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Lignin-Polylactic Acid Biopolymer Blends for Advanced Applications – Effects of Microwave-Assisted Acetylation of Lignin

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Received: 4 December 2025 | **Revised:** 24 September 2026 | **Accepted:** 5 October 2026

Keywords: biocomposite | impact resistance | Lignin modification | mechanical property | microwave-assisted acetylation | poly (lactic acid) | sustainable material | thermal stability

ABSTRACT

In this study, the effects of microwave-assisted acetylation of lignin on the properties of lignin/poly (lactic acid) (PLA) biocomposites have been developed and investigated. Acetylation was selected to reduce the hydrophilicity of lignin and improve its compatibility and dispersion within the hydrophobic PLA matrix. Microwave irradiation was employed as an alternative to conventional acetylation, providing a substantially shorter active treatment period without the use of a catalyst. The modified lignin was then blended with PLA and Biomax® Strong SG 120, an impact modifier, to produce biopolymer blends. The characterisation of the acetylated lignin was performed using Nuclear Magnetic Resonance (NMR) and Attenuated Total Reflectance Fourier-Transform Infrared (ATR-FTIR) spectroscopy, which confirmed successful modification through the appearance of ester signals and reduction of hydroxyl groups. Tensile and impact tests, conducted in accordance with ISO standards, demonstrated that the addition of acetylated lignin and the impact modifier improved the properties of the modified PLA-lignin blends, increasing impact strength, ductility and thermal stability. These findings suggest that microwave-assisted acetylation of lignin is a viable method to enhance the compatibility of lignin with PLA, leading to biopolymer blends with enhanced mechanical and thermal properties. This study further highlights the potential of these sustainable, high-performance materials for a range of advanced applications, promoting the use of renewable resources in the development of eco-friendly biopolymer blends and composites.

1 | Introduction

Imitating nature's use of lignin in material production represents a logical and sustainable approach. Lignin, a naturally abundant polyphenolic macromolecule found in vascular plants, exhibits structural complexity and functional diversity [1]. By leveraging the principles underlying lignin's role in plant physiology—particularly its contributions to structural support and defence mechanisms—we can derive inspiration for the design and synthesis of biomimetic materials with tailored properties and functionalities [2]. This approach capitalises on the evolutionary optimisation of lignin's structure and function over millions of years, offering a blueprint for developing sustainable, multifunctional materials that align with natures principles [3–5]. The properties of lignin make it far too valuable to be used primarily for energy recovery.

Lignin is a promising candidate for enhancing the properties of biopolymer blends. Extracted from sources like wheat straw

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through methods such as the organosolv process, lignin provides a renewable and cost-effective feedstock for materials. However, its highly branched structure and inherent hydrophilicity pose challenges when blending with polymers like polylactic acid (PLA), leading to issues with compatibility and mechanical performance. Creating single-phase network structures with lignin requires complementary functionality and component miscibility. This is typically achieved by modifying lignin with molecular entities that promote secondary interactions, such as hydrogen bonds, with the continuous polymer phase. Alternatively, reactive functional groups such as phenols, acrylates, epoxies, amines, and vinyl groups can be attached to lignin to enhance its reactivity and compatibility [3, 6, 7]. Chemical modification offers a versatile approach to tailoring lignin for various applications [8]. Processes like amination and propylation render lignin hydrophobic, making it suitable for use in polyurethane foam formulations [9]. Phenolation enhances lignin's reactivity in phenol-formaldehyde resin adhesives. However, esterification stands out as a well-established and promising strategy for modifying lignin's properties.

To address compatibility challenges, chemical modification techniques like acetylation have been employed to improve lignin's miscibility with PLA. Acetylation converts lignin's hydroxyl groups to acetyl groups by an esterification reaction, enhancing its compatibility with PLA and improving lignin's dispersion within the PLA matrix by reducing agglomeration [10]. Recent advancements show that microwave-assisted acetylation have the possibility to increase the efficiency of this process by reducing reaction times and energy consumption, making it more practical for large-scale applications [11]. Microwave-assisted modification is environmentally friendly, often requiring fewer or no solvents and operating at lower temperatures, which reduces chemical usage and hazardous waste production [12–15].

