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ORIGINAL PAPER

Exploring lignin types in circular by design polyethylene blends for injection moulding applications: interactions and properties

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Abstract

In the context of developing circular by design lignin-based linear low-density polyethylene (LLDPE) blends, the interactions between lignin-lignin and lignin-LLDPE using three different types of lignin—hardwood and softwood kraft lignin, and hardwood sulphite lignin (designated as SUZ, IND, and VIX, respectively)—were studied. This work focuses on improving both mechanical properties and biodegradability to design products that minimize plastic waste and enhance environmental performance, in alignment with the principles of a circular economy. The unmodified lignins were thoroughly characterized and reduced in size (38–75 µm) before melt blending with LLDPE in a twin-screw extruder in proportions up to 10%. The pelletized blends were further processed into dumbbell-shaped specimens by injection moulding. Thermal, morphological, mechanical and biodegradation tests were performed on the specimens. The LLDPE blend containing 10% VIX exhibited good dispersion (particles less than 200 nm) and combination of stiffness (0.7 GPa), tensile strength (11 MPa), elongation at break (47%) and thermal stability (455 °C). Additionally, biodegradation tests conducted through soil burial and *Aspergillus niger* solid medium revealed a weight loss ten times greater than that of neat LLDPE over 90 and 180 days, respectively, at a 10% lignosulfonate content. Tensile strength was poor for the SUZ-based blends. The LLDPE-IND blends exhibited comparable tensile strength to LLDPE-VIX although biodegradation and thermal properties were lower. The Coulomb forces in sulphite lignins, with monovalent counterions, promote lignin disaggregation and miscibility during the melt and thermal processing, enhancing interfacial interactions and the final properties of the LLDPE blends.

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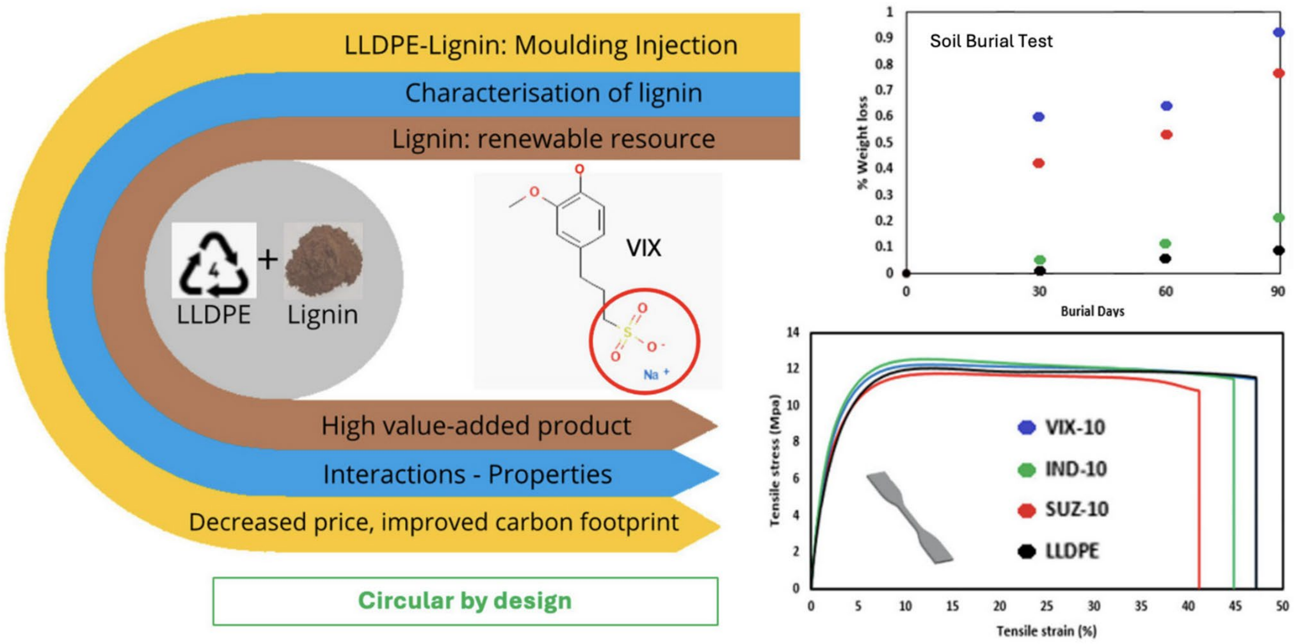
Graphical abstract



Keywords Kraft lignin · Sodium lignosulfonate · Thermoplastics · Injection moulding · Biodegradability

Introduction

Lignin is the second most abundant biopolymer of lignocellulosic biomass after cellulose, and itself is "circular" with a slow biodegradation in soils (Parit and Jiang 2020; Tardy et al. 2023). In a composting environment, thermophilic micro-fungi and actinomycetes break down lignin in the presence of oxygen at temperatures ranging from 40 to 50 °C. Insufficient mineralization leads to the utilization of lignin-derived compounds as starting materials for humus formation (Tuomela et al. 2000). In fact, "circular" highlights lignin's potential to be reused and recycled in biological systems, aligning with the principles of the circular economy that aim to minimize waste and maximize the reuse of materials.

Industrial lignin is a common "by-product" used as a cost-efficient energy source in the pulp and paper sector that could be efficiently converted into value-added products such as fine chemicals, carbon materials, and lignin-based materials. Since the demand for sustainable raw materials is growing quickly, the global lignin market valued USD 808.82 Billion in 2022 is predicted to grow to around USD 1474 Billion by 2030 corresponding to an average annual growth of 5.9% between 2023 and 2030 (Zion Research 2014).

The role of lignin and polyolefins in circularity follows different paradigms. For polyolefins, the focus lies in reducing their environmental footprint, while for lignin, the emphasis is on transitioning from an energy source to a valuable material resource. Incorporating lignin into polyolefins like linear low-density polyethylene (LLDPE) can enhance biodegradation, providing a substrate that microorganisms can break down more easily compared to pure polyethylene. Lignin biodegradation can be facilitated by fungi, among lignocellulosic fungi, *Basidiomycetes* (white- and brown-rot fungi), *Ascomycetes* and *Deuteromycetes* (soft-rot fungi), and anaerobic (rumen) fungi are the most important (Madadi and Abbas 2017). Soft-rot fungi degrade wood very slowly as compared to white-rot and brown-rot fungi and are the most efficient fungi to degrade lignin in mixed microbial populations (Madadi and Abbas 2017). Moreover, blending lignin with polyolefins can lower the carbon footprint and avoid the end of life (EoL) problems associated with conventional plastics by replacing a portion of petroleum-based materials with a renewable by-product from the pulp and paper industry (Tardy et al. 2023).

