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Scale up coating process of PBAT with modified lignin for paper packaging: Barrier properties, and screening volatile/semi-volatile compounds

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ABSTRACT

To replace fossil-based plastics with circular alternatives, paper packaging requires high-performance functional barriers. This study evaluates coatings composed of poly(butylene adipate-co-terephthalate) (PBAT) and lignin to address this performance gap from paper for food packaging applications. Specifically, paper coatings based on PBAT and esterified lignin (E.Lignin) as compatibilizer were developed and scaled up by extrusion coating. Lignin esterification with propionic acid increased compatibility with the PBAT matrix, as confirmed by FT-IR and ^{1} ^{3}C CP/MAS NMR and GC-MS. At laboratory scale, adding 1 wt% E.Lignin to PBAT reduced water and oxygen transmission rates (WVTR and OTR) relative to neat PBAT coatings by 65%. The use of lignosulfonates (LS) as alternative compatibilizer (avoiding esterification) was explored at laboratory scale. Low loadings improved lignin dispersion and comparable moisture-barrier performance was achieved as for the E.Lignin. The selected formulation (PBAT + 1 wt% E.Lignin) was validated by pilot-scale extrusion coating at grammages of 8–24 g/m^2, achieving WVTR values of 250–150 g/m^2·day (23 °C, 50% RH) and OTR values down to 200 cc/m^2·day at the highest grammage, achieving the same performance as obtained at lab scale. GC–MS screening of lignin and E.Lignin identified additional volatile/semi-volatile compounds, including Cramer Class III substances, highlighting the need for dedicated migration testing of final coated papers before food-contact use.

1. Introduction

The intensive use of synthetic plastics in food packaging has raised significant environmental concerns due to their low recyclability (e.g., 30% worldwide) and accumulation in landfills (Geyer et al., 2017; Poças & do Céu Selbourne, 2023). Their widespread use is driven by excellent performance in protecting a wide variety of food systems, as it is easy to tailor specific synthetic materials with different barrier properties against oxygen, water vapor, and grease (Jahangiri, et al., 2024). This ability to extend food shelf life using petroleum-based plastics is difficult to replicate with bio-based materials. For years, the research community has been searching for bio-based food packaging systems that match the performance of synthetic plastics (Silva et al., 2020). Several studies have demonstrated improvements in critical parameters such as mechanical properties, reduction in oxygen permeability, and reduction in water vapor permeability using more sustainable systems. However, their performance still does not fully match petroleum-based plastics (Silva et al., 2020; Álvarez-Chávez et al., 2012; Tardy et al., 2022).

Paper and board, known to be recyclable and abundant, are hydrophilic and porous in structure, and necessitate a coating to improve their surface properties for resistance to moisture and fat (Kunam et al., 2024; Hubbe & Heitmann, 2007). Polyfluoroalkyl substances (PFAS) have historically been used to improve paper resistance to oil, grease, and water (Glenn et al., 2021). However, both the European Food Safety Authority (EFSA) and the U.S. Environmental Protection Agency (EPA) have identified PFAS as harmful to human health and the environment (EFSA Panel on Contaminants in the Food Chain EFSA CONTAM Panel et al., 2020; Sunderland et al., 2019). Therefore, alternative strategies providing similar barrier performance using bio-based materials, organic solvent-free, scalable, and not negatively affecting mechanical

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performance have been under active investigation. Additionally, the application of coatings is expected to broaden the suitability of paper for food packaging, especially for products other than dry foods.

Conventional synthetic coatings, such as polyethylene (PE), ethylene-methacrylic acid copolymers), styrene-acrylic emulsions and waxes, offer good barrier performance but are not biodegradable (Singh et al., 2025; Al-Gharrawi et al., 2022, Adibi et al., 2022). Alternative strategies include coating with bio based polymers, such as polyhydroxyalkanoates (PHAs) and urethane copolymers (Liu et al., 2024); and chemically modifying the cellulose surface for hydrophobization (Rodríguez-Fabià et al., 2022); coating with inorganic materials (silica-based) to improve barrier performance (Nunes et al., 2021; Roy et al., 2024; Singh et al., 2024; Shorey & Mekonnen, 2022; Venkatesan et al., 2025; Wang et al., 2024; Ogihara et al., 2012; Jiang et al., 2021). Fibre densification through deposition of micro- or nanofibrilated cellulose to reduce porosity and enhance oil and air resistance is also applied (Singh et al., 2025; Kathuria & Zhang, 2022).

As the demand for sustainable materials in food packaging grows, biodegradable polyesters have gained attention in food packaging applications. Poly(butylene adipate-co-terephthalate) (PBAT) has attracted significant interest due to its biodegradability, flexibility, ease of processing, and strong heat-sealability (Roy et al., 2024). Furthermore, cost and commercial availability are strong arguments for selecting PBAT over other biodegradable polyesters. While PBAT is primarily fossil-based, synthesized using petrochemical-derived monomers such as butanediol, adipic acid, and terephthalic acid, advancements were done to replace these petrochemical-derived monomers with bio-based ones. Bio-based butanediol is already produced through industrial fermentation; sebacic acid (derived from castor oil) can replace adipic acid; and 2,5-furandicarboxylic acid (a bio-based aromatic monomer) is considered as a replacement for terephthalic acid. These changes allow the production of a fully bio-based PBAT (Jian et al., 2020). The above-mentioned properties make PBAT a good candidate for coating paper for food packaging applications. Several studies have shown that PBAT coatings enhance paper-based food packaging by improving water and grease resistance, and oxygen barrier properties compared to uncoated papers (Shorey & Mekonnen, 2022; Kim et al., 2023; Qiu et al., 2021). PBAT applied on kraft paper by bar coating, improved water and mechanical performance (Shankar & Rhim, 2018). Despite improving the water resistance of paper, the properties obtained are still insufficient to protect the integrity of most foods, highlighting the need to further improve this coating with hydrophobic additives (Shankar & Rhim, 2018). Additionally, these studies are at lab-scale only and the challenges of scalling up were not addressed.

One promising candidate for improving water resistance in PBAT coatings is lignin, a natural aromatic macromolecule derived from lignocellulosic biomass. Its structure, however, varies across biomass types (softwoods, hardwoods, grasses), with differences in monolignol composition and linkages influencing reactivity and compatibility (Zhang et al., 2022; Georgs et al., 2025). Lignin has attracted attention as a bio-based additive for coatings and films due to its antioxidant, antimicrobial, and hydrophobic characteristics, as potential enhancer of the functional performance of biopolymer-based coatings (Camargos et al., 2022; Boarino & Klok, 2023). Lignin can reduce oxygen and water vapor transmission, especially when the base material is hydrophilic, as lignin's chemical structure contains hydrophobic groups, such as aromatic rings and methoxy (-OCH_3) groups, that repel water. However, lignin itself also contains hydrophilic groups, such as hydroxyl (-OH) and carboxyl (-COOH) groups (Marques et al., 2025; Zadeh et al., 2018). In hydrophilic matrices, these groups facilitate compatibility. However, for relatively hydrophobic materials such as PBAT—which contains terephthalate units, aliphatic methylene groups, and ester bonds—the hydrophilic functionalities in lignin can hinder compatibility, making it necessary to modify lignin or incorporate compatibilizing additives (Boarino & Klok, 2023). Several strategies were explored to improve lignin compatibility with PBAT, including esterification (Liu et al., 2019), acetylation (Sameni et al., 2017), grafting (Eraghi Kazzaz et al., 2019), adding compatibilizers (Han & Wu, 2019), and physical modifications such as particle size reduction (Camargos et al., 2022). These strategies have been shown to improve compatibility with hydrophobic matrices; however, many involve toxic reagents such as acid chlorides or anhydrides (Ahmad et al., 2018). Emerging strategies, such as esterification with organic acids or the use of natural compatibilizers like Lignosulfonates (LS), offer safer, simple and sustainable alternatives (Liu et al., 2019; Szabó et al., 2017). These modifications are considered less hazardous, although esterification may still introduce additional safety concerns, which also need to be addressed.