The growing demand for sustainable materials has led to an increasing interest in biopolymers, which are derived from renewable resources and offer significant environmental and economic benefits compared to traditional petroleum-based polymers. Among the biopolymers, PLA, stands out due to its biodegradability and favourable mechanical properties, making it suitable for a wide range of polymer applications [16]. PLA is one of the most widely utilised biopolymers, distinguishing itself from petroleum-based alternatives. Its popularity stems from several key advantages, including its low extrusion temperature, minimal warpage, non-toxicity, and, from a sustainability standpoint, its biobased origin and biodegradability [17]. However, despite these strengths, PLA has inherent limitations that restrict its applicability, including low thermal stability, brittleness, and limited toughness, which pose challenges for applications requiring higher durability and resilience [18]. Incorporating acetylated lignin into PLA matrices is expected to improve mechanical properties such as impact strength and ductility, as well as enhance thermal stability. These improvements are critical for applications requiring durable, heat-resistant materials [10].

The automotive industry, among others, stands to benefit significantly from the development of high-performance, low weight sustainable materials. Currently, the industry relies heavily on petroleum-based plastics, which have considerable environmental impacts. By replacing these materials with biopolymer blends of PLA and acetylated lignin, the automotive industry can reduce its carbon footprint and improve the sustainability of its products. Components such as interior panels, trim, and under-the-hood parts could be manufactured using these advanced biopolymer blends, with the potential for further advancements into more complex applications [18–24].

This work represents the first stage of our investigation into microwave-assisted acetylation of lignin in PLA matrices; in subsequent research, we extended this concept by combining acetylated lignin with regenerated cellulose fibres, achieving further improvements in mechanical performance and broadening the application potential of the resulting biocomposites [25].

The primary aim of this study is to evaluate how microwave-assisted acetylation of lignin influences its compatibility with PLA and the resulting mechanical and thermal performance of PLA–lignin biopolymer blends. In our previous studies, lignin acetylation has shown the potential to improve mechanical and thermal properties [10, 26], making them suitable contenders for demanding applications in the automotive industry.

This paper details the materials and methods used for acetylation and blending, with a focus on the benefits of microwave-assisted acetylation, compared with the conventional base catalysed acetylation with pyridine. We present the results of our mechanical and thermal property evaluations and discuss the implications for the development of sustainable materials, while comparing them to previous obtained results. By demonstrating the potential of these biopolymer blends and highlighting the advantages of microwave-assisted acetylation, we aim to contribute to the advancement of environmentally friendly, high-performance materials [17–22].

2 | Materials and Experimental Methods

2.1 | Materials

The PLA used in this study was Nature Works Ingeo™ 2003D, a general-purpose extrusion grade PLA, supplied by RESINEX Nordic AB, Sweden. This grade is particularly suitable for blending applications. Lignin, extracted from wheat straw using the organosolv method, with a molecular weight of Mw-3650, Mn-1620, and a polydispersity index of 2.3, was generously provided by Fortum Power and Heat Oy in Espoo, Finland. Acetic anhydride (> 99%) was procured from Sigma Aldrich®. Biomax® Strong SG 120 was kindly supplied by Dow HPC in Switzerland.

2.2 | Acetylation of Lignin

Acetylation is a chemical modification process used to improve the compatibility of lignin with polymer matrices. This section describes two distinct acetylation methods employed in this study: the conventional pyridine-catalysed method and a microwave-assisted approach. Both methods aim to enhance

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the reactivity and functionality of lignin while optimising reaction efficiency and product quality. The detailed procedures for each method, including reaction conditions and equipment, are provided to describe the preparation of the modified lignin for further comparison.