Lignin is an amorphous biopolymer with a very complex random structure based on guaiacyl (G), syringyl (S) and p-hydroxyphenyl propane (H) moieties linked by C–C and C–O–C bonds. The ratio of lignin moieties depends on their (softwood, hardwood, or non-wood) source. Hardwoods contain both S and G units with S in its majority, softwoods mainly contain G units, while H units predominate in nonwood lignins.

Any process of separation of the cellulose-hemicellulose-lignin assembly, modifies and degrades the components. The main commercial source of technical lignin currently comes from the pulp and paper industry. The term "technical lignin" refers to the lignin-rich fraction obtained after a biomass separation process. Among the most relevant types are kraft lignin and sulphite lignin (or lignosulfonate), which are sulphur-containing lignins derived from the kraft and sulphite processes, respectively. Kraft lignins are typically obtained by acid precipitation of black liquor followed by drying, resulting in a product with a residual ash content of 2–6% and a high phenolic hydroxyl group (Ph-OH) content of 2.6–4.5%. This type of lignin is heavily condensed, with molecular weights ranging from 1000 to 5000 g mol^{-1} (Kai et al. 2016). In contrast, lignosulfonates are isolated through organic solvent extraction and recovered by the addition of a base and subsequent drying. Unlike kraft lignins, lignosulfonates are polysalts that exhibit mixed polyelectrolyte-ionomeric behaviour in aqueous solutions (Lugovitskaya and Naboychenko 2020). Furthermore, lignosulfonates have higher ash content, molecular weight, and a broader dispersity index (Đ) compared to kraft lignins.

The main chemical groups present in technical lignins are nonpolar groups (aromatic moieties and residual aliphatic chains), polar groups (ether linkages, ketones, methoxy and aliphatic hydroxyl groups) and ionizable groups (phenolic hydroxyl and carboxylic groups) (Ruwoldt 2020). Kraft lignin sulphur content (1–2%) is in the form of polar aliphatic thiol groups (Kai et al. 2016) meanwhile (up to 5%) lignosulfonate sulphur content is in the form of ionizable sulfonate groups (Ruwoldt 2020). Sulfonate groups contribute to the high solubility of lignosulfonate in water, which is different from kraft lignin that requires alkaline aqueous solutions for solubility (pH > 10).

Several attempts have been conducted on the use of lignin in polyolefins blends over the last decades (Toriz et al. 2002, Bozsódi et al. 2016, Szabó et al. 2017, Dias et al. 2019, Romhányi et al. 2018, Pregi et al. 2022, Alexy et al. 2000, Jeong et al. 2012, Pucciariello et al. 2004, Olsson et al. 2011, Diop et al. 2015, Bula et al. 2019, Samal et al. 2009, Ghozali et al. 2017, Chiappero et al. 2021, Dehne et al. 2016, Sameni et al. 2018), see Table S1. These studies have focused on improving the weak interactions between polar lignin and nonpolar polyolefins through various strategies, including plasticization, chemical modification of lignin (e.g. esterification), the use of coupling agents, and, more recently, combining lignin with reinforcement materials, fillers, or fibres to create hybrid materials. Most of the previous studies assume that variations in lignin type do not have a substantial impact on the behaviour of polyolefin blends (Szabó et al. 2017). Additionally, variations in polyolefin characteristics such as melt mass-flow rate (MFR), melt blending systems (e.g. bowl mixer, internal mixer, single and twin-screw extruders), and thermal processing methods (e.g. extrusion, compression, and injection moulding), as well as processing conditions complicate the ability to draw a general conclusion about the impact of lignin on processing performance and final material properties. Despite the discrepancies about the preparation of lignin/polyolefin blends, stiffness usually increases in larger or smaller extent, but tensile strength and deformability often decrease as result of poor interactions in the heterogeneous structure.

The melt blending and thermal processing are directly affected by the glass transition temperature (T_g) and thermal decomposition temperature of lignin. Impurities, repolymerization and depolymerization, hydrogen bonding and linkages, molecular weight and Đ are some of the features that affect melt properties (Akpan and Adeosun 2019). The G units promote crosslinking through reactive C5 sites when the temperature is increased above the lignin T_g. A low Đ means high molecular size homogeneity and fusibility of all molecules at the same time. While adsorb water and aliphatic hydroxyl groups form intermolecular hydrogen bonding with a restriction in mobility, phenolic hydroxyl groups tend to form intramolecular hydrogen bonding with methoxy groups avoiding aggregation and favouring fusibility (Akpan and Adeosun 2019). The presence of carbohydrates can contribute to increase hydroxyl groups and adsorb water (Compere et al. 2001).

The strong interactions and the usually small molecular weight of technical lignin result in a stiff and brittle material that conduct to the formation of heterogenous polyolefin blends resulting in a large lignin aggregates dispersion. In the self-association lignin process the formation of noncovalent interactions play a significant role. Such interactions include van der Waals forces (< 1 and 4 kJ·mol − 1), hydrogen bonding (between 4 and 30 kJ·mol − 1), π–π interaction (between 4 and 30 kJ·mol − 1) and chain entanglement (Dhotel et al. 2013). Additionally, electrostatic interactions are present in lignosulfonates, where divalent counterions like Ca^{2+} serve as electrostatic bridges between molecules, promoting the formation of aggregates (Lugovitskaya and Naboychenko 2020; Myrvold 2015).

As far as the authors are aware, comparative studies on the effects of technical lignins with different noncovalent forces on the final properties of the polyolefin blends are scarce (see Table S1). Understanding the assembly and molecular architecture of lignin aggregates in polyolefin blends, correlating them with the final properties of the blends, as well as the molecular composition and structure of various types of lignin, is crucial for the development of tailor-made blends and circular 'by design' lignin-based products.

In this sense, a deeper knowledge of the competitive lignin-lignin and lignin-polyolefins interactions, may help to choose the right lignin that promotes a better interfacial adhesion and contribute to the circularity of lignins through lignin-dependent implementation of circular processes. In addition, literature that compares different sources of lignin on biodegradation are seldom reported (Ghozali et al. 2017; Rusu and Tudorachi 1999; Tudorachi et al. 2020) and more investigation is needed for the development of blends that maximize this property.

This study presents a novel approach by analysing three types of lignin—hardwood kraft, softwood kraft, and hardwood lignosulfonate—blended with a widely used and easily processable thermoplastic, LLDPE. While previous studies have extensively explored lignin as a filler, they often focus on a single type without considering how variations in lignin structures and interactions influence the material's properties. This work addresses that gap, providing a comprehensive analysis of how different lignin interactions affect the performance of the blends. Moreover, this study emphasizes lignin's role in circular economy strategies, going beyond the mechanical enhancements typically targeted in previous research. It evaluates the potential of lignin to improve biodegradability, reducing the environmental impact of the blends. This dual focus on mechanical properties and sustainability makes this study a significant contribution beyond the established use of lignin as a simple filler.