While PBAT- and lignin-based coatings have been widely investigated as sustainable alternatives for paper packaging, most reported lignin-containing PBAT systems have been evaluated only at laboratory scale, by casting and limited information exists regarding their processability under industrially relevant extrusion-coating conditions. Moreover, many studies focus primarily on barrier enhancement without examining the formation of volatile or semi-volatile compounds that may arise from lignin chemical modification—employed to improve compatibility—which is critical for food-packaging applications. Consequently, there remains a need for scalable PBAT–lignin coating systems that integrate improved barrier performance, robust processing compatibility, and preliminary safety-oriented chemical screening.

This study investigates the incorporation of modified lignin, prepared using a direct propionic acid esterification process, into PBAT for the development of paper coatings with enhanced barrier performance. The objectives are to (1) evaluate the chemical and physical characteristics of esterified lignin (E.Lignin) and its compatibility with PBAT; (2) assess the barrier properties, morphology, and surface wettability of coated papers; (3) examine the feasibility of scaling the process through pilot extrusion coating; and (4) screen potential harmful volatile/semi-volatile compounds generated by lignin modification. Additionally, LS were explored as an alternative additive to mitigate compatibility between PBAT and lignin and safety concerns by avoiding chemical modification.

2. Materials and methods

2.1. Materials

The materials following described were used for the development of the biodegradable paper coating. Alkali lignin (CAS 8068–05–1) and lignosulfonate (CAS 8061–52–7) were purchased from Sigma Merck (Germany). For the esterification, propionic acid (CAS 79–09–4) was also acquired from Sigma Merck (Germany), while sulfuric acid (CAS 7664–93–9) and acetone were from Fischer (United States). Ecoflex® F Blend C1200 was the PBAT used from BASF (Germany). For lab-scale coatings, the PBAT was dissolved using chloroform from Fischer (CAS 67–66–3), and the paper substrate used was non-bleached 40 g/m^2. For pilot scale extrusion, the same PBAT and lignin were used, and the paper substrate was kraft extra white 80 g/m^2.

2.2. Lignin esterification

Esterification was adapted from a procedure previously published (Liu et al., 2019). Lignin was esterified using propionic acid in a 1:7 lignin-to-acid ratio, with 10% (v/v) acetone added to enhance dispersion. Sulfuric acid (5% w/w relative to lignin) was used as a catalyst. The suspension was stirred for 3 h and then transferred to an autoclave for thermal treatment at 121 °C for 4 h. The modified lignin was then thoroughly washed with distilled water and centrifuged multiple times at 4000 rpm for 15 min until neutral pH, following air-drying until completely dry and milled prior to incorporation into PBAT. Approximately 90% of the propionic acid was recovered using a rotary evaporator. Lignin esterification was carried out in multiple batches until the necessary mass for pilot extrusion was achieved, all these batches were

mixed and then assessed as one batch.

2.3. Incorporation of lignin (neat and esterified) and lignosulfonate on PBAT and coating at lab scale

Solutions of PBAT for blade coating were prepared in chloroform. For PBAT- E.lignin coating formulations, E.Lignin (1%, 5%, and 10% w/w lignin/PBAT) was first added to the chloroform solvent and mixed. Then, PBAT was added (20% w/v) at room temperature and magnetically stirred (200–300 rpm). After PBAT was fully dissolved, the solution was ready for blade coating. The coatings were applied using an automatic film applicator (Sheen Instruments, UK) under specific conditions: a speed of 50 mm/s, with the blade height adjusted to achieve the desired pick-up grammage (5 or 15 g/m^2). The PBAT solution was kept under constant agitation to ensure homogeneous dispersion of lignin. After application and full evaporation of chloroform, the coated samples were heated at 120–140 °C in an oven for 2 min to melt the PBAT on the paper surface. For the incorporation of lignin and lignosulfonate into PBAT, the same preparation procedure was used, with the slight difference of lignin and lignosulfonate being premixed prior to dispersion in chloroform and PBAT dissolution. Lignin content was fixed at 1% w/w relative to PBAT, while lignosulfonate concentrations of 1%, 5% and 10% relative to PBAT were used (lignosulfonate/lignin mass ratios of 1:1, 5:1, and 10:1, corresponding to total particle loadings of 2%, 6%, and 11% w/w in the PBAT). PBAT incorporation and coating were then carried out as described in this section.

2.4. Pilot extrusion coating

The pilot extrusion coating of PBAT–E.lignin on paper involved two main stages: masterbatch preparation and extrusion coating. In the first stage, E.lignin was incorporated into PBAT at a concentration of 10% to create a masterbatch. This compounding was performed using a 21 mm LAB Twin extruder with five temperature zones: 155 °C (T1), 160 °C (T2 and T3), 165 °C (T4), and 165 °C at the die. The resulting fibre was then cut into pellets. For extrusion coating, the masterbatch pellets were mixed with neat PBAT at a 10:1 PBAT/masterbatch ratio, resulting in a final lignin content of 1 wt% in the coating layer. Extrusion coating trials were carried out on an extrusion coating line (Periplast, Portugal) equipped with a single-screw extruder (30 mm diameter, L/D 30), driven by a 5.5 kW motor and capable of operating up to 171 rpm. The barrel includes four heating zones (up to 350 °C), complemented by four additional temperature-controlled zones in the adapter and die head. The system is fitted with a 250 mm flat die with adjustable lips, which were set to a 0.7 mm opening during the trials. The grammage of the coating (or coating pick-up values in g/m^2) can range between 5 and 130 g/m^2, with operating line speeds from 2 to 50 m/min and a maximum coating width of 250 mm. The coating process was performed at paper line speeds between 20 and 40 m/min, while maintaining a constant extruder screw speed of 40 rpm, resulting in coated papers with coating pick-up values ranging from 8 to 24 g/m^2.

2.5. PBAT and lignin characterization

Fourier-Transform Infrared Spectroscopy (FT-IR) - FTIR analysis of lignin, E.lignin and lignosulfonate was carried out in a Bruker FTIR spectrometer ALPHA II (Bruker Corporation, Billerica, MA, USA) in transmission mode, operating at a resolution of 4 cm^{-1}. The spectra were taken between 4000 and 300 cm^{-1} by averaging 60 scans for each spectrum. All samples were scanned twice.

Nuclear magnetic resonance (NMR) - NMR analysis of Lignin and E. lignin was carried out with 1 H with rotation at the magic angle (MAS) and 1H–13 C of cross-polarization/rotation at the magic angle (CP/MAS NMR) were obtained in a Bruker Avance III spectrometer of 9.4 T wide bore, with Larmor frequency of 400 MHz for 1 H. A 4 mm dual-resonance MAS probe was used, operating at 400.1 MHz for 1 H and 100.6 MHz for 13 C. The samples were inserted into ZrO2 rotors and subjected to a rotation rate of 10 kHz. The 1 H MAS spectra were acquired with a time of 5 s and an excitation pulse of 90° for 1 H with a duration of 2.5 ms. For the 13C-CP/MAS NM spectra, an amplitude variation in cross-polarization contact was used, ranging from 100% to 50% at 100 points, with SPINAL−64 uncoupling, 5 s recycle time, 2.0 ms contact time, and a 90° excitation pulse for 1 H lasting 3 ms. Chemical displacements were referenced in ppm relative to TMS (tetramethylsilane).

Thermal characterization - was performed by differential scanning calorimetry (DSC) using a DSC 6000 from Perkin Elmer (Boston MA, USA), under nitrogen atmosphere (gas flow of 20 mL/min) using a sample of about 5–8 mg sealed in aluminium pans. Two cycles were performed: heating from 0 to 200 °C at a of 10 °C/min and cooling 10 °C/min from 200 to 0 °C. The thermal history of PBAT was eliminated in the first heating and determinations were taken from the cooling and second heating cycles. The melting point (Tm) and crystalization temperature (Tc) were estimated for both PBAT and PBAT-E.lig.

