Performance of Lignin as Filler in Composites of Low Density-Polyethylene and Lignosulfonate

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Low-density polyethylene (LDPE) composites were developed using unmodified kraft lignin and lignosulfonate at varying mass ratios to evaluate their effects on mechanical, thermal, and environmental performance. At low filler content, lignin enhanced LDPE crystallinity and stiffness due to improved dispersion and interfacial interaction. However, higher lignin loadings led to particle agglomeration and reduced thermal stability between 100 and 400 °C. Tensile strength increased with lignin content, though no notable difference was observed between LL7.5 and LL10, which was likely due to aggregation. All composites exhibited a consistent melting point at 107 °C. Thermogravimetric analysis revealed that lignin degraded between 200 and 400 °C, while LDPE decomposed at 400 to 500 °C. Melt Flow Rate (MFR) declined with increasing filler content, from 4.92 g/10 min (LL0) to 3.53 g/10 min (LL10). FTIR analysis before and after 30 days of sunlight exposure showed no significant chemical changes, suggesting good environmental stability. These results demonstrated that unmodified lignin-based fillers can enhance the stiffness and environmental resilience of LDPE composites, although thermal stability may be compromised at higher loadings. The study offers insights into the balance between biofiller content and composite performance, supporting the development of sustainable materials for industrial use.

DOI: 10.15376/biores.21.1.1851-1868

Keywords: Composite; Filler; Lignin; LDPE; Lignosulfonate

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INTRODUCTION

Research and development of low-density polyethylene (LDPE)-based composites have been a central theme for decades due to the widespread application of LDPE materials in fields such as packaging, construction, and various industries (Zubair et al. 2024). Early studies primarily focused on the incorporation of inorganic fillers (Kurnianto *et al.* 2007; Sherkawy *et al.* 2024), including glass fiber (Kabir and Ahmed 2012; Rohit and Dixit 2016; Ichim *et al.* 2024), talc (Lee *et al.* 2020; Jing *et al.* 2024), and calcium carbonate (Adeosun *et al.* 2014; Zapata *et al.* 2018). The addition of such fillers were found to affect the mechanical and thermal character of LDPE. Over time, growing concern for environmental sustainability has led to the adoption of renewable and biodegradable fillers. These include natural fibers such as jute (Niloy Rahaman *et al.* 2019), hemp (Kozlowski 2012), and sisal (Kalaprasad *et al.* 1997), and bio-based polymers such as starch (Beg *et al.* 2016; Jayarathna *et al.* 2022; Amatullah *et al.* 2023; Wang *et al.* 2023), lignin (Diop *et al.* 2015; Huang *et al.* 2024; Ma *et al.* 2021), and cellulose (Xiang *et al.* 2009; Scholten *et al.* 2020; Song *et al.* 2022). Recent studies have increasingly explored the use of abundant and low-cost lignocellulosic materials, particularly lignin and lignosulfonate, as fillers or reinforcing agents, due to their chemical stability, compatibility with thermoplastic matrices, and ability to form covalent bonds with polymer backbones. Significant improvements in thermal stability, mechanical strength, and biodegradability have been demonstrated, while also addressing challenges related to filler dispersion, interfacial adhesion, and processability (Reddy *et al.* 2016; Ruwoldt *et al.* 2023). The compatibility of lignin and lignocellulosic materials with thermoplastic matrices has been investigated in several studies. While complete miscibility is rare, lignin has been shown to be successfully incorporated into thermoplastics such as polyethylene (PE), polypropylene (PP), and polylactic acid (PLA), either directly or with compatibilizers, leading to improvements in thermal stability, mechanical properties, and UV resistance (Kai *et al*. 2016; Gordobil *et al*. 2015; Taj *et al*. 2007).

Lignin is a complex natural biopolymer found in the cell walls of plants, functioning primarily to provide structural support, stiffness, and resistance to microbial invasion. It is the second most abundant biopolymer on Earth after cellulose and is mainly composed of phenolic units interconnected by various chemical bonds. Technical lignin is typically generated as a by-product of the pulp and paper industry, particularly during the kraft and sulfite pulping processes (Borges Gomes *et al.* 2020; Li, J. *et al*. 2025). Lignosulfonate, a water-soluble derivative of lignin, is produced during the sulfite pulping process. This complex aromatic polymer, formed through sulfonation of lignin, is considered highly versatile for various industrial applications. Due to its excellent binding, dispersing, and emulsifying properties, lignosulfonate is widely used as an additive in the construction industry (Gonçalves *et al.* 2021). The incorporation of lignin and lignosulfonate into LDPE-based composites has shown significant effects on their thermal, mechanical, and environmental performance (Pucciariello *et al*. 2004). Lignin, with its rigid and aromatic structure, serves as a reinforcing additive that enhances stiffness, tensile strength, and thermal stability (José Borges Gomes *et al.* 2020). Additionally, lignosulfonate, as a sulfonated lignin derivative, has been reported to improve dispersion within the LDPE matrix, while also contributing to greater thermal stability and higher biodegradation rates (Schneider *et al*. 2021; Ciolacu *et al*. 2024).

The synthesis of LDPE/lignosulfonate/lignin-based composites offers several advantages and presents a promising material for green applications. These composites benefit from enhanced thermal stability, improved mechanical integrity, and increased biodegradability due to the incorporation of lignosulfonate and lignin as natural fillers. Moreover, with the growing demand for eco-friendly materials, the use of renewable and cost-effective lignin derivatives aligns well with current sustainability goals. Nevertheless, certain challenges remain, including the tendency for non-uniform filler dispersion, weak interfacial bonding between LDPE and lignin-based fillers, and a relatively limited improvement in deformation resistance compared to pure LDPE. Despite these limitations, the overall benefits, increased sustainability, improved thermal properties, and potential for industrial scalability, outweigh the associated drawbacks.