The lignin-lignin interactions were investigated by a comprehensive characterization of the lignins, while interfacial interactions between lignin aggregates and LLDPE were studied using morphological and mechanical analyses. Additionally, soil burial and *in-vitro* fungal tests were conducted on the blends. Both the soil burial and *in-vitro* fungal tests aim to provide a comprehensive understanding of how the inclusion of lignin in LLDPE blends affects their biodegradability in natural environments.

Materials and methods

Materials

The LLDPE used in the experiments was supplied in granulated form by Braskem S.A. (Triunfo/Brazil) with a MFR of 29 g/10 min (190 °C, 2.16 kg) and a density of 0.924 g cm^{-3}. Three technical lignins were used in LLDPE blends: **VIX**, a eucalyptus sodium lignosulfonate (Vixilex SDX) from LignoTech (Brazil); **SUZ**, a eucalyptus kraft lignin supplied by Suzano Pulp and Paper (Brazil); and **IND**, a pine kraft lignin (Indulin AT) produced by MeadWestvaco Corporation (USA). The reagents used for the characterization of lignins were 1,4-dioxane (analytical grade, Cicarelli), NaOH (≥ 98%, Cicarelli), KH_2PO_4 (≥ 99%, Anedra), $Na_2B_4O_7 \cdot 10H_2O$ (≥ 99%, Anedra), and methanol (HPLC grade, Cicarelli).

Characterization and pre-treatment of lignins

The characterization of lignins involved the following measurements: moisture and ash contents, carbohydrates, solubility in distilled water and 0.1 N NaOH solution, analysis of functional groups using Fourier transformed infrared spectroscopy (FTIR), Ph-OH content by difference UV-spectroscopy, number-average molecular weight (*Mn*) and weight-average molecular weight (*Mw*) employing Size Exclusion Chromatography (SEC), glass transition temperature by Differential Scanning Calorimetry (DSC), and thermal stability using Thermogravimetric Analysis (TGA). See Characterization methods S1.

Before blending with the LLDPE, lignins were dried in an oven with air circulation at a temperature of 60 °C for 24 h. Then, a particle size reduction was carried out in a ball mill, and particles between 38 and 75 µm were sieved using 400-mesh and 200-mesh sieves.

LLDPE-lignin blends

The LLDPE-lignin blends shown in Table 1 were prepared by melt extrusion using a HAAKE Rheomex P332 twin-screw extruder, 16 mm and L/D = 25 rate from Thermo Scientific located at Centro de Quimica e Meio Ambiente CQMA- IPEN/CNEN-SP. The processing temperature profile was 170/170/175/180/185/185 °C and the screw rotation was 60 rpm. The extruded materials were cooled down in water at room temperature for a better dimensional stability, pelletized and dried again at 60 ± 2 °C for 48 h. The pelletized blends were further processed into dumbbell-shaped specimens by injection moulding, using an AX Plásticos® laboratory injection moulding machine, model AX16I. The temperature profile used was 170/175/180/185 °C, and the mould temperature was set to 100 °C.

When preparing the LLDPE-lignin blends, the molecular properties of LLDPE and the initial particle size distribution of lignin were carefully considered to ensure consistency across samples.

The selected LLDPE has a MFR of 29 g/10 min and a density of 0.924 g/cm^3, characteristics indicative of a moderately branched molecular structure that balances processability and mechanical properties. Since all blends were processed under the same extrusion and injection moulding conditions, variations in LLDPE molecular weight or branching density are expected to have minimal impact on the comparative analysis of different lignin types.

All lignins were milled and sieved to a particle size range of 38–75 µm before blending (Sect. "Characterization and pre-treatment of lignins"). While this preparation controls

Table 1 LLDPE-lignin blends: Composition, thermal and mechanical properties

Name	Composition	Thermal properties				Mechanical properties		
		T5% (°C)	T50% (°C)	Char (%)	TMR (°C)	Tensile strength at break (MPa)	Elongation at break (%)	Young's modulus (MPa)
LLDPE	100% LLDPE	285	415	0.10	440	11.55 ± 0.9	47.18 ± 0.7	683.32 ± 20.1
SUZ-2.5	97.5% LLDPE–2.5% SUZ	315	418	0.38	441	10.83 ± 0.9	44.31 ± 1.1	690.21 ± 15.6
SUZ-5	95% LLDPE–5% SUZ	328	434	0.13	443	10.94 ± 1.5	44.73 ± 0.9	692.44 ± 18.3
SUZ-10	90% LLDPE–10% SUZ	334	437	0.84	446	10.82 ± 1.2	41.14 ± 1.4	698.48 ± 20.6
IND-2.5	97.5% LLDPE–2.5% IND	300	452	0.76	467	11.58 ± 1.5	44.48 ± 0.8	700.12 ± 21.4
IND-5	95% LLDPE–5% IND	345	445	0.77	457	11.52 ± 1.7	43.71 ± 1.9	696.32 ± 13.3
IND-10	90% LLDPE–10% IND	344	446	0.89	453	11.40 ± 1.0	44.82 ± 1.5	710.33 ± 23.2
VIX-2.5	97.5% LLDPE–2.5% VIX	340	454	0.68	456	11.27 ± 1.2	44.31 ± 1.1	739.21 ± 10.9
VIX-5	95% LLDPE–5% VIX	341	447	0.61	457	11.40 ± 0.8	46.15 ± 1.7	764.13 ± 19.2
VIX-10	90% LLDPE–10% VIX	339	450	0.98	455	11.44 ± 1.3	47.14 ± 1.8	744.22 ± 20.2

the initial particle size, the final particle size within the polyolefin matrix is still influenced by thermodynamic and kinetic factors during melt blending and thermal processing—including lignin-polyolefin interactions and lignin's self-aggregation behaviour. These aspects will be further discussed in the results section to clarify their impact on blend performance.

Thermal stability of the blends was performed using TGA (see Characterization methods S1). Also, morphological, mechanical and degradation tests were conducted.

Field Emission Scanning Electron Microscope (FE-SEM) of cryofractured LLDPE/lignin blends under liquid nitrogen was performed using a JEOL-JSM-6701 F microscope with an accelerating voltage of 1–30 kV, using EDS Thermo-Scientific Mod. Noran System Six software, on carbon sputtered samples.