Rheological characterization - Rheological analysis was performed using a dynamic rotational rheometer (Bohlin Instruments, UK) equipped with a 40 mm diameter stainless steel parallel plate geometry and a 2 mm gap. All measurements were carried out in open air under oscillatory mode at a constant temperature of 130 °C. A frequency sweep ranging from 0.1 to 10 Hz was conducted to evaluate the viscoelastic properties of neat PBAT and PBAT-based composites containing lignin under 1% strain. The tests focused on characterizing the storage modulus (G'), loss modulus (G"), and complex viscosity (η) as a function of frequency. Duplicates were made to validate reproducibility.

2.6. Coated and uncoated paper characterization

Thickness – measurements were performed with a digital thickness gauge (Adamel Lhomargy, France) on all coated papers. The thickness of each produced sample was determined by taking the average of five measurements arranged in a systematic five-point pattern (one at the center and four at the corners of a defined square area) to ensure a representative characterization of the coating uniformity.

Surface wettability – was characterized by contact angle (Attension Theta, Biolin Scientific, USA). The dynamic contact angle analysis (video recording) was performed with the embedded software (Biolin Scientific) using the Laplace-Young approximation model and the sessile drop method. A drop of 5 μL of distilled water is positioned on the coatings's surface with a microliter syringe and observed over time (up to 100 s). Six measurements were made in each sample. The surface wettability was determined as referred on TAPPI T458–14 standard. The surface wettability (°/s) is determined by the ratio of the difference between the average contact angle values at 5 s and 100 s, and the elapsed time of 95 s.

Barrier properties – the water vapour transmission rate (WVTR) was assessed gravimetrically, adapting the water method from ASTM E96–95. The test specimen was sealed to the open mouth of a test dish containing distilled water (RH 100%) or calcium chloride (RH 0%), and the assembly was placed in controlled standard (23 °C, RH 50%) or tropical (38 °C, RH 90%) conditions. WVTR driven by the RH difference between the internal (either RH 100% or RH 0%) and external (RH 50% or RH 90%) environments was determined by plotting the capsule weight change (g) against the elapsed time (h). A climate chamber (FITOCLIMA D1200) was used to control tropical conditions (38 °C; RH 90%).

Oxygen transmission rate (OTR) was measured according to the standardised method (ASTM D3985–17). OTR tests were performed with MOCON Oxtran Model 2/21 at RH 50%, 23 °C, and an oxygen concentration of 100% in the coated face and 0% in the uncoated face of the coated paper. Sample area of 50 cm^2 was used. For each sample, duplicates were made.

Morphology analysis – Lignin particles were characterized by

scanning electron microscopy (SEM), using Phenom XL G2 SEM (Thermo Fischer Scientific—FEI; Eindhoven). Results were acquired using the Fischer scientific software. Samples were placed on observation pins with double-sided adhesive carbon tape (NEM tape; Nisshin, Japan) and coated with 9–12 nm of gold/palladium for improved conductivity, using a Polaron instrument (Bad Schwalbach, Germany). The analysis was conducted with an accelerating voltage of 5–10 kV with a varying magnification scale of 1000x to 4000x. A secondary electron detector (SED) was used for Micrographs capture.

Morphology and thickness measurements were acquired by SEM (FEI Quanta 400 FEG ESEM Microscope) operating at 15 kV under the secondary electron (SE) mode at CEMUP (Porto, Portugal). Cross-sectional freeze-fracturing of the samples was performed to expose the internal and undistorted morphology. The samples were immersed in liquid nitrogen to induce brittleness and physically broken with mount forceps. Fractured samples were mounted on aluminium pins with conductive carbon adhesive tape (Fischer Scientific). The average thickness of the coating was determined by analysis of SEM images using ImageJ v.151 software (50 measurements).

Characterisation of potential volatile and semi-volatile migrants - Lignin and E.lignin were analysed through GC-MS using a chromatography system (Bruker EVOQ TQ GC-MS), to detect volatile and semi-volatile compounds from these samples that could migrate. Two sample preparation methods were used, headspace (in polar and non-polar columns) and liquid extraction (in a non-polar columns). For headspace analysis, about 25 mg of lignin and E.lignin were thermally treated at 200 °C for 1 h. Analysis was performed using a CP-Wax 58 column (50 m × 0.25 mm ID × 0.2 μm) and a Zebron 5 ms plus column (30 m × 0.25 mm ID × 0.25 μm), with a 1 mL injection volume. The injector was set to 250 °C (split 1:10). The oven was programmed from 40 °C (2 min), ramped at 8 °C/min to 250 °C (10 min) for CP-Wax 58 column and from 40 °C (5 min), ramped at 10 °C/min to 320 °C for Zebron 5 ms column. Mass spectrometry detection was conducted with electron ionization (EI) at 70 eV, scanning *m/z* 33–350. In the liquid extraction method, volatile compounds and semi-volatile compounds of lignin and E.lignin were extracted in 3 mL ethanol for 24 h at 60 °C. A 1 μL aliquot was injected into the Zebron 5 ms plus column under splitless mode (injector at 320 °C, 0.75 min). The oven was programmed from 50 °C (3 min), ramped at 10 °C/min to 320 °C, and held for 15 min. MS detection was carried out using EI at 70 eV, with full scan range 33–700 *m/z*. Identification of compounds was performed using the NIST 2020, Version 2.4 library.

2.7. Statistical analysis

Statistical analysis was supported by Prism version 9.4.1 (GraphPad Software, La Jolla California USA), using one-way (and two-way) ANOVA and Tuckey's post-hoc analysis for pairwise comparison of more than two means. Mean differences were considered statistically non-significant (ns) when p-value was higher than 0.05 (95% of interval of confidence). The default statistical confidence level was 95% ($p < 0.05$) in all tests.

3. Results and discussion

3.1. Lignin esterification

Esterification of lignin was performed to enhance its compatibility with the hydrophobic PBAT matrix. The process involved treating kraft alkali lignin with propionic acid under controlled heat (90–120 °C) to introduce ester functional groups, following a modified approach based on Liu et al. (2019). The reaction led to structural modifications, confirmed by FT-IR (Figure S1). The first foreseen spectral change was the appearance of a strong absorption band around 1722 cm^{-1}, corresponding to C═O stretching in ester groups. This band is absent in native lignin and confirms the successful formation of ester bonds (Zhao et al., 2017). Additionally, bands observed at 2918 cm^{-1} and 2850 cm^{-1} represent asymmetric and symmetric C–H stretching, respectively, associated with the presence of propionyl alkyl groups (Sangeetha et al., 2022). Further changes were noted in the 1000–1300 cm^{-1} region, where alterations in C–O and C–O–C stretching vibrations were observed (Figure S1). ^{13}C CP/MAS NMR also allowed to confirm lignin esterification (Figure S2). The NMR spectra allowed detailed analysis of structural changes in lignin before and after esterification. Significant differences were observed in regions associated with aliphatic and carbonyl carbons, confirming the formation of ester groups. New resonances appeared at $\delta = 180–170$ ppm, corresponding to aliphatic ester carbonyl carbons, and at $\delta = 28–26$ ppm and $\delta = 10–8$ ppm, corresponding to aliphatic carbon chains of the propionate groups. The aromatic region was unaffected, thus esterification mainly affecting aliphatic hydroxyl groups (Boarino & Klok, 2023; Liu et al., 2019). As confirmed by both FT-IR and $^{1}{}^{3}C$ CP/MAS NMR, lignin was successfully esterified using propionic acid. Absolute quantification was not possible with $^{1}{}^{3}C$ CP/MAS NMR; however the significant reduction of signal intensity in the $\delta = 60–80$ ppm region (associated with aliphatic –OH carbons) indicates substantial esterification. Furthermore, the results of chemical analysis by GC-MS also confirmed the esterification through the detection of 1,2,3-propanetriol tripropanoate and other esters. The E.Lignin was subsequently incorporated into PBAT at different concentrations to evaluate its effect on barrier properties (WVTR, OTR) and surface hydrophobicity (contact angle), as detailed in the following sections.