Several hypotheses have been proposed to explain how lignin, despite its relatively low intrinsic strength, may contribute positively to composite reinforcement. The interfacial reinforcement hypothesis suggests that strong interfacial adhesion between lignin and LDPE allows efficient stress transfer across the matrix–filler boundary, thus enhancing mechanical performance. The morphology-control hypothesis posits that lignin can alter polymer crystallization behavior, potentially acting as a nucleating agent and improving stiffness. In addition, energy dissipation mechanisms such as crack deflection, void formation, or filler debonding may enhance impact resistance and toughness. Finally, in hybrid systems, synergistic interactions between lignin and other fillers may promote better dispersion and interfacial bonding, resulting in improved overall properties. These mechanisms are particularly relevant in unmodified lignin systems, where compatibilizers are not used.

In addition to mechanical properties, the compatibility between the filler and the polymer matrix plays a crucial role in determining composite performance. Good molecular contact and interfacial adhesion enable efficient stress transfer across the interface, which is especially important when the filler itself is not mechanically strong. One predictive approach to evaluating filler–matrix compatibility is through Hansen solubility parameters (HSPs) (Hansen 2000**,** which estimate the likelihood of two materials being miscible or interacting favorably based on their dispersion, polar, and hydrogen-bonding components. Studies such as by Ruwoldt *et al.* (2020) have applied HSP analysis to lignin–polymer systems, demonstrating that a lower HSP distance (R_a) between lignin and LDPE or HDPE correlates with better dispersion and interfacial adhesion. For example, Ruwoldt *et al.* reported that the calculated R_a between kraft lignin and HDPE was moderately high, indicating partial incompatibility, which could be improved *via* surface modification. Including such assessments helps predict composite morphology and optimize processing conditions for improved performance.

Recent developments in surface modification techniques, such as chemical grafting and plasma treatment, have significantly improved the dispersion and interfacial adhesion between lignin-based fillers and polyethylene matrices. These strategies help overcome compatibility challenges, making LDPE/lignosulfonate/lignin composites increasingly promising as sustainable alternatives to petroleum-based plastics. In this study, LDPE composites were formulated by incorporating sodium lignosulfonate and purified lignin as fillers. The composites were subsequently characterized using mechanical testing (tensile strength, elongation at break), differential scanning calorimetry (DSC), Fourier-transform infrared spectroscopy (FTIR), and scanning electron microscopy (SEM) to comprehensively assess their performance.

EXPERIMENTAL

Materials

Materials used in this research were LDPE (Etilinas Petlin) purchased from Malaysia (425,000 g/mol to 800,000 g/mol) (Heitsch *et al.* 2020), lignosulfonate (Sigma Aldrich from the USA; 534.5 g/mol), and lignin (Sigma Aldrich from the USA; 5% moisture).

Methods

The compounding of LDPE, lignosulfonate, and lignin was performed using a twin-screw extruder (HAAKE Thermo Fisher, Thermo Fisher Scientific Inc., Waltham, Massachusetts, USA) to prepare the composite samples. The materials were processed at temperatures ranging from 120 to 140 °C, with a screw rotation speed of 60 rpm. The compounding process was carried out for 7 min without prior drying of the lignosulfonate and lignin. Various mass of LDPE, lignosulfonate, and lignin used in this study are presented in Table 1. After compounding, the extrudates were pelletized for subsequent characterization.

Table 1. Composites Composition

No.	Code	LDPE (g)	Lignosulfonate (g)	Lignin (g)
1	LL0	50.00	5.00	0.00
2	LL5	47.50	5.00	2.50
3	LL7.5	46.25	5.00	3.75
4	LL10	45.00	5.00	5.00

Mechanical testing

Mechanical properties of the composites were evaluated using a Universal Testing Machine (UTM, Shimadzu AGS-X series, Kyoto, Japan). Prior to testing, tensile specimens were prepared and molded into a dumbbell shape using an injection molding machine (Minijet Pro, HAAKE Thermo Fisher Scientific Inc., USA) at a temperature of 120 °C and a pressure of 20 MPa. The specimens were fabricated in accordance with ASTM D638 (2024), with dimensions of 3.25 ± 0.03 mm thickness, 3.00 ± 0.05 mm width, and 25.94 ± 0.85 mm gauge length. The UTM was equipped with a 10 kN load cell and appropriate grip couplings. Tensile tests were conducted at a constant crosshead speed of 10 mm/min, applying uniaxial force until specimen failure. Three replicate specimens were tested for each composite formulation, and the average values were reported.

Differential scanning calorimetry

Differential scanning calorimetry (DSC) analysis was carried out using a DSC 4000 instrument (Perkin Elmer, Waltham, MA, USA). Approximately 5 mg of each composite sample was accurately weighed and sealed in an aluminum pan by crimping to ensure a tight closure. The sample was then placed into the DSC chamber and subjected to a single heat–cool cycle. The heating process was performed from 10 to 250 °C, followed by cooling from 250 °C back to 10 °C, at a constant rate of 10 °C/min under a nitrogen gas flow of 20 mL/min. The resulting thermograms, showing heat flow (mW) *versus* temperature, were analyzed to identify key thermal transitions, including the glass transition temperature (T_g), melting temperature (T_m), and crystallization temperature (T_c) of the composites.