The tensile strength, Young's modulus, and elongation at break were measured in quintuplicate on a Universal Testing Machine SHIMADZU and all specimens were performed according to ASTM International (2018) at room temperature and loading rates of 50 mm/min.

Biodegradation tests were conducted for neat LLDPE and LLDPE blends with 10% lignin. The soil burial test was carried out in a flowerpot containing farmland soil maintaining high relative humidity by daily sprinkling water at room temperature. Each specimen (40 × 20 mm) was buried in the soil, dug out after a period of 30, 60 and 90 days and washed with water and dried. Weight loss was measured throughout the test. Also, an *in-vitro* fungal degradation test was conducted to investigate the biodegradation of the material by *Aspergillus niger*, a widespread soft-rot fungi in soils. Specifically, the fungal growth medium for the *in-vitro* biodegradation test was prepared using the following chemicals dissolved in water: KH_2PO_4 (2000 mg/L), K_2HPO_4 (7000 mg/L), NH_4NO_3 (1000 mg/L), glucose (3000 mg/L), $MgSO_4 \cdot 7H_2O$ (100 mg/L), $ZnSO_4 \cdot 7H_2O$ (1 mg/L), $CuSO_4 \cdot 5H_2O$ (0.1 mg/L), $FeSO_4 \cdot 7H_2O$ (10 mg/L), and $MnSO_4 \cdot H_2O$ (2 mg/L). The sterilized agar medium was poured into a sterile Petri dish, onto which sterilized samples were placed, followed by the inoculation of *Aspergillus niger* spores. The samples were incubated for 180 days at 30 °C, with an intermediate sample taken at 90 days. Upon removal, the samples were washed with water and dried before weight loss measurements.

The biodegradation tests were performed on a single sample to evaluate trends from preliminary results rather than to obtain precise quantitative values. By examining a single sample, we assessed the overall biodegradation performance and determined whether the blend exhibits favourable characteristics, such as improved degradation rates or enhanced interactions with microbial populations. This approach can guide further research and help refine hypotheses for subsequent studies.

Results and discussion

Characterization of lignins

Chemical properties

Table 2 presents the chemical characterization of lignins. IND is the purest lignin, with ash and carbohydrate contents almost 5 and 30 times lower, respectively, than those of SUZ and VIX. The moisture content of VIX is the highest, attributed to the highly polar sulfonic groups present in lignosulfonate, which interact strongly with water, rendering it water-soluble despite its high *Mn* and *Mw*. IND is water-insoluble meanwhile SUZ is water-soluble. This difference in solubility can be explained based on the low *Mn* and *Mw*

Table 2 Lignin Characterization

	SUZ	IND	VIX
Chemical properties:			
% Moisture	7.88	4.72	13.33
% Ash (dry basis)	17.84	4.31	22.16
% Carbohydrate (dry basis)	3.48	<0.01	4.42
% Purity (dry basis)[a]	78.7	96.7	73.42
Solubility			
Water	soluble	insoluble	soluble
NaOH 0.1 N	soluble	soluble	soluble
Mw(g mol^{-1})	784	8389	6857
Mn(g mol^{-1})	716	1800	1412
Đ (Mw/Mn)	1.09	4.66	4.86
Functional groups:			
Aliphatic to phenolic OH ratio [b]	0.67	0.61	0.71
Phenolic OH [c] (OH/C9)	0.53	0.50	0.25
G/S [c]	60/40	84/16	59/41
Total (OH/C9)	0.89	0.81	0.43
Thermal properties:			
T_g (°C)	162	133	186
16–200 °C	7	4	12
Weight loss (%)			
600–800 °C	18	6	12
Char (%)	33	47	39

[a]%Purity = 100—%Ash (dry basis)—%Carbohydrate (dry basis), [b] From FTIR measurements, and [c] From UV-spectroscopic measurements

which favour solubility in water. The high Đ of IND reflects a broader Mw. Softwood lignin, rich in G units, has more reactive positions for forming C–C and C–O–C linkages, leading to a more condensed structure (Sharma and Kumar 2020). In contrast, hardwood lignin contains more S units, which have methoxy groups that limit crosslinking and result in a more linear structure, thus yielding a lower Đ.

Functional groups

In accordance with the literature, Table 2 shows that the Ph-OH content of SUZ and IND kraft lignins is twice that of VIX, while the G/S ratio of hardwood lignins (SUZ and VIX) is lower than that of the softwood IND lignin, which is primarily composed of G units (Bula et al. 2019).

The VIX, IND and SUZ FTIR spectra are given in Fig. 1. Despite the differences in intensities and widths of the absorption bands all spectra of Fig. 1a show typical lignin patterns. The wide band in the range of 3500–3100 cm^{-1} (peak 1) is characteristic of alcoholic and phenolic hydroxyl groups involved in hydrogen bonds.

The two absorption bands (peaks 2 and 3) in the range of 3100–2800 cm^{-1} are related to the asymmetric stretching vibration meanwhile the band at 1457 cm^{-1} (peak 6) corresponds to the in plane bending of C-H in methyl and methylene structures. The corresponding bands at 1609, 1512, 1420 cm^{-1} and 1599, 1512, 1427 cm^{-1} and 1600, 1516, 1421 cm^{-1} (peak 4, peak 5 and peak 7) for VIX, IND and SUZ are assigned to aromatic skeletal vibrations of the aromatic rings. Additionally, VIX exhibits the characteristic S–O band of lignosulfonate at 652 cm^{-1} (peak 8) (Wibowo and Park 2023), meanwhile the signals at 619 and 623 cm^{-1} (peak 9) for kraft lignins are assigned to C–S bending (Fodil Cherif et al. 2020).

The characteristic G and S signals are displayed in Fig. 1b. Signal absorptions at 1207, 1218, 1217 cm^{-1} and 1042, 1034, 1043 cm^{-1} for the corresponding VIX, IND and SUZ are attributed to G bands. Also, IND exhibits a quite intense absorbance of G band at 1271 cm^{-1} compared to those of hardwood lignins which suggests a higher G content. The moderate signal at 1331 cm^{-1} for SUZ, with absence in IND and VIX, is attributed to S band with C = O bending. Also, SUZ exhibits a quite intense peak at 1119 cm^{-1} characteristic of S band.

Relative quantification was performed by comparing the intensities of aliphatic/phenolic hydroxyl signals within the same spectrum to establish their relationships. The aliphatic/Ph-OH ratio presented in Table 2 was calculated using the ratio of peak 2 to peak 5 intensities, and it increases in the following order: IND < SUZ < VIX, with higher values observed for hardwood lignins.