3.2. Optimization of PBAT lignin-based coatings at lab scale

3.2.1. Incorporation of E.Lignin on PBAT

The incorporation of E.Lignin into PBAT was optimized to achieve the best balance between processability and barrier properties. PBAT and PBAT–E.Lignin formulations in chloroform were successfully applied to paper, producing coatings with a grammage of 15 g/m^2. The concentration of E.Lignin was optimized to efficiently improve the barrier performance of the coated paper. The PBAT and PBAT–E.Lignin coatings were assessed for barrier properties, primarily water vapor and oxygen transmission rates, and surface wettability, as illustrated in Fig. 1.

Fig. 1 highlights the positive effect of incorporating E.Lignin on PBAT. Uncoated paper exhibited the highest WVTR, reflecting expected poor moisture barrier properties. Coating with neat PBAT significantly reduced WVTR, yet a significant reduction in WVTR to as low as 250 $g/m^2{\cdot}day$ is observed when PBAT was blended with 1% E.Lignin ($p < 0.05$). The increase of the concentration of E.Lignin in the PBAT matrix led to lower reduction of the WVTR relative to the coating with PBAT only, likely due to particle agglomeration within the matrix, which compromises the coating integrity. Particle agglomeration may induce micro pinholes and cracks in the coating layer, thus affecting the performance of the barrier layer (Zhan et al., 2021; Lim et al., 2021). This agglomeration also impacted OTR, with higher concentrations of E. Lignin causing a marked increase in OTR values ($p < 0.05$). At 1% E. Lignin, this negative effect was not observed; in fact, the OTR was slightly lower than that of neat PBAT ($p > 0.05$), measuring 55 $cc/(m^2{\cdot}day)$ versus 133 $cc/(m^2{\cdot}day)$, respectively (Fig. 1). Values of transmission rate for PBAT–lignin coatings on paper are very scarce in the literature. Shorey and Mekonnen (2022) reported improved oxygen barrier properties for such coatings, but their data were limited to thickness-normalized permeability coefficients (4.28 down to 1–2 cc. m/m2.day.Pa). Most values are reported on standalone PBAT and PBAT–lignin films and not coatings. In those studies, neat PBAT films typically show values of 250–400 g/m^2.day for WVTR and 400–800 cc/m^2.day for OTR, which drop to 100–250 g/m^2.day and 200–400 cc/m^2.day upon optimized lignin addition (Kim et al., 2023; Wang et al., 2024). Values considerably higher than those obtained in the present work. The chemical modification of the lignin through esterification (as confirmed by FTIR and NMR) reduced the interfacial tension between

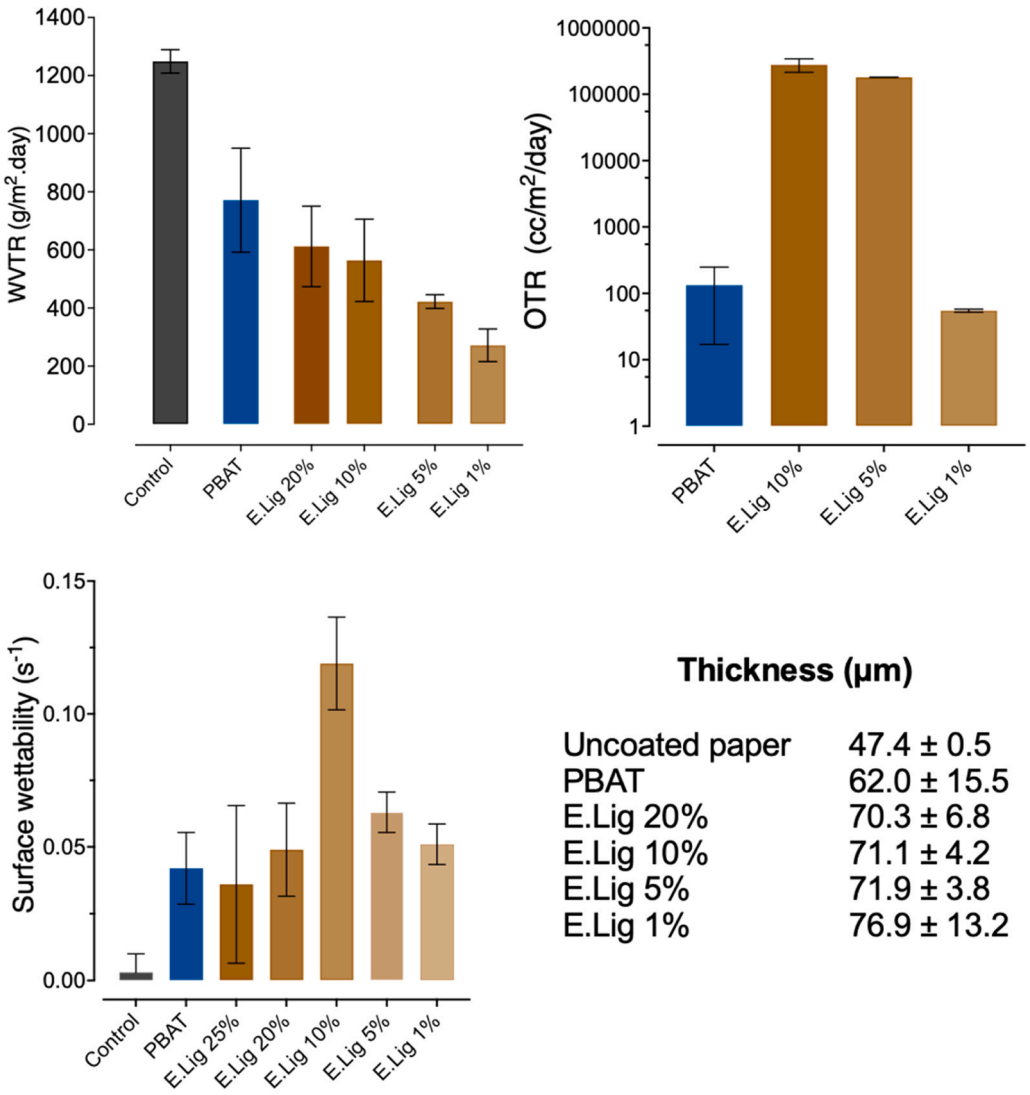

Fig. 1. Water vapor transmission rate (WVTR), oxygen transmission rate (OTR), surface wettability and thickness of paper and paper coated with PBAT and PBAT with E. lignin; results for OTR of uncoated paper (control) were not possible to obtain due to equipment range limitation.

the E.Lignin and the PBAT matrix, suppressing lignin agglomeration and forcing gas molecules to follow a more tortuous path, ultimately leading to the observed reductions in WVTR and OTR (Fig. 1).

Regarding surface wettability, both PBAT and PBAT–E.Lignin coatings exhibited low wettability values, reflecting the hydrophobic nature of the PBAT matrix and the hydrophobic contribution of E.Lignin.

Based on these results, the formulation consisting of 99% PBAT and 1% E.Lignin demonstrated enhanced barrier performance, particularly concerning WVTR and OTR. Other studies also claimed lack of compatibility of PBAT with lignin, similarly emphasizing the necessity of chemically modifying kraft lignin to improve its compatibility (Kim et al., 2023). In their study, increasing the concentration of acetylated lignin led to progressively lower WVTR and OTR values, contrasting with the trend observed in this study. This discrepancy may be explained by differences in the degree of substitution, as the esterification process used in our study affected mainly the aliphatic region (Figure S2). With a higher degree of esterification, higher lignin concentrations could be incorporated without compromising compatibility and barrier performance. As a result from the lab scale studies, the 1% E.lignin concentration was selected for further evaluation at pilot scale using extrusion coating, to validate the hydrophobization effect of the coating on paper.