Thermogravimetric analysis

Thermogravimetric analysis (TGA) was carried out using a TGA 4000 instrument (Perkin Elmer, Waltham, MA, USA). The procedure began with sample preparation, which involved drying the composite to remove moisture and milling it into small, uniform pieces. Approximately 5 to 10 mg of the sample was accurately weighed and placed into a ceramic crucible. The thermal analysis was performed under a nitrogen atmosphere with a flow rate of 20 mL/min, using a constant heating rate of 10 °C/min from 25 to 500 °C. The analysis recorded the weight loss as a function of temperature, enabling the identification of thermal degradation steps and evaluation of the composite's thermal stability.

Melt flow rate

Melt flow rate (MFR) of the composites was measured using a CEAST 7026.000 melt flow indexer (Norwood, MA, USA), following the ASTM D1238-23 (2020) standard method. The sample was weighed carefully and then placed in the preheated hopper of the hot machine. The test was conducted at a temperature of 190 °C under a standard load of 2.16 kg. The polymer melt was allowed to stabilize according to the manufacturer's recommended preheating protocol before testing commenced. The MFR was determined by measuring the mass of material extruded through a standard die (2.095 mm diameter, 8.000 mm length) over a 10-min period. This measurement is important for understanding how easy the process is and how well it melts.

Fourier transform infrared spectroscopy

Thin film samples of LL5 and LL10 composites were subjected to Fourier Transform Infrared Spectroscopy (FTIR) analysis utilizing a Spectrum Two instrument (Perkin Elmer, Waltham, MA, USA) both before and after 30 days of exposure to sunshine. A hot-press machine was used to create uniformly thin sheets of the composite films. For analysis, a sample of around 1 cm × 1 cm was put on the FTIR sample holder. To guarantee correct calibration, a background scan was carried out before every measurement. The samples were examined in transmission mode with a wavenumber range of 4000 to 400 cm^{-1} and a resolution of 4 cm^{-1}. Functional groups and potential chemical alterations brought on by exposure to sunshine were identified and contrasted using the obtained spectra.

RESULTS AND DISCUSSION

Mechanical Properties Analysis

Tensile testing of LDPE/lignosulfonate/lignin composites provides valuable insight of the mechanical properties of the material, in particular tensile strength, elongation at break, and modulus elasticity. In general, the values of tensile strength and modulus elasticity were found to increase with increasing concentration of added lignin, while elongation at break tended to decrease. Although compatibilization is commonly required to achieve good performance, several studies have shown that even unmodified (pristine) lignin, when added at moderate loadings, can contribute positively to mechanical behavior in polyethylene composites. Menta *et al*. (2020) studied tobacco lignin blended with HDPE; when up to 15 wt% lignin was added, tensile strength remained statistically unchanged, while Young's modulus increased by as much as 29%. Degryse *et al*. (2022) investigated low density LDPE lignin membrane composites and observed that at lignin contents of ~40 wt%, tensile strength reached 19.6 MPa and elongation at break ~120%, performance comparable to neat LDPE, despite the absence of lignin modification. Construction of high-content lignin/LDPE composites (without surface grafting) revealed that tensile modulus steadily increased with lignin content up to 30 wt%, although tensile strength decreased slightly at higher loadings—suggesting potential for stiffness enhancement even without compatibilization (Hong and Hwang 2022).

As shown in Fig. 1 and Table 2, the tensile strength, elastic modulus, and elongation at break of LDPE composites (LL0, LL5, LL7.5, and LL10) generally improved with the incorporation of lignin and lignosulfonate. This enhancement is attributed to the reinforcing effect of the fillers: lignin's rigid and aromatic structure increases stiffness, while lignosulfonate's amphiphilic nature improves particle dispersion and interfacial interaction with the hydrophobic LDPE matrix (Szabó *et al.* 2018). However, at higher filler concentrations, agglomeration may occur, which can hinder uniform stress distribution and reduce mechanical performance (Ridho *et al.* 2022). Although chemical bonding with LDPE is limited, the more uniform distribution of fillers reduces weak points in the matrix, enabling more efficient stress transfer. Additionally, minor polar–nonpolar interactions, and the use of compatibilizers, can further enhance mechanical reinforcement (Gou and Guo 2019).