Thermal properties

Table 2 shows that the T_g of SUZ is higher than that of IND. Despite having low molecular weights and a low G/S ratio, factors that typically favour chain mobility, the presence of impurities and higher aliphatic hydroxyls in SUZ significantly hinder thermal mobility, leading to an increase in T_g (Akpan and Adeosun 2019). Carbohydrates are not free but as lignin carbohydrate complexes which can contribute to rise in the amount of aliphatic OH groups in SUZ. On the other hand, VIX exhibits the highest Tg. Pendent sulfonate groups in VIX elevate T_g due to the ionomeric associative effect (intramolecular interaction) and the bulkiness of the sulfonate groups hinder rotation about the polymer chain (McGrath et al. 2005).

Figure 2 shows the TGA curves of lignins during the pyrolysis process, while the weight loss percentages and char are given in Table 2.

According to the literature, the thermal decomposition of lignin occurs over a wide temperature range (200–500 °C) under nitrogen due to the complex lignin structure (Brebu and Vasile 2010; Klapiszewski et al. 2016; López-Beceiro et al. 2021). Below 200 °C, the weight loss involves the desorption of bound water and volatiles release such as guaiacol derivates

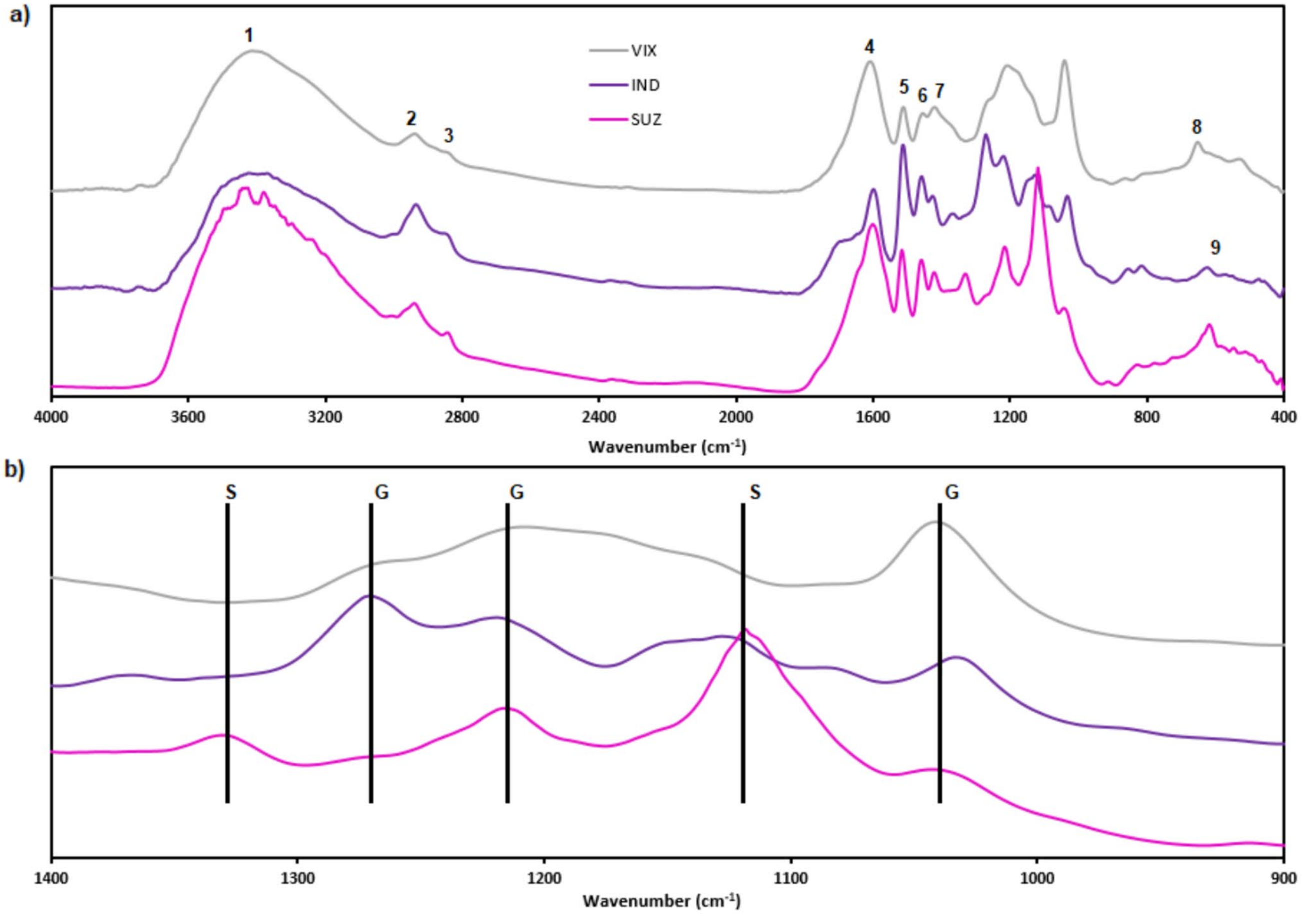


Fig. 1 FTIR spectra of lignins: **a** 4000–400 cm^{-1}, and **b** 1400–1000 cm^{-1}