3.2.2. Preliminary assessment of lignosulfonate as compatibilizer for lignin on PBAT

As alternative to the esterification of lignin, the incorporation of lignosulfonate as compatibilizer was also explored. Owing to their amphiphilic nature and functional group diversity (Ruwoldt, 2020), lignosulfonates are potential compatibilizers to improve the dispersion of unmodified lignin within the PBAT matrix without requiring chemical modification. This section explores the feasibility of using LS to enhance lignin incorporation in PBAT, with the goal of maintaining or improving further the barrier performance while avoiding chemical modification. This preliminary assessment focused on the morphology of lignin-based particles and FT-IR analysis, to evaluate whether LS promote better lignin dispersion in PBAT.

Incorporation of 1% lignin (PBAT-Lig), 10% lignosulfonate (PBAT-LS), or 10% LS with 1% lignin slightly increased WVTR compared to neat PBAT (Fig. 2-a). On the other hand, the addition of a lower lignosulfonate concentration (1% w/w) together with lignin reduced WVTR relative to PBAT-Lig, indicating a synergistic interaction that improved coating uniformity and filler dispersion. Although LS exhibits hydrophilicity at higher loadings, at low concentrations it promoted uniform lignin dispersion in the PBAT matrix, achieving performance comparable to E.Lignin ($p > 0.05$) (Figs. 2-a and 1).

The FTIR spectrum of lignosulfonate exhibited marked differences

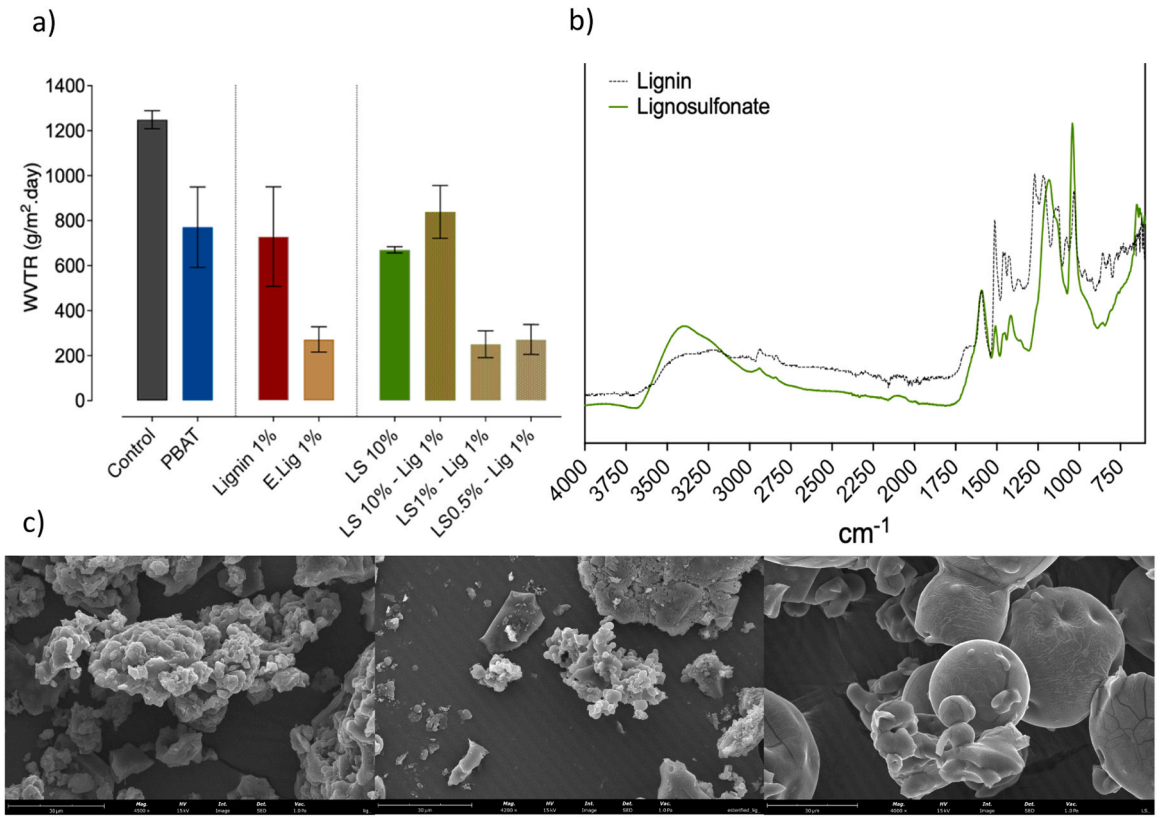

Fig. 2. a- Water vapor transmition rate (WVTR) of paper substrates coated with various PBAT-based formulations; b- FTIR spectrum of lignin and lignosulfonates, normalized in the peak 1700 cm^{-1}; **c**-SEM images of lignin (left), esterified lignin (middle) and lignosulfonates (right);.

compared to lignin, mainly due to the presence of sulfonic groups introduced by sulfonation (Fig. 2-b). Two prominent regions were observed: 1000–1080 cm^{-1} and 1100–1250 cm^{-1} . The latter is a broad, structured band that includes overlapping vibrational modes such as C–O stretching, C–C–O and C–O–C linkages, and symmetric S═O stretching associated with sulfonate ($–SO_3^-$) groups (Karimov et al., 2021). The 1030–1060 cm^{-1} region also reflects symmetric S═O stretching (Karimov et al., 2021). The presence of $–SO_3^-$ groups can give dispersion abilities to LS in polyesters such as PBAT. The use of lignosulfonate with low amounts of sulfonate groups, may result in less hindrance of hydrophobic adsorption between the hydrocarbon backbone of lignin and the material to which it adsorbs (Aro & Fatehi, 2017). Additionally, LS retain hydroxyl (–OH) and ether (C–O–C) functionalities, which can form hydrogen bonds with lignin hydroxyl groups (Aro & Fatehi, 2017). These combined interactions enable LS to act as compatibilizers between lignin and PBAT, promoting improved dispersibility, interfacial adhesion, and a more homogeneous and stable composite material (Bova & Naskar, n.d.).

SEM images revealed clear morphological differences between unmodified lignin, E.Lignin, and LS (Fig. 2-c). Unmodified lignin displayed rough, aggregated particles, while E.Lignin exhibited smaller, more uniform structures, likely due to structural modifications from esterification (Panzarasa et al., 2018). In contrast, LS formed larger, spherical, and homogeneous particles, indicative of higher solubility and enhanced potential for dispersion within the polymer blend (Panzarasa et al., 2018). Although this section is exploratory, the observed improvement in lignin compability with PBAT suggests that LS should be considered a potential additive in future work to better evaluate its potential to enhance coating homogeneity at higher lignin loadings and in scalable paper-coating applications.

3.3. PBAT-E.lignin extrusion coating

The pilot-scale extrusion coating process was performed to validate the feasibility of incorporating PBAT–E.Lignin (PBAT–E.lignin) as a barrier layer. In the prior laboratory-scale tests, chloroform was used for PBAT and lignin blending, which may have influenced compatibility, particle distribution, and the performance of PBAT–E.lignin coatings. To validate and scale the laboratory results, the optimal formulation was further studied via extrusion coating. E.Lignin was first incorporated into PBAT by extrusion compounding to form a masterbatch with 10% E. Lignin, which was subsequently diluted to achieve a final concentration of 1% in the extrusion coating formulation. Before coating, the properties of PBAT and PBAT containing 10% E.Lignin relevant for processing were analysed in the masterbatch pellets.