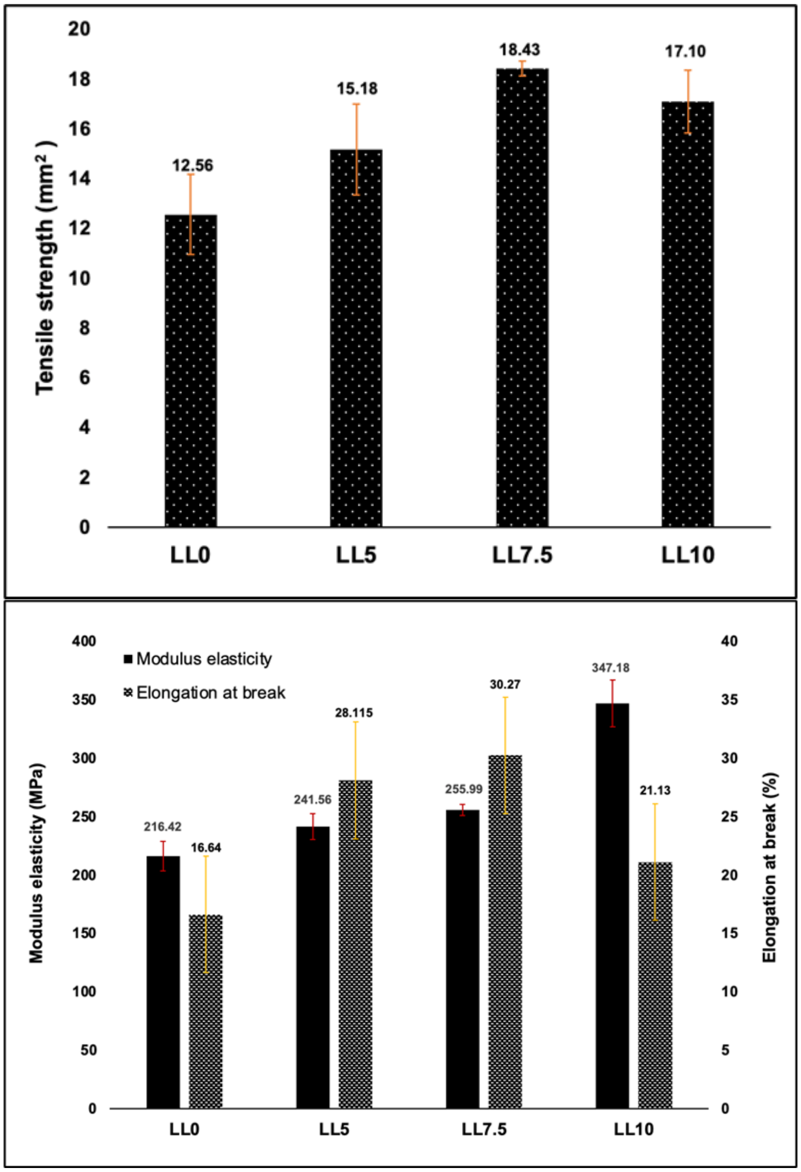

Fig. 1. Tensile strength, modulus elastic, and elongation at break of composites LL0, LL5, LL7.5, and LL10

Nevertheless, the effect on elongation at break is usually more subtle. Along with increased stiffness of the material, lignin can decrease the flexibility and elongation of the composite because of its rigidity. In contrast, lignosulfonate might contribute to maintaining some degree of flexibility through improved dispersion of lignin in the matrix. The general rise in modulus elasticity, an estimate of resistance to deformation by a material, is the indication of the reinforcing action of these natural fillers (Diop *et al.* 2015). However, the specific effect of lignin and lignosulfonate on tensile properties is not only influenced by these parameters related to filler content, dispersion, and the ability of the polymer and fillers to be compatible with each other. Despite the possibility for a decrease in elongation, the increase in tensile strength and modulus indicates that these composites can be used in applications with the need for improved mechanical properties, as well as consistent environmental sustainability.

Table 2. Mechanical Properties of LDPE/Lignosulfonate/Lignin Composites

Source	N	Sample	Mean	Std. Dev	Min	Max	Neat LDPE (ASTM D-638)
Tensile Strength	4	LL0	12.56	1.61	10.77	13.90	8 to 12
(N/mm^2)	4	LL5	15.18	1.82	13.18	16.75	
	4	LL7.5	18.43	0.31	18.11	18.73	
	4	LL10	17.10	1.26	16.20	18.54	
Modulus elastic	4	LL0	216.42	12.68	204.28	229.58	200 to 400
(MPa)	4	LL5	241.56	11.00	229.76	251.52	
	4	LL7.5	255.99	4.71	251.38	260.79	
	4	LL10	347.18	20.13	324.52	363.00	
Elongation at break	4	LL0	16.64	1.90	14.47	18.02	200 to 600
(%)	4	LL5	37.24	16.22	24.50	55.49	
	4	LL7.5	30.27	3.00	28.51	33.73	
	4	LL10	21.13	1.99	16.45	20.01	

The presence of lignosulfonate in the LDPE/lignin composite plays an important role in improving dispersion of lignin particles. Although lignosulfonate is inherently hydrophilic, its sulfonate groups impart electrostatic repulsion between particles, thereby preventing agglomeration and facilitating a more uniform distribution in the polymer matrix (Schneider *et al.* 2021). Additionally, due to its low molecular weight and amphiphilic structure, lignosulfonate can act as a dispersing agent, enhancing the spatial separation of lignin particles within the hydrophobic LDPE phase (Ruwoldt *et al.* 2023). When compatibilizers are used, the polar–nonpolar interactions at the interface may be further improved, contributing to better interfacial adhesion and composite integrity.