2.3 | Acetylation of Lignin Using Pyridine

Prior to acetylation, the lignin was dried overnight in a vacuum oven (Vacucell, MMM Medcenter Einrichtungen GmbH, Munich) at 40°C to minimise its moisture content. Lignin was acetylated using pyridine as a catalyst according to previously conducted studies [10, 26]. Briefly, lignin (10 g) was reacted with 100 mL of pyridine and 30 mL of acetic anhydride at room temperature for 24 h in a 200 mL Erlenmeyer flask. The solution was added dropwise to cold water to precipitate the lignin. The solids were collected by vacuum filtration and extensively washed with deionised water to remove unreacted reagents, by-products, and residual catalyst species, followed by vacuum drying for a minimum of 24 h. The reaction conditions, including reactant ratios and reaction time, were selected based on previously reported studies and our earlier work, where these parameters were shown to provide effective acetylation of lignin [10, 26].

2.4 | Microwave-Assisted Acetylation

Acetylation of oven-dried lignin was conducted by reacting lignin with acetic anhydride in the absence of a catalyst using a high-performance microwave digestion system (Ethos Up, Milestone s.r.l., Italy). Lignin (10 g) was introduced into a 100 mL Teflon pressure-sealed vessel together with acetic anhydride at a 1:5 (w/w) lignin-to-acetic anhydride ratio. The rotor contained eight pressure-sealed vessels, corresponding to a total of 80 g of lignin subjected to acetylation simultaneously.

The temperature programme consisted of a 5 min heating ramp followed by isothermal heating at 130°C for 10 min, during which a fraction of the fixed power was applied to maintain the target temperature. The selected temperature, reaction time, and reactant ratio were based on previous studies on microwave-assisted lignin acetylation, which demonstrated effective modification under similar conditions.

[12–15] These parameters were chosen to achieve effective acetylation while minimising the active treatment time and avoiding the use of catalysts.

Following microwave irradiation, the sealed vessels were left to cool naturally to room temperature for 12–24 h before opening and further processing. The extended cooling period was chosen for practical convenience and was not considered part of the active microwave-assisted treatment time. No active microwave heating was applied during this period. However, the reaction kinetics during cooling were not monitored; therefore, it cannot be excluded that some residual acetylation occurred while the reaction mixture cooled.

The reaction mixture was slowly poured into cold water and stirred for 24 h using a magnetic stirrer until the lignin precipitated. The solid residues were collected by vacuum filtration and extensively washed with deionised water to remove unreacted reagents and by-products, followed by vacuum drying at 40°C for a minimum of 24 h.

2.5 | Extrusion and Injection Moulding

Prior to blending PLA, lignin, and the impact modifier, each component was dried overnight in a vacuum oven set to 40°C to minimise moisture content. Blends containing modified lignin, PLA, and the impact modifier were subsequently prepared according to the compositions detailed in Table 1. These mixtures were manually fed into a 15 cm^3 twin-screw micro compounder (Xplore Instruments, the Netherlands).

Uniform processing conditions were applied to all blends. Each batch involved processing approximately 8 grams of the mixed components, and this procedure was repeated multiple times until a sufficient quantity of the compounded blends was produced. The micro compounder's barrel temperature was maintained at 200°C, and the die temperature was set at 180°C. During the feeding phase, the screw speed was 75 rpm, which was then increased to 125 rpm during the mixing phase. The mixture was recirculated in the barrel for 3 min. These conditions, deemed optimal in our previous study [10, 26], were used to ensure effective mixing. For each blend, at least five replicates were prepared for subsequent characterisation.

Following extrusion, samples for mechanical property evaluation were created using injection moulding at a temperature of 200°C. The molten blends were fed into a micro injection moulding machine (Xplore Instruments, the Netherlands), with the mould temperature set at 70°C. This process yielded dumbbell-shaped specimens for tensile testing (ISO 527-2) and rectangular specimens for Charpy impact testing (ISO 179-1). Uniform conditions for injection moulding were applied to all

TABLE 1 | Composition of the PLA–lignin blends used in this study (wt.%).