DSC analysis confirmed that the thermal stability of PBAT–E.lignin was comparable to that of pure PBAT, with a slight increase in melting temperature (Tm). Incorporation of lignin significantly affected crystallization behavior, where the crystallization temperature (Tc) increased from 36.6 °C (neat PBAT) to 75.2 °C (PBAT–E.lignin 10%) (Fig. 3-a). This shift toward higher Tc indicates that lignin acted as an efficient nucleating agent for PBAT crystallization (Kargarzadeh et al., 2020; Terzopoulou et al., 2025).

Rheological properties of the coating are relevant for the processability and scaling-up process. Results indicate that no significant particle agglomeration occurred in the lignin-containing formulations. This is observed by the increase in viscoelasticity, both storage modulus (G′) and loss modulus (G″) as well as an overall increase in complex viscosity, when compared to neat PBAT (Fig. 3-b). The increased viscosity indicates a good dispersion of lignin within the polymer matrix and supports the viability of using the 10% masterbatch for diluting to 1% in extrusion application. In terms of complex viscosity behaviour, incorporation of lignin increased the overall viscosity of PBAT. For the 1% lignin formulation, viscosity remained shear-thinning and followed a

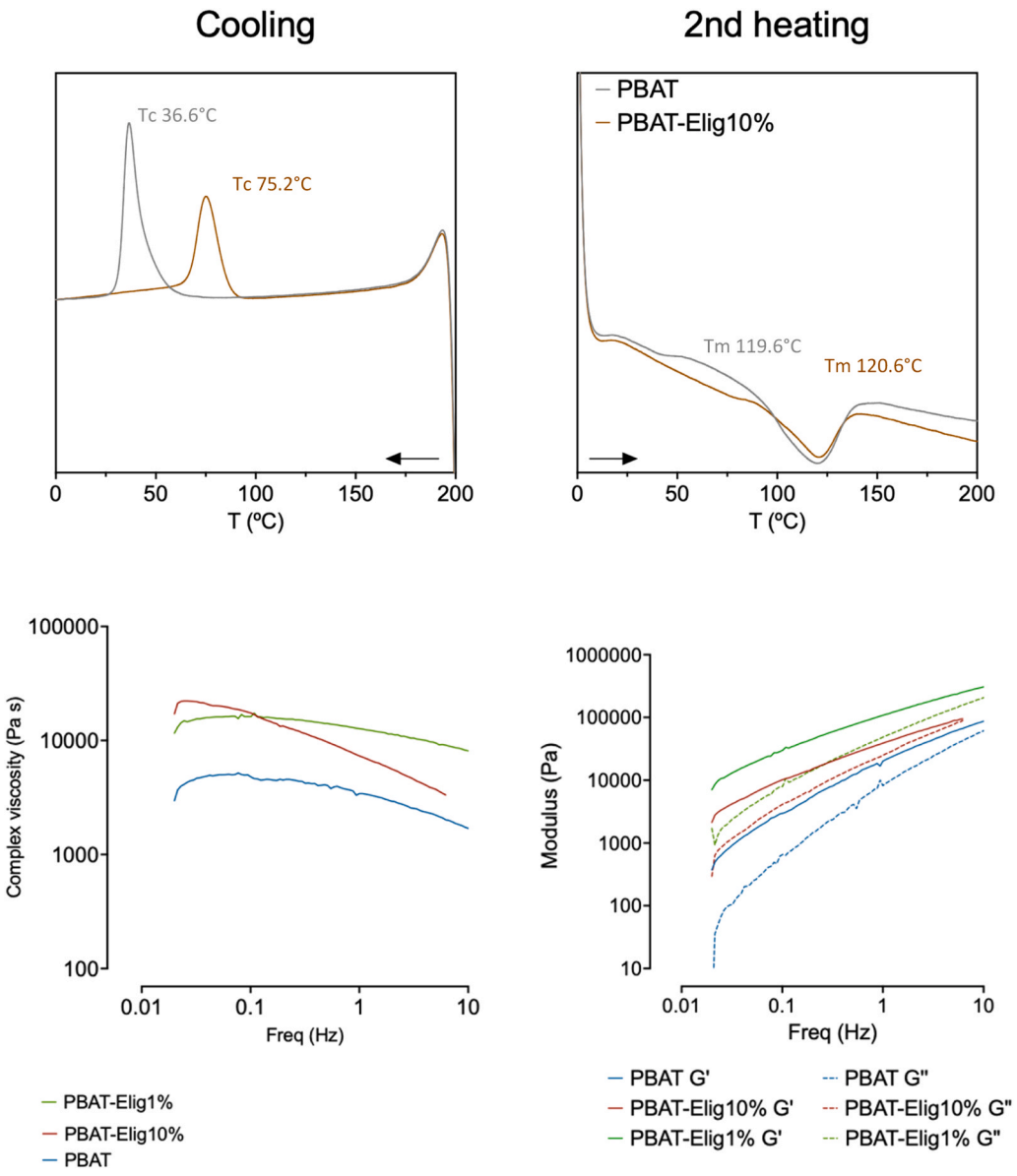

Fig. 3. a-DSC thermograms of PBAT (grey line) and PBAT-E. lignin (brown line) with thermal transitions: temperature crystallization (Tc) and melting temperature (Tm); b- Rheological properties of PBAT (green line), PBAT-E.lig 10% (red line) and PBAT-E.lig 1% (blue line);.

similar frequency-dependent decrease as neat PBAT, indicating that the polymer network retained its characteristic flow behaviour (Fig. 3-b). In contrast, the 10% lignin formulation exhibited a more pronounced viscosity drop at higher frequencies, suggesting stronger interactions between lignin and PBAT and more restricted chain mobility at this higher loading (Terzopoulou et al., 2025). Overall, these results demonstrate that incorporating 1% E.Lignin increases viscosity and viscoelastic moduli without significantly altering the shear-dependent rheological behaviour. This ensures that PBAT–E.lignin 1% remains processable under shear, during extrusion coating.

3.3.1. *Barrier performance of extrusion coated paper*

Extrusion coating was performed on paper kraft (extra white 80 g/m^2), producing coatings with varying pick-up levels of 8, 12, and 24 g/m^2 (Table 1). To evaluate the performance of the coatings, the coated papers were analysed through physical characterization, SEM, and barrier performance tests.

Cross-sectional SEM images of coated papers were further analysed and compared with those obtained at lab-scale coating (Fig. 4). SEM images showed a thicker coating layer for the lab-scale coating (21.99 ± 0.57 μm) when compared with the one produced by the pilot-scale process (18.05 ± 0.53 μm).

Table 1
Physical characteristics of the PBAT coated paper (pilot scale).

Material	Pick-up (g/m^2)	Thickness (μm)	Adhesion to paper?
PBAT-E.lignin	8	100 ± 1.44	Yes
	12	105 ± 2.25	Yes
	24	116 ± 2.71	No

Moreover, cross-sectional SEM images revealed differences in interfacial interaction and adhesion between lab-scale and pilot-scale processes. Better adhesion was observed for the lab-scale coating relative to the pilot extrusion coating, which can be attributed to the dissolution-based coating approach employed at the lab scale (using chloroform, as described in the materials & methods section). In this case, dissolved PBAT likely enhanced penetration and interfacial contact with the fibrous substrate, leading to stronger adhesion (Fig. 4-a vs Fig. 4-b).