Thermal Properties Analysis by DSC

Figure 2 presents the DSC curve of LL0, LL5, LL7.5, and LL10 composites. The curves of LDPE/lignosulfonate/lignin composites exhibited a single melting peak at around 102 °C and were in a similar range of values. Composite without lignin (LL0) showed the most intense sharp melting peak, consistent with a very high crystallinity. Previous research indicates that neat LDPE typically exhibits a melting peak at ~107 °C (Kudelytė *et al*. 2025). Interestingly, the addition of the lignin mixture led to a slight decrease in the crystallinity of LDPE, as indicated by the reduction in the intensity and sharpness of the diffraction peaks (Fig. 2). This phenomenon can be attributed to the interference of lignin particles with the regular folding and packing of LDPE chains during crystallization. Polar functional groups of lignin may interact with the polymer chains, disrupting lamellar formation. Nevertheless, this reduction in crystallinity did not negatively impact the mechanical properties of the composite. In fact, improved mechanical performance was observed, which might be attributed to the better dispersion of the lignin particles and enhanced interfacial adhesion between the lignin and LDPE. These interactions likely facilitate more efficient stress transfer and energy dissipation under mechanical loading, compensating for the loss in crystallinity. With increasing lignin content there was a shift and widening of the melting peak, especially on the LL5 curve, in which an entirely changed heat flow pattern is evident. The reduction in crystallinity is likely due to the disruption of LDPE chain packing by the presence of dispersed lignin particles, which act as physical barriers to crystal growth during solidification. Nevertheless, the mechanical enhancement arises from the rigid aromatic backbone of lignin and its ability to act as a stress transfer medium within the polymer matrix. Hence, improved mechanical performance in this case is not primarily dependent on crystallinity, but rather on effective filler–matrix interactions and uniform particle distribution (Ruwoldt *et al.* 2023; Kaur *et al.* 2021). This indicates that lignin competes with LDPE crystallization, which may come at the cost of reduced crystallinity on account of polymer-filler interactions. Furthermore, the widening of the baseline between the melting peak could be interpreted as moisture evaporation or another structural deformation in the composite. Previous research also obtained the similar results, where the effect of lignin filler concentration on the LDPE/MgO composite produced a DSC graph whose value was almost the same; so that the filler addition had a negligible effect on the composite (Bula *et al.* 2021). Previous research on the analysis of LDPE/graphene nanoplatelet composites obtained uniform DSC curve results, having a single melting peak (Yusof *et al.* 2018).

The melting temperature (T_m) values were approximately the same for all samples, ranging between 107.3 and 107.8 °C. This indicates that the presence of lignin did not significantly influence the thermal stability of the crystalline domains within the LDPE matrix. These limited changes suggest that lignin primarily affects the degree of crystallinity rather than the crystal structure itself, which is known to be the principal determinant of T_m (Ghozali *et al.* 2017). In comparison, however, enthalpy of fusion (ΔH_f) and the degree of crystallinity showed more evident and nonlinear changes with increasing lignin loading. Both ΔH_f and crystallinity decreased compared to the composite without lignin sample (LL0) at 5% lignin loading (LL5). This initial decrease was likely due to the amorphous and irregular nature of lignin, which disrupts the packing of LDPE chains and inhibits the crystallization process. It may also result from phase incompatibility caused by the polar nature of lignin, which is only marginally soluble in the nonpolar LDPE. This leads to limited miscibility and a reduced level of crystallization (Dörrstein *et al.* 2018).

However, at higher lignin contents (7.5% and 10%), ΔH_f values increased, even surpassing those of the unfilled LDPE. This points to some interesting effects of lignin when it is present in higher amounts. Greater rough dispersion of lignin particles facilitates crystallite formation better. Such behavior has been observed in other polymer–biopolymer composites, where lignin serves as a heterogeneous nucleating agent when its dispersion is well-controlled (Kun and Pukánszky 2017). At low concentrations it mainly just messes up the neat crystalline shape. However, high levels help the molecules grow into crystals themselves. The balance between these opposing effects likely depends on the dispersion quality, interfacial adhesion, and processing conditions employed during melt mixing (Zhang 2024). Based on supplier data, the particle size of technical lignin used ranged from 50 to 500 µm, while lignosulfonate particles were finer, typically <150 µm, and they formed colloidal structures when dispersed, especially under melt-mixing or solvent-assisted conditions (Sigma-Aldrich 2023; Ruwoldt *et al.* 2023). The DSC analysis showed that the melting temperature of LDPE remained largely unchanged after lignin incorporation, indicating the absence of strong thermodynamic miscibility.