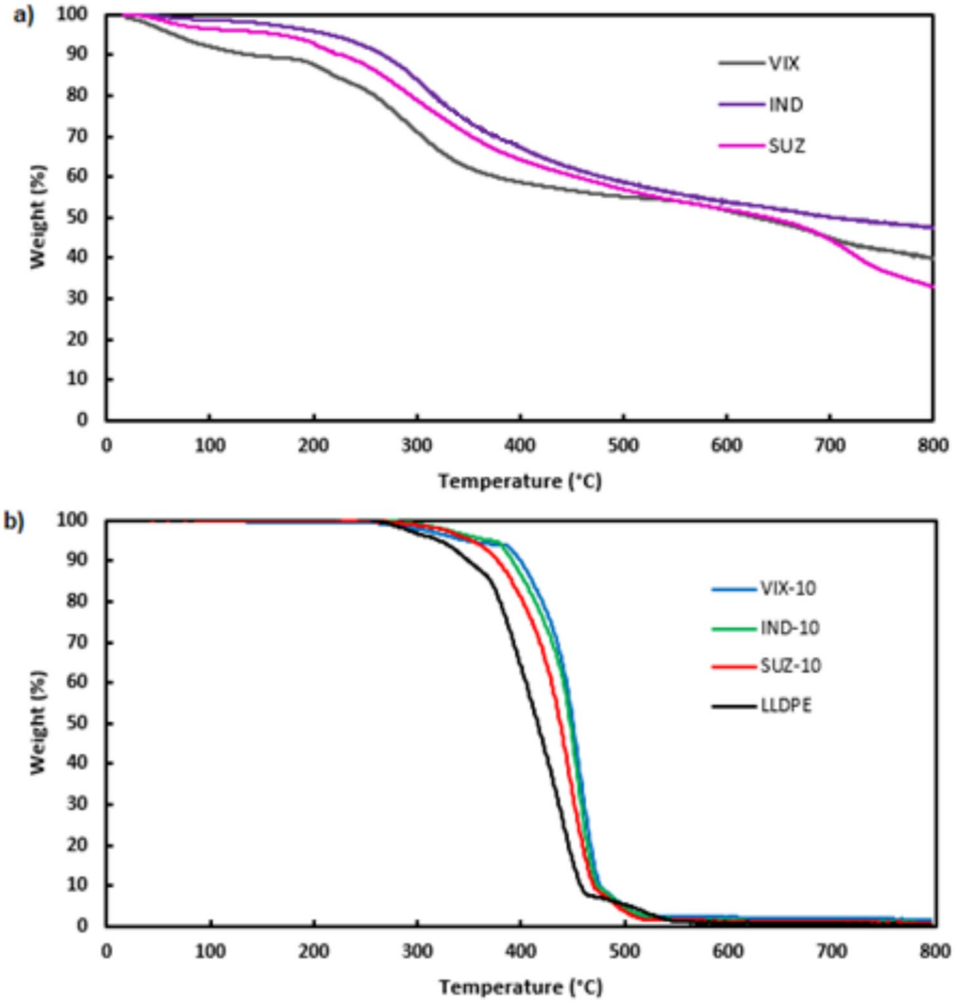
(Brebu and Vasile 2010; Shi et al. 2012). The weight loss percentages given at the bottom of Table 2 are in accordance with the moisture content of each lignin shown at the top of Table 2. Between 200 and 600 °C, the maximum rate of weight loss (T_{MR}) is around 300 and 315 °C for hardwood (SUZ and VIX) lignins and IND, respectively. Above 600 °C, fragmentation and degradation occur. In contrast to IND, both VIX and SUZ follow the trend that a lower ash content correlates with a lower carbon residue. The distinct behaviour of IND suggests that further decomposition and recondensation reactions may be occurring, which are likely more pronounced in softwood lignins due to their higher content of G units. These reactions could result in a more condensed structure that influences the residual carbon content after pyrolysis (Tejado et al. 2007; Zhao and Liu 2010; Monteiro et al. 2021).

Characterization of blends

Thermal properties

Table 1 summarizes the TGA and DTG results including the degradation temperatures at which 5 and 50% of the initial mass are lost (T5 and T50%), the TMR, and the percentage of char produced at 800 °C for neat LLDPE and the lignin-based blends. The neat LLDPE degraded completely in a single step due to the cleavage of carbon atoms (C–C) with a residue of 0.1% as reported by Shebani et al. (2009). The 10% lignin-based blends exhibited a significant char residue approximately 10 times higher than for neat LLDPE. The temperature at which half of the initial mass of the sample is lost increases in the following order

Fig. 2 TGA curves: **a** Lignins, and **b** neat LLDPE and 10% lignin-based LLDPE blends



LLDPE < LLDPE-SUZ < LLDPE-IND < LLDPE-VIX. Interestingly, the thermal behaviour trend of pristine VIX is not the same in LLDPE blends. Despite the low thermal stability of VIX (Fig. 2a) the LLDPE-VIX blend (Fig. 2b) exhibits the best thermal stability revealing an enhanced matrix-lignin interaction.

Morphological properties

As shown is Fig. 3, the surface morphology of all LLDPE-lignin blends is heterogeneous, lignin spheres dispersed in the polyolefin matrix at all compositions.

The original lignin particles of about 75 µm size break up during melt blending and thermal processing to smaller particles dispersed in the matrix. The average particle size of lignin spheres is around 4, 1.5 µm and 200 nm for IND, SUZ and VIX, respectively. The smaller the particles the stronger the LLDPE-lignin interactions and miscibility. According to Fig. 3b interactions between LLDPE and VIX are stronger (smaller spherical lignin particles and thicker interphase) than between kraft lignins and LLDPE (Fig. 3a and c). The final size of particles depends on thermodynamic and kinetic effects (Szabó et al. 2017). For the same mixing conditions (shear stress and time) and thermal processing (pressure and time) the size of particles mainly depends on interactions. The low average molecular weight (weak entanglement forces) and the low Đ (high homogeneity) makes SUZ better dispersed than IND in the polyolefin matrix. Despite the high average molecular weight and Tg of VIX, particles break up into smaller fragments due to the repulsive Coulomb forces between the like monovalent charges redistributed by friction during melt blending and thermal processing (Mimini et al. 2019).

Mechanical properties

Figure 4 shows the tensile stress–strain curves for a representative specimen (out of five) from the 10% lignin-based LLDPE blends.