Composition (WT. %)	PLA	Microwave-assisted lignin	Pyridine acetylated lignin	Impact modifier
Blend 1	75	20	—	5
Blend 2	75	—	20	5
Blend 3	80	15	—	5
Blend 4	80	—	15	5
Blend 5	95	—	—	5
Reference	100	—	—	—

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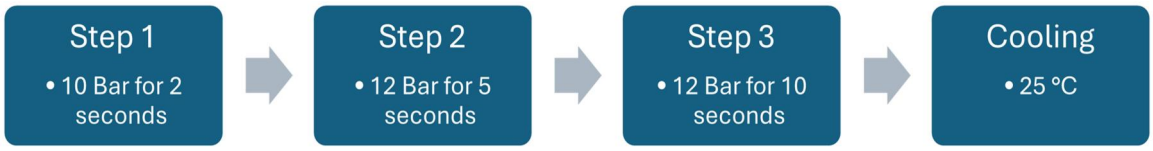

FIGURE 1 | Injection-moulding conditions used for preparation of the test specimens.

blends, they consisted of three pressure steps followed by a cooling step where the specimens were extracted from the mould and cooled between two metal plates to room temperature to prevent deformation, with a typical cooling time of 20 min (Figure 1).

2.6 | Characterisation Methods

2.6.1 | *ATR-FTIR Spectroscopy*

To evaluate the degree of acetylation of the hydroxyl functional groups in lignin, we employed an ATR-FTIR spectrophotometer (Nicolet iS10, Thermo Scientific, US). Measurements were performed in absorbance mode with a resolution of 4 cm^{-1}, covering a range from 4000 to 400 cm^{-1}, and each sample was scanned 16 times. All measurements were done in triplicates. Pre-processing of the ATR-FTIR spectra was performed using Python. The baseline correction was done by asymmetric least squares (ALS) [27] using the *irfpy* library [28]. The degree of acetylation (conversion, α) was calculated based on the normalised absorbance ratio of the hydroxyl group stretching band (AOH) to the aromatic reference band at 1510 cm^{-1} (Aref), according to Equation (1) [12, 29].

$$\alpha = [1 - (\mathrm{AOH}/\mathrm{Aref})\mathrm{Acetylated}/(\mathrm{AOH}/\mathrm{Aref})\mathrm{Pristine}] * 100 \quad (1)$$

2.6.2 | *NMR and 1H NMR Spectroscopy*

The acetylation of the lignin was analysed by solid state and solution NMR spectroscopy. The solid state ^{13}C CP MAS NMR spectra were recorded on Bruker AVANCE-II spectrometer at 14.1 T magnetic field using home built double resonance magic-angle-spinning probe for 4 × 25 mm Si_3N_4 rotors. The spinning speed of the sample was set to 13.5 kHz. The spectrum was recorded with ordinary cross polarisation (CP) pulse sequence, where the duration of ramped polarisation transfer pulse was 2 ms, and the relaxation delay between the excitations was 5 s. The number of averages in all three spectra was around 17000.

Solution ^{1}H and ^{13}C NMR spectra were obtained by dissolving the samples in DMSO-d_6 (5% to 10% solutions) and recorded at 298 and 328 K temperatures on a Bruker Avance III 800 MHz spectrometer with cryo probe. The chemical shifts were referenced to TMS using solvent signals at 2.50 and 39.5 ppm for ^{1}H and ^{13}C, respectively.

The degree of acetylation was estimated from the ^{1}H NMR spectra by integrating the signal corresponding to the methyl protons of the acetyl groups (~ 2.0–2.2 ppm) and comparing it to the integral of the aromatic proton signals of lignin. The ratio of these integrals was used to assess the relative extent of acetylation.