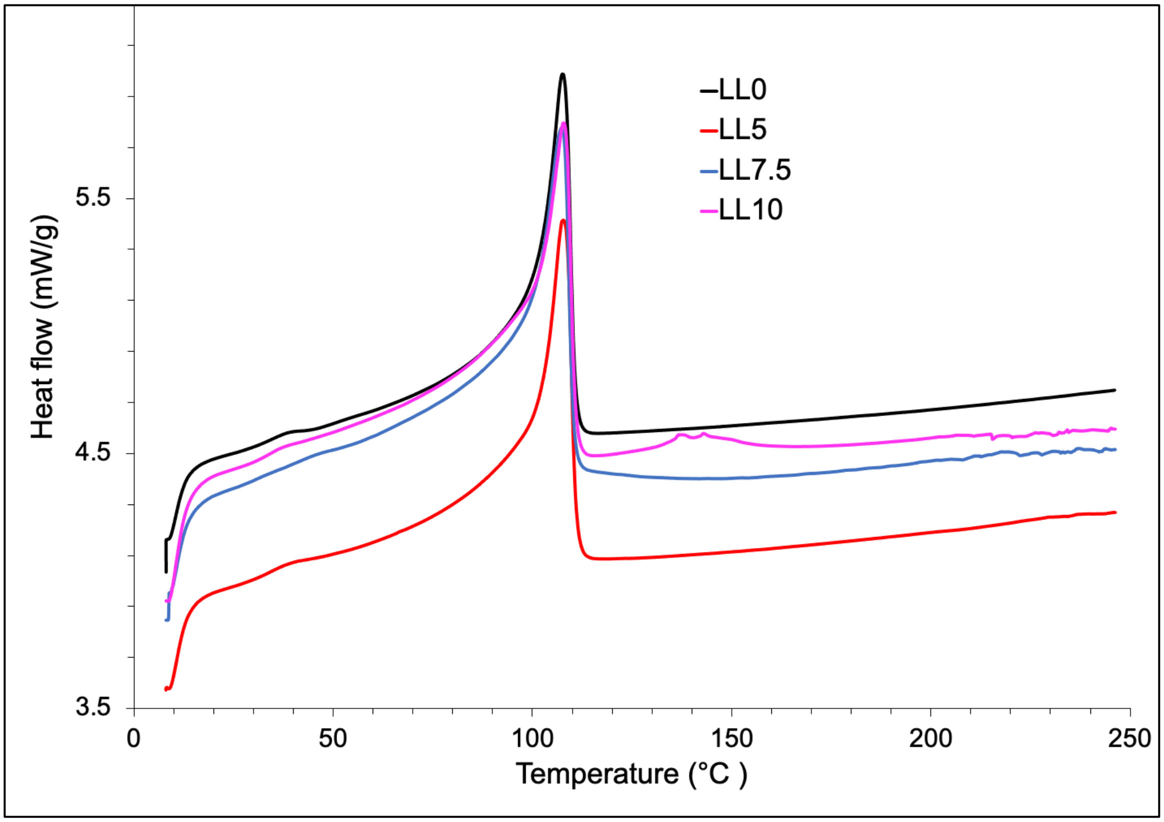

Fig. 2. DSC curve of LDPE/lignosulfonate/lignin composites LL0, LL5, LL7.5, and LL10

Thermal Properties by Thermal Gravimetry Analyzer

The TGA curves describe the thermal degradation properties of LDPE, lignosulfonate, lignin, and their composites by the weight loss with increasing temperature. Figure 3 presents the TGA and DTG curves of pure LDPE, lignosulfonate, lignin, LL0, LL5, LL7.5, and LL10 composites. Composites and LDPE exhibited the same curve trend. Pure LDPE (black curve) showed a clear break between 450 to 500 °C, which is the most general thermal degradation regime. Composite samples (LL0, LL5, LL7.5, and LL10) showed similar behavior, indicating that the addition of lignosulfonate and lignin did not drastically modify the primary thermal stability of LDPE. These results are in accordance with previous research that stated that at a temperature of 400 to 500 °C, LDPE or plastic material degrades (Kudelytė *et al.* 2025).

In contrast, lignin (blue curve) and lignosulfonate (red curve) displayed continuous weight loss from 200 to 400 °C, which is attributed to the breakdown of oxygenated functional groups within the bio-fillers. These degradation events were also reflected in the composite curves, particularly LL5, LL7.5, and LL10, which show a multi-step degradation pattern. Interestingly, despite the observed increase in crystallinity at moderate lignin loadings, the composites with higher filler contents exhibited a reduction in thermal stability within this 200 to 400 °C range. This discrepancy may be explained by the fact that crystallinity and thermal stability are governed by different mechanisms: while lignin may act as a nucleating agent promoting crystallite formation in LDPE, it simultaneously introduces thermally labile domains that degrade earlier than the LDPE matrix (Ruwoldt *et al.* 2023; Kaur *et al.* 2021).

Furthermore, the higher residual weight above 600 °C in the composites compared to LDPE indicates increased char formation due to the aromatic structure of lignin and lignosulfonate, which may contribute to enhanced flame retardancy. Overall, while lignin-based fillers may reduce thermal stability at intermediate temperatures, they do not significantly alter the principal degradation regime of LDPE and may even improve high-temperature char yield.

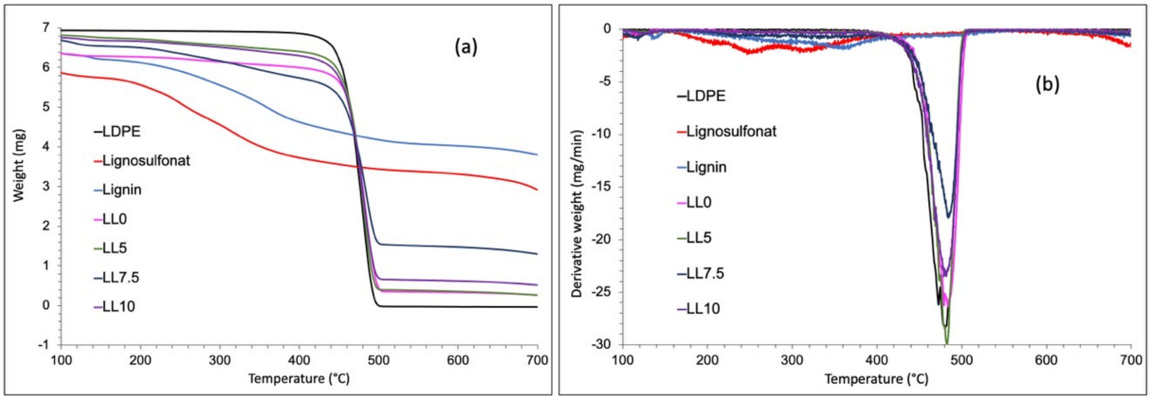

Fig. 3. TGA (a) and DTG (b) curves of LDPE, lignosulfonate, lignin and composites LL0, LL5, LL7.5, and LL10

Thermal Properties by MFR Analysis

Figure 4 shows the Melt Flow Rate (MFR) values of LL0, LL5, LL7.5, and LL10 composites, illustrating a progressive decline in flowability with increasing lignin content. The LL0 sample, containing only lignosulfonate, exhibited the highest MFR value, indicating superior melt flow behavior.