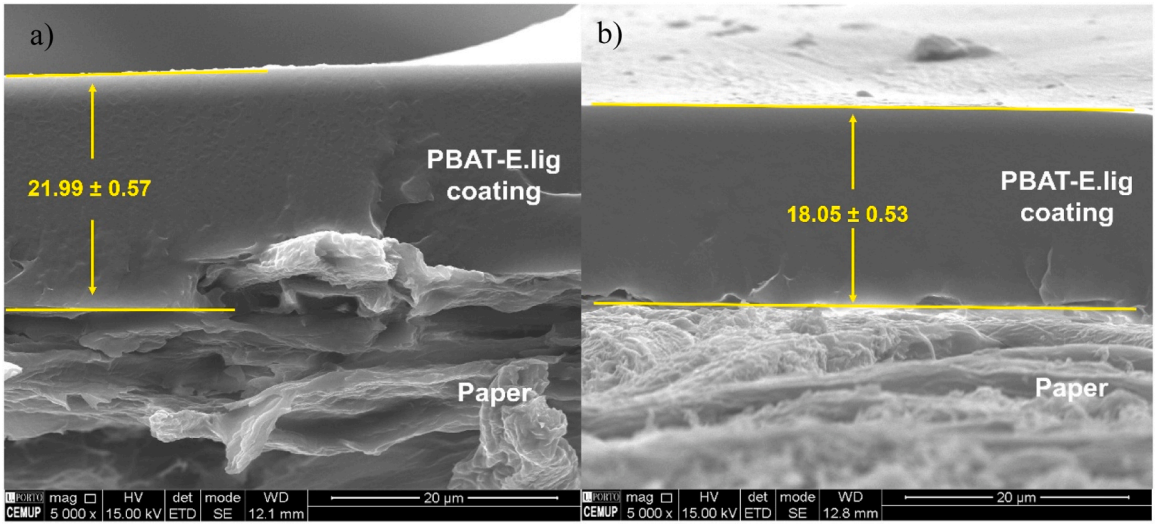

Fig. 4. a SEM images of the cross-section of lab coated paper; b- SEM images of the cross-section of coated paper using pilot extrusion using PBAT and 1% E.lignin.

Although these differences in adhesion did not affect WVTR measurements, they significantly influenced OTR. Lab-coated papers exhibited lower OTR values compared to papers coated by pilot extrusion (Fig. 1 vs. Fig. 5-a).

Barrier performance tests showed that coating pick-up level significantly affected both WVTR and OTR as expected ($p < 0.05$). Under tropical conditions (38 °C, 90% RH), WVTR for papers coated at 8 and 12 g/m^2 was approximately 1400 g/m^2·day (Fig. 5-a). Increasing the pick-up to 24 g/m^2 reduced WVTR to approximately 700 g/m^2·day. Under moderate storage conditions (23 °C, 50% RH), WVTR values were substantially lower: 250 g/m^2·day for 8 and 12 g/m^2, and 150 g/m^2·day for 24 g/m^2. These WVTR values were significantly lower than those of uncoated paper and PBAT-only coated paper at 23 °C, 50% RH as anticipated by the lab tests. At elevated temperature and humidity (38 °C, 90% RH), WVTR values were higher for all coatings, but the effect of temperature and RH was lower for the higher pick-up coating of 24 g/m^2 ($p < 0.05$). This is likely due to the combined effects of water molecule diffusion at higher temperatures, and a higher water vapor concentration gradient, which forces more water vapor through the PBAT–E.lignin layer (Wu et al., 2021). Additionally, both E.Lignin and PBAT are partially hydrophobic but still capable of absorbing moisture at humidity, which can slightly plasticize the matrix and consequently increase permeability (Chinma et al., 2015). Despite these effects, PBAT–E.lignin coatings provided a clear barrier improvement, achieving nearly a 50% reduction in WVTR at the lowest tested pick-up level (8 g/m^2) and approximately a 75% reduction at 24 g/m^2.

A similar trend was observed for OTR, where increasing the coating pick-up led to decreased oxygen permeability ($p < 0.05$), likely due to reduced porosity and improved film continuity (Sabo et al., 2024; Mujtaba et al., 2022). Specifically, increasing pick-up from 8 to 12–24 g/m^2 resulted in OTR reductions from nearly 1200 cc/m^2·day to 500 cc/m^2·day and 200 cc/m^2·day, respectively (Fig. 4-c).

Surface wettability tests demonstrated that PBAT–E.lignin coatings significantly increased the contact angle relative to uncoated paper, confirming an improved hydrophobic surface ($p < 0.05$). This result is consistent with the WVTR findings, reinforcing the water-repellent properties of lignin-modified PBAT coatings. These results demonstrate that the barrier improvements are maintained even when transitioning from the laboratory set up (solvent casting) to continuous pilot extrusion coating. This transition presents challenges, with two inherently incompatible materials under high-shear extrusion conditions would typically induce severe filler agglomeration. However, the esterification modified the blend's structural response, providing the enhanced thermal stability required to withstand extrusion temperatures and preserving a shear-thinning behavior identical to neat PBAT without compromising viscosity, which ensured the required processability to achieve effective barrier coatings.

Compared to other biodegradable coatings, the PBAT-E.lignin system obtained demonstrates moderate barrier performance. Reported values for neat PBAT films show OTR around 1000 cc/m^2·day and WVTR above

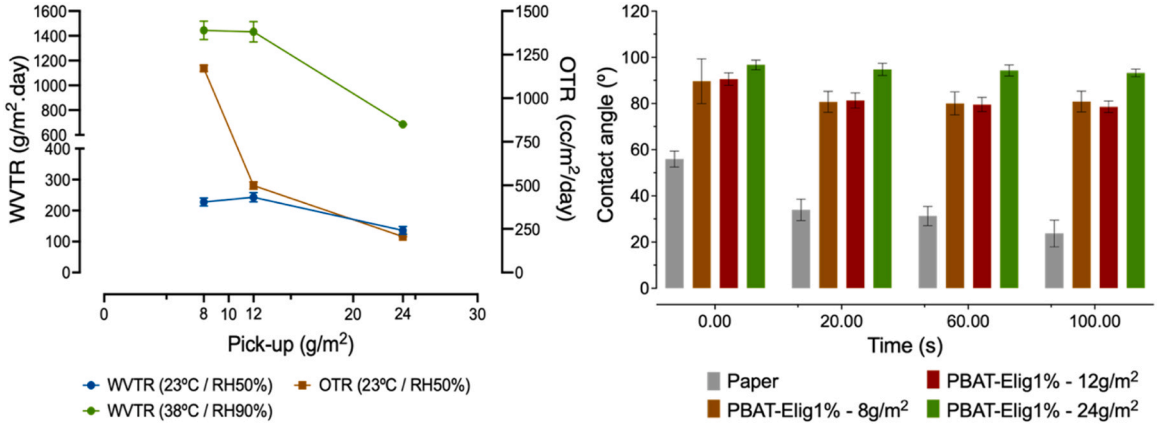

Fig. 5. a- WVTR and OTR values coated paper with PBAT-E.lignin 1% with different pick-up (8–24 g/m^2); WVTR tested at two conditions, 23°C RH50% and 38°C RH90%; b- Contact angle of uncoated and coated paper with PBAT-E.lignin 1% with different pick-up (8–24 g/m^2).

140 g/m²·day (Venkatesan et al., 2023a; Venkatesan et al., 2023b). PLA films typically exhibit OTR in the range of 1500–400 cc/m²·day and moderate moisture barrier (WVTR <300 g/m²·day) (Silva et al., 2020; Yuniarto et al., n.d.; Wang et al., 2021). Despite the improvements, the barrier levels achieved here remain insufficient for high-barrier food applications. For example, packaging of dry foods (e.g., coffee, dry pasta) requires OTR < 1 cc/m²·day and WVTR < 5 g/m²·day to ensure shelf stability and prevent oxidative or moisture-induced degradation (Silva et al., 2020; Silva et al., 2023; Singh et al., 2017). The best-performing PBAT-E.lignin coating in this study (24 g/m²) achieved an OTR of 200 cc/m²·day and WVTR of 150 g/m²·day at 23 °C, 50% RH—well above the above-mentioned requirements. To extend applicability to dry food packaging, further optimization is needed—either by increasing lignin concentration while maintaining compatibility and uniform distribution, or by incorporating additives able to significantly reduce both oxygen and water vapour transmission. LS can improve compatibility and enable higher lignin loading without promoting particle agglomeration (Mukherjee & Mukhopadhyay, 2023), offering a promising strategy for enhancing barrier performance.