2.6.3 | *Elemental Analysis*

In preparing the samples for analysis, the samples were dried in a 40°C vacuum-oven overnight to remove any moisture. 2-3 mg sample of unmodified and acetylated lignin samples were used for determining carbon, hydrogen, nitrogen contents of the samples. The C, H, N and S contents were determined in triplicate by A FlashSmart™ Elemental Analyzer (Thermo Fisher Scientific Inc., USA). The oxygen content was calculated from the difference between the C, H, N and S contents and was based on the assumption that the samples only contain the C, H, N, and O elements.

2.6.4 | *Charpy Impact Testing*

Charpy impact testing was performed following the ISO 179-1 standard using a QC-639D mechanical impact tester from Cometech Testing Machines, Taiwan. The tests were conducted on un-notched specimens oriented edgewise and using a 5 J pendulum. To ensure the results were accurate and representative, five replicate samples, each measuring 80 × 10 x 4 mm, were tested.

2.6.5 | *Tensile Testing*

Tensile testing was performed using a Tinius Olsen H10KT universal testing machine. Specimens were tested at room temperature, loaded at a speed of 10 mm/min until failure. The initial distance between the clamps was set to 25 mm, with a load range of 5 kN. The results were averaged from five replicate tests. Data analysis to determine tensile strength, elongation at break, and Young's modulus was conducted using Horizon software. To minimise the effects of potential sample slippage during testing, the modulus was manually calculated from the measured data.

2.6.6 | *Thermogravimetric Analysis (TGA)*

TGA was performed using a TGA Q500 instrument from TA Instruments. Approximately 9 mg of each sample was heated at a rate of 10°C/min under a nitrogen atmosphere, spanning a temperature range from 25°C to 900°C. Consistent test conditions were maintained for all samples. The TGA aimed to identify the thermal decomposition phases of the lignin as well as the blends. The T_{50} value indicates the temperature at which a 50% mass loss occurs, while the temperature at maximum mass loss ($T_{D\text{-}max}$) is derived from the peak of the derivative thermogravimetry (DTG) curve. Additionally, the char residue remaining at 600°C and 800°C was measured. Weight loss curves and DTG versus temperature plots were generated and analysed using TA Universal Analysis 2000 software. The results presented are averages from five replicate measurements.

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2.6.7 | *Differential Scanning Calorimetry Analysis (DSC)*

DSC was performed using a TA Instruments Q2000 differential scanning calorimeter. The glass transition temperature (Tg) of acetylated lignin, PLA and impact modifier were determined, as well as for the blends. The analysis was performed under a nitrogen atmosphere with aluminium pans, and sample weights ranged from 5 to 10 mg. Two heating cycles at a rate of 10°C/min were conducted: the first cycle heated the sample from 0°C to 150°C to remove residual moisture and thermal history, followed by cooling to 25°C and then reheating to 200°C at a rate of 20°C/min. The results were processed using TA Universal Analysis 2000 software, and the data presented represent the average of five replicate measurements.

3 | Results and Discussion

3.1 | Acetylation

The acetylation of lignin was confirmed through ATR-FTIR and NMR analyses, which are presented and discussed in detail in Sections 3.3 and 3.4. An overview of the main findings is provided here, while the corresponding spectroscopic results are presented in the subsequent sections. ATR-FTIR results showed a significant reduction in the hydroxyl group absorption band (3000–3650 cm^{-1}), indicating successful substitution of hydroxyl groups.

This reduction in hydroxyl group content is expected to decrease the hydrophilicity of lignin, which may lead to reduced moisture uptake. Although moisture absorption was not directly measured in this study, the observed reduction in hydroxyl group content (48–57%) is consistent with decreased hydrophilicity, which is commonly associated with reduced moisture uptake in lignin-based systems [10].

These changes were accompanied by the appearance of characteristic ester peaks at approximately 1740–1760 cm^{-1}, corresponding to C = O stretching vibrations.