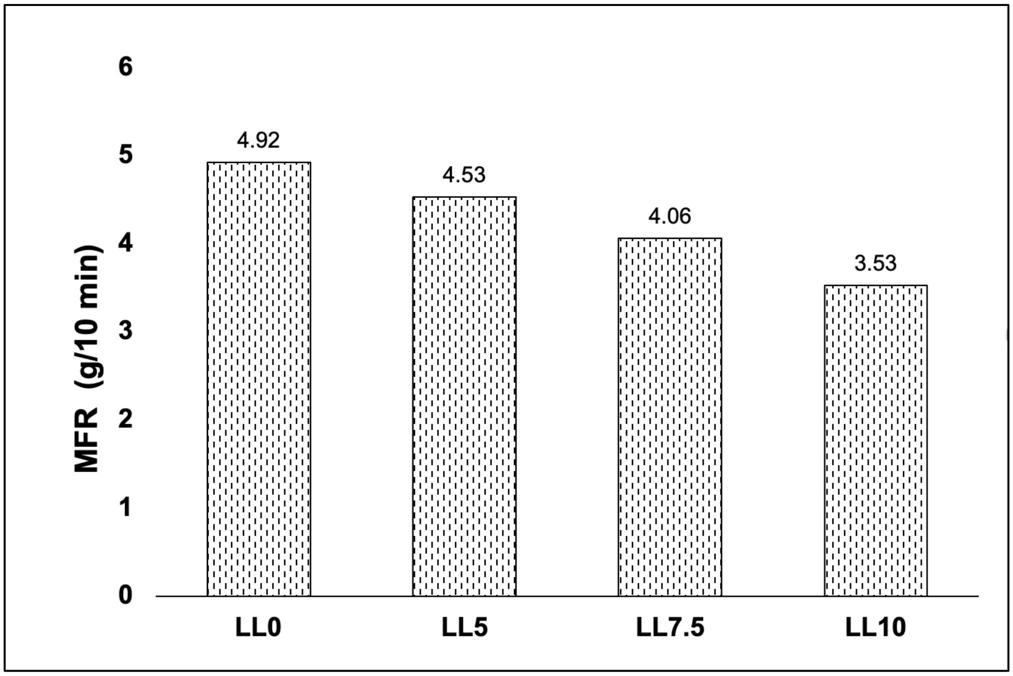

Fig. 4. MFR of LDPE/lignosulfonate/lignin composites LL0, LL5, LL7.5, and LL10

As lignin content was increased from LL5 to LL10, the MFR values decreased monotonically, reflecting a rise in melt viscosity. This trend can be attributed to the physical restriction of polymer chain mobility due to lignin insertion, which promotes intermolecular interactions and possible interfacial adhesion within the polymer matrix (Park *et al.* 2018 and Simionescu *et al*. 2024). Specifically, the increase in viscosity was likely caused by a combination of physical entanglement and weak intermolecular forces, such as Van der Waals forces and dipole-induced interactions, between LDPE and the polar functional groups present in lignin and lignosulfonate. Moreover, hydrogen bonding among filler particles and interfacial friction with the hydrophobic LDPE matrix may further hinder polymer flow and reduce chain flexibility (Ruwoldt *et al.* 2023; Kaur *et al.* 2021). While this viscosity increase may challenge melt processing, it can be advantageous for applications requiring improved dimensional stability and reduced flow under heat.

Hong and Hwang (2022) reported that the MFI of one commercial LDPE in Korea was 0.8 g/10 min. Alexy *et al.* (2000) reported that one commercial LDPE in Slovakia had an MFI value of 1.7 to 2.3 g/10 min. This value is far from the composite produced. Therefore, the addition of lignin filler had observable effect on the MFI of the composite. Previous research about study on the thermal properties of LDPE/Palm Kernel Shell (PKS) composites, showed that the higher the concentration of PKS added, the lower the MFI value of the composite (Salmah *et al.* 2013).

Chemical Structure Stability of Composite under Sunlight Exposure by FTIR Analysis

The FTIR characterization of LDPE/lignosulfonate/lignin composites yielded important information for understanding the chemical interactions between polymer matrix and natural fillers. Figure 5 presents the FTIR spectra of LL5 and LL10 composite before (0) and after thirty days (30) exposure to the sunlight. Spectra often show the characteristic absorption bands of LDPE, including the stretching vibrations of the C-H at 2800 to 3000

cm^{-1} and the bending vibrations at approximately at 1460 to 1470 cm^{-1} area (Boeriu *et al.* 2004). The appearance of either new peaks or intensity changes in the presence of lignosulfonate and lignin may reflect interactions between LDPE and the fillers.

The four curves (LL5(0), LL5(30), LL10(0), and LL10(30)) appear similar, indicating that the basic chemical structure remained the same despite differences in treatment or composition. Peaks associated with -OH groups in lignin and lignosulfonate are typically found in the 3200 to 3500 cm^{-1} range, indicating hydrogen bonding or some other interaction.

Furthermore, the peak due to the sulfonate $-SO_3^-$ groups of lignosulfonate may also lead to a characteristic peak in the range of 1100 to 1200 cm^{-1}, thereby confirming the existence of the lignosulfonate (Karimov *et al.* 2021). These alterations in the FTIR spectrum show successful embedding and (potential) chemical compatibility of the components, which is important for the improvement of the composite properties. Small differences related to intensity can be caused by differences in lignin concentration in the composite and can also be caused by light degradation of the dried composite samples. FTIR spectra did not exhibit any new peaks or significant shifts, suggesting that no chemical bonding occurred between lignin and polyethylene. These results imply that lignin did not dissolve at the molecular level into the LDPE matrix, but rather acted as a physically dispersed filler phase.