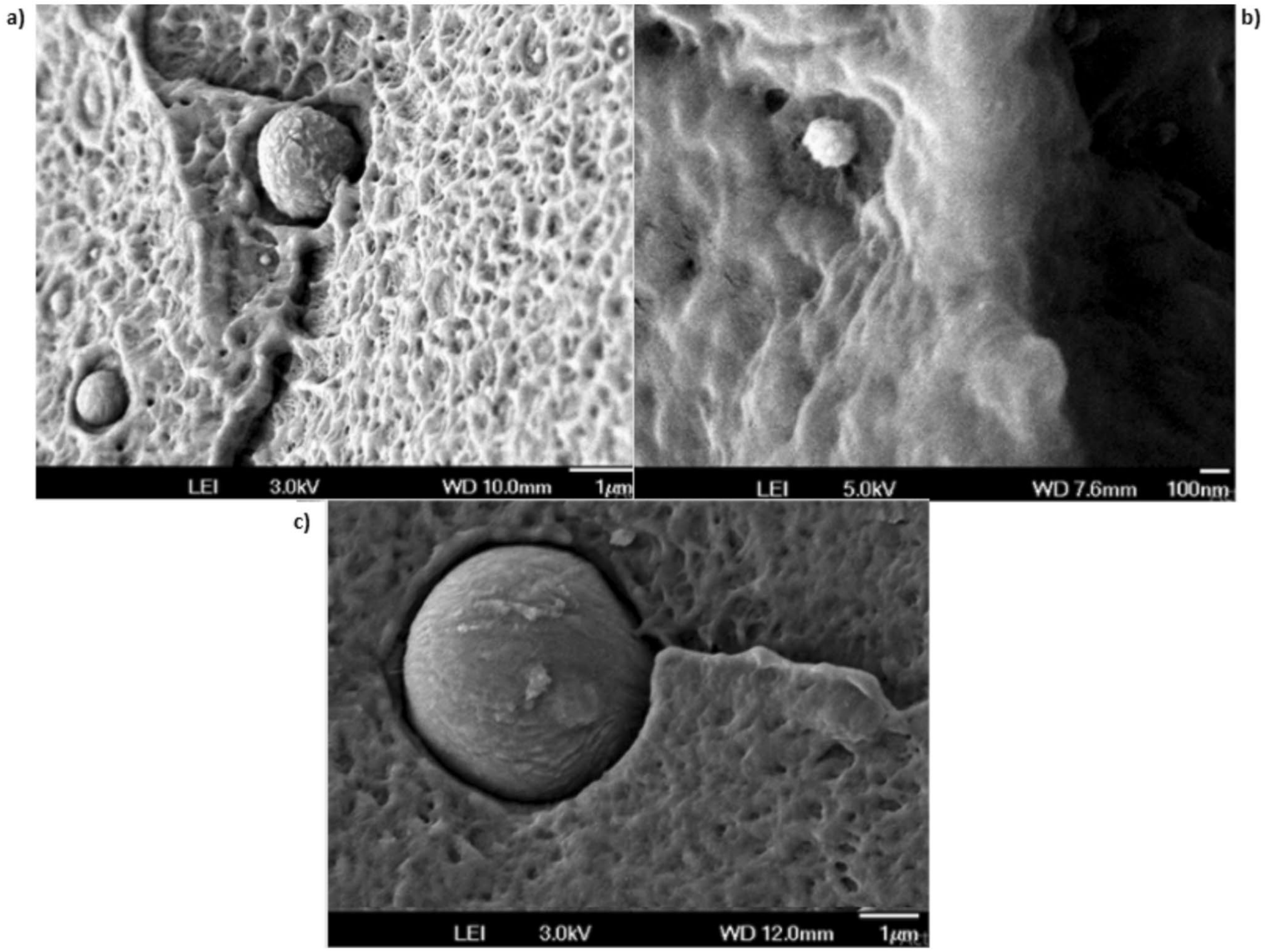
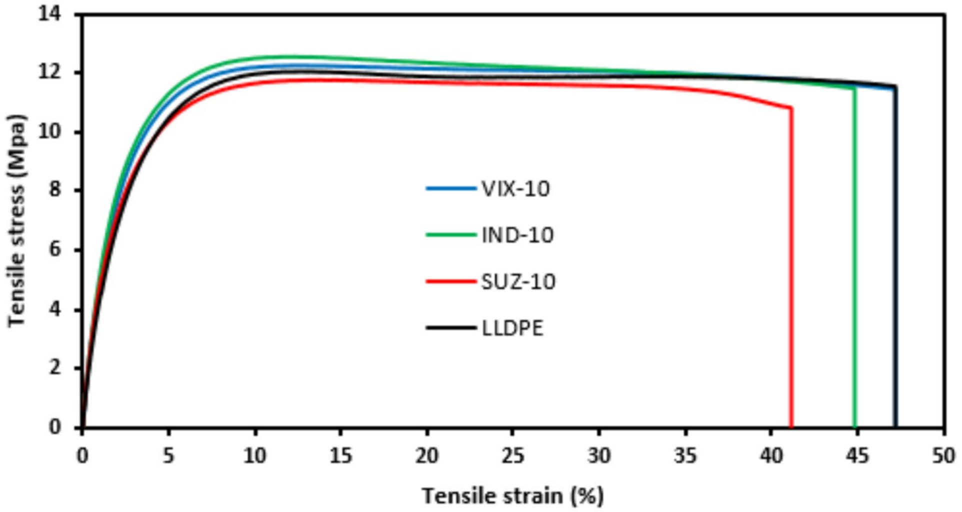


Fig. 3 FE-SEM images: **a** SUZ-10, **b** VIX-10, and c) IND-10

Fig. 4 Tensile strain–stress curves for neat LLDPE and 10% lignin-based LLDPE blends



To enable effective comparisons between the materials, the five measurements of tensile strength at break, elongation at break, and Young's modulus were analysed using analysis of variance (ANOVA), with average values shown in Table 1. These results were compared using Fisher's test at a significance level of 0.05. The statistical

Table 3 Statistical comparison of mechanical properties among different materials

Tensile strength at break	LLDPE = IND-2.5 = IND- 5 = IND-10 = VIX-5 = VIX-10 = VIX-2.5 > SUZ-2.5 = SUZ-5 = SUZ-10
Elongation at break	LLDPE = SUZ-2.5 = SUZ-5 = IND-2.5 = IND- 5 = IND-10 = VIX-2.5 = VIX-5 = VIX-10 > SUZ-10
Young's modulus	VIX-2.5 = VIX-5 = VIX-10 > IND-2.5 = IND- 5 = IND-10 = SUZ-10 > LLDPE = SUZ-2.5 = SUZ-5

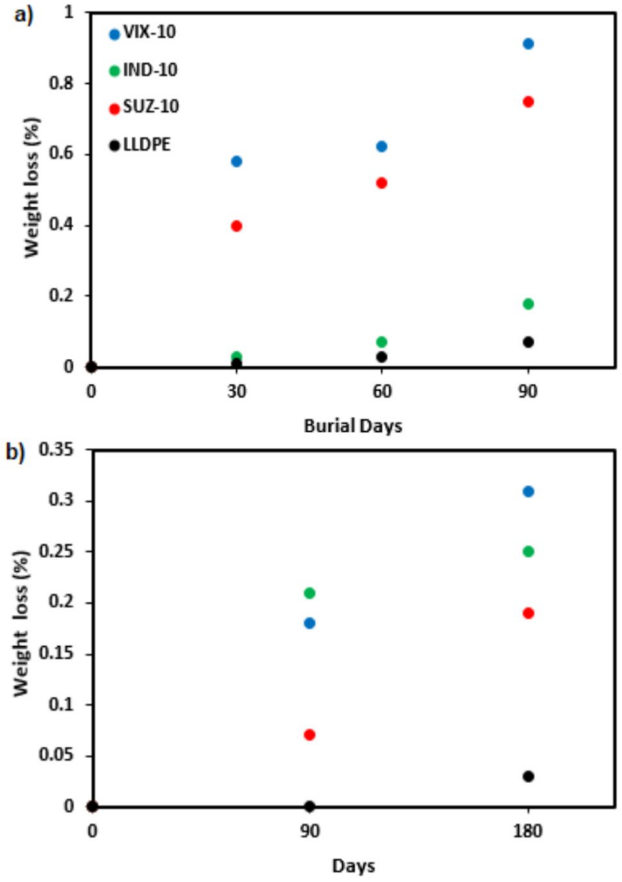


Fig. 5 Biodegradation: **a** soil burial test, and **b** *Aspergillus niger in-vitro* test

analysis was conducted using INFOSTAT statistical software (version 2017), and the results are presented in Table 3.