Quantitative analysis of the integrated hydroxyl stretching band revealed reductions of approximately 57% and 48% for pyridine-acetylated and microwave-assisted acetylated lignin, respectively (Figure 3). The calculated degree of conversion was approximately 65% for pyridine-assisted acetylation and 45% for microwave-assisted acetylation. The OH-band reduction was calculated directly from the integrated OH peak areas relative to pristine lignin, whereas the degree of conversion was calculated after normalisation of the OH band to the aromatic reference band at approximately 1510 cm^{-1}, as described in Section 2.6.1. Consequently, the two calculations yield different absolute values but show the same trend, with pyridine-acetylated lignin exhibiting a greater extent of hydroxyl substitution than microwave-assisted acetylated lignin.

The acetylation of lignin also plays a critical role in modifying its interaction with the PLA matrix at the molecular level. Pristine lignin contains a high concentration of hydroxyl groups, resulting in a hydrophilic character that limits its compatibility with the relatively hydrophobic PLA. Upon acetylation, these hydroxyl groups are replaced by acetyl functionalities, reducing polarity and increasing hydrophobicity. This is expected to enhance the interfacial compatibility between lignin and PLA, potentially promoting improved dispersion of lignin within the polymer matrix. Furthermore, the presence of ester groups in both acetylated lignin and PLA may facilitate intermolecular interactions, such as dipole–dipole interactions, contributing to improved interfacial adhesion and overall material performance.

3.2 | Microwave-Assisted Acetylation

Microwave-assisted acetylation involved a substantially shorter active treatment period than the reaction period used for the conventional pyridine-catalysed method. The microwave treatment consisted of a 5 min heating ramp followed by 10 min at 130°C, corresponding to an active microwave treatment time of approximately 15 min, compared with the 24 h reaction period used for the conventional method. The 15 min period refers specifically to active microwave treatment and does not include the subsequent cooling, precipitation, washing, and drying steps. Following microwave treatment, the reaction vessels were allowed to cool naturally to room temperature for 12–24 h before further processing. As the reaction kinetics during this cooling period were not monitored, continued acetylation during cooling cannot be excluded.

Despite the substantially shorter active treatment period and the absence of a catalyst, successful acetylation was achieved using the microwave-assisted method, as confirmed by the ATR-FTIR and NMR analyses presented in Sections 3.3 and 3.4. NMR results showed similar spectral features for both acetylation methods, with characteristic signals corresponding to acetyl carbonyl groups (~169 ppm) and methyl groups (~20 ppm). However, slightly lower relative intensities of the acetyl-related signals were observed for microwave-assisted acetylation, consistent with its somewhat lower degree of substitution compared with pyridine-assisted acetylation.

Microwave-assisted acetylation offers a substantially shorter active treatment period and eliminates the need for a catalyst. Rapid microwave-assisted lignin esterification has also been reported by Monteil-Rivera and Paquet [15], who achieved effective lignin esterification using 10 min of microwave irradiation without solvent or catalyst. However, no direct measurements of energy consumption were performed in the present study. Moreover, the microwave-assisted route included heating to 130°C and subsequent precipitation with 24 h stirring, in addition to cooling, washing, and drying steps. Therefore, the present results do not provide sufficient evidence to conclude that the microwave-assisted route reduces either the overall processing time or the overall energy demand compared with the conventional method. A comprehensive process and energy assessment would be required to establish such advantages.

3.3 | ATR-FTIR Spectroscopy

To detect the structural disparities among lignin acetylated using pyridine as a catalyst, microwave-assisted acetylated lignin, and unmodified lignin, the samples were analysed using ATR-FTIR spectroscopy (Figure 2).

The ATR-FTIR spectra clearly confirm the occurrence of acetylation. The pristine lignin exhibits a broad O–H stretching

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band in the range of 3000–3650 cm^{-1}, corresponding to hydroxyl groups. After acetylation, a significant reduction in the intensity of this band is observed, indicating the consumption of hydroxyl groups during the esterification reaction.