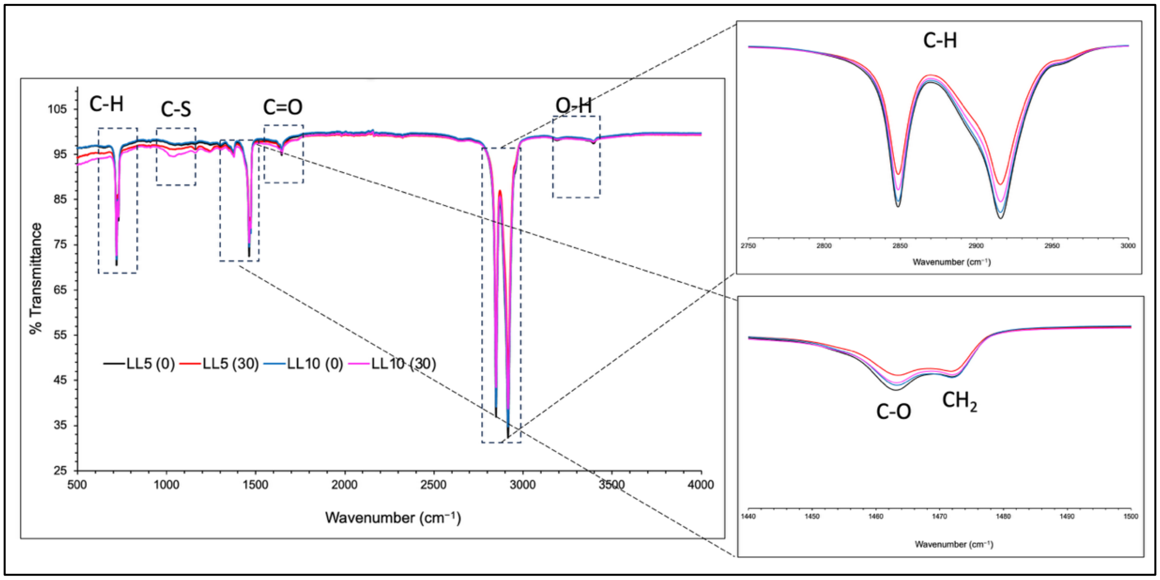

Fig. 5. FTIR spectra of LDPE/lignosulfonate/lignin composites LL5 and LL10 before and after sunlight exposure

CONCLUSIONS

1. Low density polyethylene (LDPE)-lignosulfonate composites reinforced with varying concentrations of lignin were successfully fabricated.
2. Mechanical property analysis indicated that increasing lignin concentration enhanced the tensile strength of the composites, although this effect became limited at higher loadings due to potential lignin agglomeration.

3. There was no significant difference in tensile strength between the LL10 and LL7.5 composites, likely due to lignin agglomeration. The effect was attributed to filler agglomeration and reduced interfacial adhesion at high lignin concentrations.
4. The differential scanning calorimeter (DSC) analysis revealed that all samples (LL0, LL5, LL7.5, and LL10) exhibited a single melting peak at 107 °C, indicating that the addition of lignin and lignosulfonate did not significantly alter the crystalline phase of LDPE.
5. Thermogravimetric analysis (TGA) results showed similar thermal degradation profiles among composites and pure LDPE (400 to 500 °C)**,** while lignin and lignosulfonate degraded earlier (200 to 400 °C). The earlier degradation step in composites was linked to the presence of these bio-fillers, although the main thermal stability of LDPE remained largely unaffected.
6. The melt flow rate (MFR) analysis demonstrated that LL0 had the highest value (4.92 g/10 min), while LL10 had the lowest MFR (3.53 g/10 min). The decreased flow rate is attributed to increased melt viscosity resulting from weak intermolecular interactions, such as Van der Waals forces and dipole-induced interactions, between LDPE and polar functional groups in lignin/lignosulfonate, along with possible hydrogen bonding and interfacial friction
7. The presence of lignosulfonate was found to improve the dispersion of lignin in the hydrophobic LDPE matrix, potentially due to electrostatic repulsion and reduced particle agglomeration. This enhances stress transfer and uniformity in mechanical performance, particularly when assisted by compatibilizers.
8. The Fourier transform infrared (FTIR) analysis before and after 30 days of sunlight exposure showed no significant differences, indicating minimal effects of lignin concentration or exposure duration on the chemical structure.
9. The compatibility between fillers and the LDPE matrix was partially supported by Hansen solubility parameters, which suggest limited miscibility but allow weak interaction potential. Surface modification or compatibilization may be considered in future work to improve interfacial bonding and performance.

ACKNOWLEDGMENTS

This research was supported by the RIIM LPDP Grant and BRIN, grant number B-803/II.7.5/FR/6/2022 and B-1373/III.5/PR.03.08/6/2022. We also thank the Research Organization for Life Sciences and Environment. The authors acknowledge the facilities and technical support from Advanced Characterization Laboratories Cibinong – Integrated Laboratory of Bioproduct, National Research and Innovation Agency.

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Article submitted: May 5, 2025; Peer review completed: June 30, 2025; Revised version received: August 3, 2025; Accepted: October 6, 2025; Published: January 13, 2026.
DOI: 10.15376/biores.21.1.1851-1868