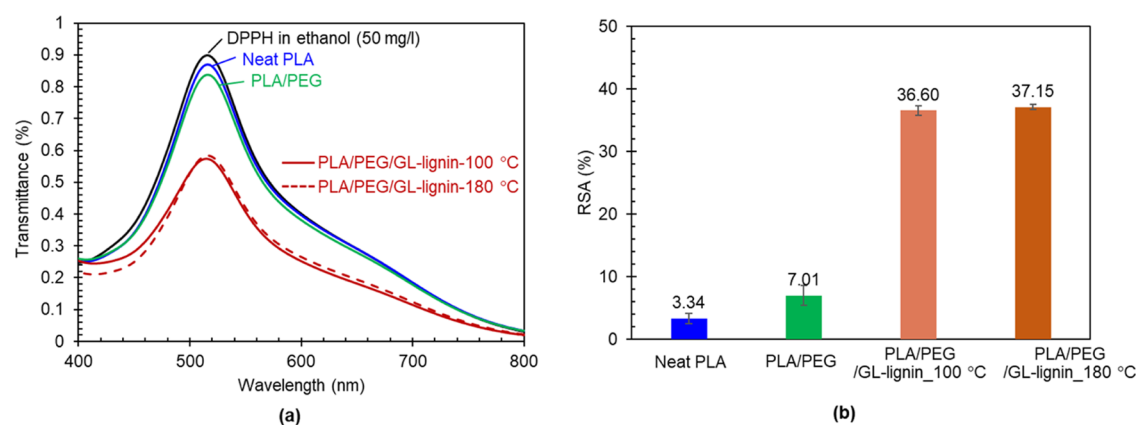
Figure 7. Evaluation of antioxidant ability: (a) absorbance of DPPH-ethanol solutions after the film immersion test for 24 h and (b) free radical scavenging activity (RSA).

Table 1. Overall Migration of PLA/Self-Formed Lignin Composite Films in Different Food Simulants[a]: Simulant A (Ethanol/ Water (1:9, v/v)), Simulant B (3%w/v Acetic Acid), Simulant C (Ethanol/Water (2:8, v/v)), Simulant D1 (Ethanol/Water (1:1, v/v)), and Simulant D2 (*n*-Heptane)

	overall migration (mg/kg)				
samples	simulant A	simulant B	simulant C	simulant D1	simulant D2
neat PLA	44.2 ± 11.2^a	$48.4 \pm 9.1^{a,b}$	36.2 ± 4.0^b	36.0 ± 1.4^b	33.7 ± 6.5^c
PLA/PEG	46.6 ± 12.1^a	55.0 ± 10.5^a	$37.5 \pm 3.4^{a,b}$	47.9 ± 2.1^a	$44.6 \pm 3.3^{a,b}$
PLA/PEG/GL-lignin_100 °C	45.1 ± 10.1^a	$45.2 \pm 9.2^{a,b}$	47.8 ± 6.6^a	46.9 ± 2.2^a	41.6 ± 4.8^a
PLA/PEG/GL-lignin_180 °C	47.3 ± 11.8^a	40.4 ± 10.1^b	47.3 ± 5.1^a	45.5 ± 1.6^a	$38.2 \pm 11.1^{b,c}$

[a]Significant difference at *p*-value <0.05 (95% confidence interval).

after immersing different film specimens for a duration of 24 h. After immersion, the DPPH solutions exhibited lower absorbance with the lowest absorbance recorded from the solution containing PLA/self-formed lignin composite films. Further analysis in Figure 7(b) reveals the free radical scavenging activity, RSA, which indicates the antioxidant activity of the films. Neat PLA and PLA/PEG exhibited poor antioxidation ability, with RSA values of 3.34 ± 0.8 and 7.01 ± 1.57%, respectively. This aligns with the poor antioxidation performance of PLA reported in previous studies.[60] Remarkably, PLA composite films with self-formed lignin exhibited significantly higher RSA values, reaching approximately 36−37%. The addition of 0.5 wt % of self-formed lignin particles enhanced the antioxidant activity by over 30% compared to PLA/PEG films over a 24 h duration. Increasing the dissolution temperature of lignin in PEG from 100 to 180 °C did not have a significant effect on antioxidant performance, which correlated well with the chemical composition of lignin determined by ^{31}P NMR. The antioxidation performance of PLA/self-formed lignin composite films is primarily related to the presence of phenolic hydroxyl groups in lignin, which act as inhibitors to stabilize reactive oxidized radicals.[40,61] Due to their high antioxidant activities, abundance, and low toxicity, lignin could serve as a promising natural antioxidant in food packaging applications.