When adding VIX and IND at concentrations of up to 10% in LLDPE blends, there were no significant statistical differences observed in tensile strength and elongation. However, Young's modulus increased in the following order: LLDPE < IND < VIX. In contrast, the addition of SUZ reduced tensile strength due to its lower average molecular weight. SUZ concentrations of up to 5% showed no significant changes in elongation at break or Young's modulus compared to neat LLDPE, while a 10% lignin content decreased ductility and increased stiffness.

Biodegradation

Figure 5a shows the weight loss of 10% lignin-based blends and neat LLDPE after 90 days of soil burial. Final samples revealed a weight loss of 0.08, 0.77, 0.21, and 0.93% for LLDPE, SUZ-10, IND-10, and VIX-10, respectively. For the *in-vitro Aspergillus niger* test (Fig. 5b), the weight loss percentages after 180 days were 0.03, 0.19, 0.25, and 0.31% for LLDPE, SUZ-10, IND-10, and VIX-10, respectively.

While molecular weight is a crucial factor in lignin degradation, the overall process is multifactorial, and a combination of factors should be considered. Despite the high molecular weight of VIX, its biodegradation rate is higher than that of kraft lignins. This behaviour may be attributed to the greater hydrophilic character of lignosulfonate and the higher sulphur content available for microorganisms. The degradation rates of kraft lignins in soil differ from those observed in *in-vitro* experiments. In the *in-vitro* fungal study, IND demonstrated a higher biodegradation rate than SUZ, indicating that S units are more resistant to degradation than G units (Lu et al. 2022). Conversely, the soil burial test revealed the opposite trend, likely due to the lower molecular weight of SUZ, which facilitates lixiviation and dissolution, thereby increasing its availability for other microorganisms.

Discussion

The investigation of LLDPE blends with various lignin types revealed significant insights into their biodegradation, mechanical and thermal properties. The following observations highlight the performance of these blends:

Lignosulfonates with monovalent counterions, such as VIX, contain sulfonate groups that introduce electrostatic repulsion. Despite VIX's high *Mw* and T_g, its high miscibility is attributed to these electrostatic interactions. During melt blending and thermal processing, the electrostatic repulsion of VIX promotes the disaggregation of lignin particles, preventing agglomeration and facilitating a finer dispersion within the LLDPE matrix. This electrostatic stabilization continues during cooling, reducing lignin aggregation and maintaining its finely dispersed state. As observed in the SEM images (Fig. 3), the dispersed VIX particles reached an average size of less than 200 nm, significantly smaller than those of the kraft lignins (SUZ and IND). This improved dispersion enhances interfacial adhesion between lignin and LLDPE, which is crucial for mechanical performance. The smaller lignin domains act as reinforcing elements, distributing stress more effectively. This is reflected in the fact that LLDPE-VIX blends maintained comparable tensile strength (~ 11 MPa) and elongation at break (~ 47%) to neat LLDPE, while also exhibiting a higher Young's modulus. Additionally, VIX can influence molecular mobility through induced dipole interactions, which may restrict the movement of polyolefin chains near the lignin interface. This limitation on mobility can indirectly promote crystallization by reducing chain flexibility and facilitating the ordered arrangement of polyolefin segments, a phenomenon that will be further explored in future investigations. Furthermore, the more uniform dispersion of the lignin particles facilitates more even heat distribution during processing, contributing to greater resistance to thermal degradation. Finally, these interactions not only affect the mechanical and thermal properties but also influence biodegradation. The hydrophilic nature of sulfonate groups enhances water uptake, promoting microbial colonization and enzymatic attack. This explains the significantly higher weight loss observed in LLDPE-VIX blends during both the soil burial and *Aspergillus niger* biodegradation tests, where the weight loss was ten times greater than that of neat LLDPE after 90 and 180 days, respectively.

In comparison, the kraft lignin-based blends showed that SUZ exhibited better miscibility, as indicated by its low Đ and a particle size of approximately 1.5 µm, in contrast to IND, which had a particle size of 4 µm. However, the tensile strength of LLDPE-SUZ was poor due to the low molecular weight and impurities present in the lignin. The discrepancies in degradation rates between kraft lignins in soil and those observed in *in-vitro* experiments underscore the influence of environmental conditions on biodegradation. For instance, the *in-vitro* fungal study indicates that IND has a higher biodegradation rate than SUZ, suggesting that S units in SUZ are less susceptible to microbial attack compared to G units. However, the soil burial test produced contrasting results, with SUZ demonstrating a higher degradation rate. This may be attributed to SUZ's lower molecular weight, which facilitates its dissolution and leaching in soil, making it more accessible to microorganisms.

Weight loss during the biodegradation of lignin-LLDPE blends primarily results from lignin degradation, as this biopolymer is more susceptible to microbial action. In contrast, LLDPE is generally resistant to biodegradation and remains largely unchanged under normal conditions. However, oxidative degradation of LLDPE can occur due to environmental factors like UV light and heat, potentially fragmenting the polyolefin into smaller pieces that may be more easily assimilated by microbes. Thus, while the blend demonstrates some degree of biodegradation, it is important to specify that this primarily reflects the degradation of the lignin fraction rather than the entire blend.

Conclusion

This work provides valuable insights into the interactions between different types of lignin and LLDPE in the development of sustainable materials. The results indicate that incorporating lignin, a by-product of the pulp and paper industry, particularly hardwood sulphite lignin with monovalent counterion, into LLDPE blends significantly reduces plastic waste while maintaining acceptable mechanical properties and lignin biodegradation. The biodegradation tests demonstrated that lignin not only contributes to weight loss but also promotes microbial activity, indicating its potential for improving the environmental performance of conventional plastics. This approach not only addresses the pressing issue of plastic waste but also supports the transition to eco-friendly materials that align with sustainable development goals demonstrating the potential contributions of lignin-based LLDPE blends to sustainability through circularity, including a design that ensures the biodegradability of lignin.

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Author contributions V.N. and E.M. conceived and planned the experiments. L.C. carried out the experiments and characterizations, and wrote the paper with input from all authors. R.O. and J.B. assisted with FE-SEM measurements. V.N. supervised the project.

Data availability No datasets were generated or analysed during the current study.

Declarations

Competing Interests The authors declare no competing interests.

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