3.4. Potential volatile and semi-volatile migrants

While the incorporation of E.Lignin into PBAT significantly enhances the barrier properties of coated paper, it may also introduce potential concerns regarding chemical safety. Esterification modifies the lignin structure to improve compatibility with the hydrophobic polymer matrix, yet these chemical changes can also generate new compounds. For materials intended for food-contact applications, such modifications raise critical questions about the potential migration of uncharacterized substances into food (EFSA Panel on Food Contact Materials, Enzymes, Flavourings and Processing Aids CEF, 2016). Therefore, a chemical safety assessment of E.Lignin is essential to evaluate its regulatory compliance for use in sustainable food packaging. GC-MS analysis of lignin and E.lignin identified several compounds, which were classified according to their toxicity using Cramer's Decision Tree classification (Roberts et al., 2015). This system categorizes compounds into Class I (low toxicity), Class II (moderate toxicity), and Class III (high toxicity) based on their chemical structure.

In Supplementary Information a table with the compounds detected in Lignin and E.lignin and their toxic classification according to Cramer is presented (Table S1). For reference, the chromatograms are presented (Figure S4). Table 2 presents the main results showing the peaks corresponding to higher intensity in the chromatograms, the respective Cramer class and information about the origin of the substance. This preliminary analysis revealed the appearance of new peaks, that need to be considered to rule out potential concerns regarding the safety of E. Lignin for food-contact use. Esterification of lignin significantly altered its chemical composition, leading to the formation of new esters, transformation of guaiacol-derived compounds, and degradation of certain volatile components.

Table 2
Key Compounds found in Lignin (GC-MS) and their toxic classification according to Cramer.

Cramer	Compounds	Observations
Class III	**Diethyl sulfate**	IARC Group 2 A carcinogen; formed via sulfuric-acid alkylation
	Methanesulfonic acid methyl ester	Formed on the presence of sulfuric acid
	Dimethyl sulfone	Formed on the presence of sulfuric acid
	Furfural	Thermal degradation of carbohydrates or lignin fragments
	Dehydroabietic acid	Conversion of abietic acid into its dehydrogenated form
Class II	**H-Pyrrole−2-carboxaldehyde**	Nitrogenous degradation product
Class I	**4-Acetoxy−3-methoxyphenethyl alcohol, acetate**	Ester formed
	Propanoic acid, ethyl ester	Ester formed
	Naphthalene, 2,3-dimethoxy	Detectable after esterification
	Phenol, 4-(2-propenyl)- (4 Allyphenol)	Detectable after esterification
	1-Hydroxy−2-butanone	Detectable after esterification

Beyond the safety concerns, the detection of 1,2,3-propanetriol tripropanoate and other esters further supports the successful incorporation of hydrophobic groups, as observed earlier in FT-IR (Figure S1) and 13 C CP/MAS NMR (Figure S2), enhancing lignin–PBAT compatibility and contributing to improved water-repellent performance.

New esters such as diethyl sulfate and propanoic acid ethyl ester were formed as a result of reactions catalyzed by sulfuric and propionic acids. Guaiacol and its derivatives partially reacted to form more complex structures, such as 3-(4-allyl−2-methoxyphenoxy)−1,2-propanediol, while coniferyl alcohol was converted to higher-molecular-weight phenylpropanoid derivatives (Table 2). Thermal degradation also contributed, producing furfural and other furan derivatives (Table 2). Several phenolic and guaiacol-based compounds decreased or disappeared, indicating their participation in esterification or volatilization. For example, vanillin may have been converted to 3,4-divanillyltetrahydrofuran, while hydroquinone and coniferyl alcohol disappeared, likely due to decomposition or structural transformation (Table S1). In contrast, some lignin-related compounds increased, such as dehydroabietic acid, suggesting oxidative transformations (Table S1). Analysis of lignin revealed that most compounds belonged to Class I, indicating low toxicity (Table 2). These included natural phenolic derivatives such as vanillin, eugenol, creosol, benzenepropanol derivatives, and trans−13-octadecenoic acid. These compounds are naturally present in plant materials reported to been found elsewhere (Takada et al., 2004; Ehara et al., 2005; Lucejko et al., 2020). Nevertheless, certain Class III compounds were detected, including resin acids (dehydroabietic acid, abietic acid), sulfur-based compounds (dimethyl trisulfide, 2-thiophenecarboxaldehyde), and products of thermal degradation (Borella et al., 2024). The presence of sulfur-containing compounds suggests byproducts of esterification may contribute to increased toxicity risk (Boarino & Klok, 2023). Following esterification, the GC-MS analysis confirmed the formation of additional Class III compounds (Table 2). The most concerning were diethyl sulfate, methanesulfonic acid methyl ester, and dimethyl sulfone—none of which were detected in unmodified lignin. Diethyl sulfate is classified as a Group 2 A carcinogen (IARC, 1992). The presence of these compounds suggests that further purification steps may be required to remove residual byproducts prior to food-contact applications. Other Class III compounds detected included furfural and 5-methylfurfural, typically formed during thermal degradation of carbohydrates and lignin (Jilani & Olson, 2023). These are known to pose potential health concerns at elevated concentrations. While lignin esterification introduces valuable hydrophobic functionality, the increase in Class III compounds highlights the need for careful evaluation of migration potential and regulatory compliance. It should also be considered that formation of volatiles and semi-volatile substances by thermal degradation can be a result of a combined effect of the chemical modification process of the lignin and of the extrusion process. This preliminary assessment was performed only on lignin extracts, although submitted to the heating process required for GC analysis.

Further work is required to assess whether these compounds migrate from the final PBAT–E.lignin coatings themselves. Given that E.Lignin represents only 1% of the final coating formulation, the overall risk may be mitigated. Nevertheless, migration studies are necessary to confirm this scenario. This preliminary assessment showed that quantification and migration should focus on sulphur-containing compounds, propionic acid itself and esterification products, namely esters of phenolic compounds with or without methoxy groups (consistent with lignin-based) and dimers of these compounds.

4. Conclusion

This study demonstrated that incorporating E.Lignin into PBAT coatings on paper substrates can significantly enhance water vapor and oxygen barrier properties. The esterification of lignin with propionic acid successfully increased lignin's hydrophobicity and compatibility with the PBAT matrix (confirmed with FTIR and NMR), with similar observations in the literature. The key novelty of this study lies on transitioning to pilot-scale extrusion coating, where the optimized formulation (1% E.Lignin in PBAT) was validated in terms of processability and barrier performance. While the incorporation of E.Lignin into PBAT demonstrated promising improvements in barrier performance, GC-MS analysis revealed that esterification also introduced potentially harmful compounds, including Class III substances such as diethyl sulphate and furfural derivatives, that needs to be fully addressed to rule out safety concerns for food-contact applications.

LS were explored as an alternative strategy and their amphiphilic nature and functional groups enabled improved lignin dispersion within PBAT, leading to similar water vapor barrier performance to E.lignin, if low lignosulfonate loadings are used.

Despite the improved barrier performance under a pilot scale set up, the developed materials show a barrier able to protect foods with medium protection requirements only. Further optimization is required, with the goal of improving compatibility of lignin to increase loadings. Quantification of new compounds detected in the modified lignin and migration studies on the final coatings should be performed to ensure regulatory compliance and recyclability tests to assess whether PBAT-E. lignin layer does not hinder fibre recovery and can be integrated into existing recycling streams.

CRediT authorship contribution statement

Carlos Granadeiro: Writing – original draft, Formal analysis. **Tomás Duarte:** Writing – original draft, Methodology, Investigation, Formal analysis. **Francisco Soares Silva:** Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Joel Pereira:** Writing – original draft, Methodology, Investigation. **Fátima Poças:** Writing – review & editing, Validation, Supervision, Resources, Methodology, Funding acquisition, Conceptualization.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.fpsl.2026.101799.

Data availability

Data will be made available on request.

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