The overall migration (OM) of PLA/self-formed lignin composite films was evaluated to assess their suitability for food packaging applications.[62] OM tests were conducted in accordance with the guidelines outlined in Commission Regulation EU No. 10/2011 using a total immersion test. The overall migration limit (OML) set by the regulation is 10 mg/dm^2 or 60 mg/kg of food simulant.[63,64] After 10 days of incubation at 40 °C in various food simulants, the overall food migration results are presented in Table 1. These results provide critical information regarding the suitability of the composite films for use in food packaging.

The PLA used in this study is food-grade and is recommended for use with all food types. The highest overall migration was observed in food simulant B, with a migration value of 48.1 mg/kg. This value is well within the acceptable limit established by the current European legislation for food contact materials, which is set at 60 mg/kg. In the case of food simulant A (ethanol/water 1:9, v/v), the overall migration of the neat PLA film was measured at 44 mg/kg, and this value aligns well with the results reported in the literature.[23]

An increasing trend in overall migration was observed when low-molecular-weight PEG was added to PLA. This may be attributed to the migration of PEG from the PLA/PEG films into the food simulants. The highest migration value detected was 55 mg/kg, which was observed in the case of simulant B. Furthermore, with the addition of lignin, the PLA/self-formed lignin composite films exhibited migration values below the OML (60 mg/kg).[63,64] It emphasizes that all the migration values of the produced PLA/self-formed lignin composite films are within the acceptable range, indicating their potential for use in food packaging for a variety of food types, including aqueous food (pH > 4.5), acidic food (pH ≤ 4.5), alcoholic food (up to 20% v/v), dairy products, and fatty foods. These findings support the suitability of the PLA/self-formed lignin composite films for use in food packaging, as their overall migration values are within the acceptable limits established for food contact materials.

4. CONCLUSIONS

In this study, a simple practical process for producing self-formed lignin particles within a poly(lactic acid) (PLA) matrix

was demonstrated for the first time. This process involves several steps: (I) dissolution of lignin in low-molecular-weight poly(ethylene glycol) (PEG), (II) feeding the lignin-PEG solution into a twin-screw extruder via a liquid feeder, and (III) mixing the solution with molten poly(lactic acid) using a twin screw extruder, leading to the spontaneous self-formation of lignin particles within the PLA matrix. These self-formed lignin particles exhibited a spherical shape and ranged in submicron size. Importantly, individual self-formed lignin particles were well dispersed and distributed throughout the PLA matrix without agglomeration issues. The resulting PLA/self-formed lignin composite films demonstrated excellent UV-barrier capabilities and antioxidant activity compared with neat films. Additionally, their optical and mechanical properties were comparable to those of neat PLA. The overall migration values of these composite films in various food simulants were found to be lower than the limit value (60 mg/kg) established by current European legislation. This suggests that these composite films have the potential to be used in food packaging applications. The process of self-forming lignin particles holds promising implications for utilizing lignin in plastic products and offers a sustainable approach to enhancing the properties of biodegradable materials like PLA.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.3c10113.

Functional groups determined by 31P NMR of as-received lignin (GL-lignin) and its derivative lignins dissolved in PEG at different temperatures (Table S.1); optical and mechanical properties of neat PLA film and its composite films (Table S.2); DSC thermogram of as-received lignin (GL-lignin) and its derivative lignins dissolved in PEG at different temperatures (Figure S.1) (PDF)

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Notes
The authors declare no competing financial interest.

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