Simultaneously, new absorption bands appear in the region of 1740–1760 cm^{-1}, attributed to the C = O stretching vibrations of ester groups formed during acetylation. The presence of these peaks provides direct evidence of successful esterification. Additionally, an increase in intensity at approximately 1190 cm^{-1} is observed, corresponding to C–O stretching vibrations in ester linkages.

Non-acetylated lignin exhibited all typical bands, including aliphatic C–H stretching vibrations (2850–2950 cm^{-1}) and characteristic aromatic skeletal vibrations in the range of 1600–1425 cm^{-1}. These peaks were present in all samples and did not show significant variation, indicating that the aromatic backbone of lignin remained largely unaffected by the acetylation process.

Quantitative analysis of the integrated hydroxyl stretching band revealed reductions of approximately 57% and 48% for pyridine-acetylated and microwave-assisted acetylated lignin, respectively (Figure 3). The calculated degree of conversion was approximately 65% for pyridine-acetylated lignin and 45% for microwave-assisted acetylated lignin, indicating a higher extent of hydroxyl substitution for the pyridine-assisted process [12, 13]. The OH-band reduction was calculated directly from the integrated OH peak areas relative to pristine lignin, whereas the degree of conversion was calculated after normalisation of the OH band to the aromatic reference band at approximately 1510 cm^{-1}, as described in Section 2.4.1. Consequently, the two calculations yield different absolute values but show the same trend, with pyridine-acetylated lignin exhibiting a greater extent of hydroxyl substitution than microwave-assisted acetylated lignin.

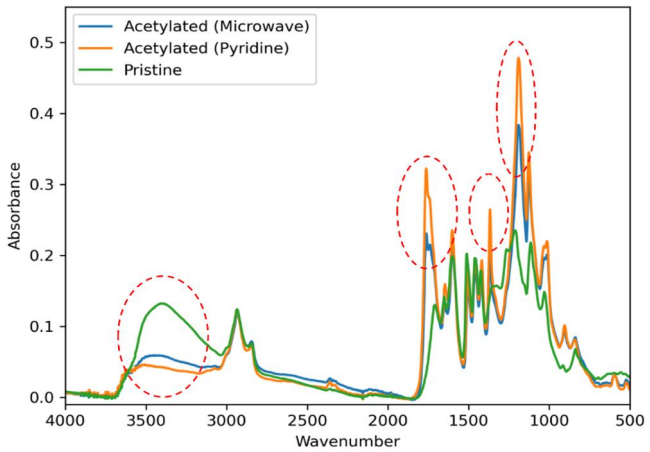

FIGURE 2 | ATR-FTIR spectra of pristine, pyridine-acetylated, and microwave-assisted acetylated lignin.

Differences in peak intensities were also observed between the two acetylation methods, with pyridine-acetylated lignin exhibiting higher intensities for the ester-related peaks (Figure 4), consistent with its higher degree of conversion. Both acetylated lignins displayed characteristic ester signals, including C = O stretching at 1740–1760 cm^{-1}, C–H bending at 1367 cm^{-1}, and C–O stretching at 1190 cm^{-1}, confirming the successful introduction of acetyl groups into the lignin structure.

Residual hydroxyl groups were observed in the range of 3620–3510 cm^{-1} (Figure 2), which are attributed to sterically hindered hydroxyl groups incapable of forming hydrogen bonds [15]. Overall, the observed spectral changes confirm successful acetylation for both methods, although the quantitative analyses indicate a higher extent of hydroxyl substitution for pyridine-assisted acetylation.

There is a visual difference in the colour of the different lignin samples. Lignin acetylated using acetic anhydride and pyridine appears lighter in colour compared to pristine lignin, while microwave-assisted acetylated lignin exhibits a darker colour (Figure 5). The difference in colour between the two types of acetylated lignin is likely due to variations in structural alteration, including differences in conjugation and chromophore formation induced by each acetylation method.

The observed colour differences may have implications for potential applications of the material. The darker colour of

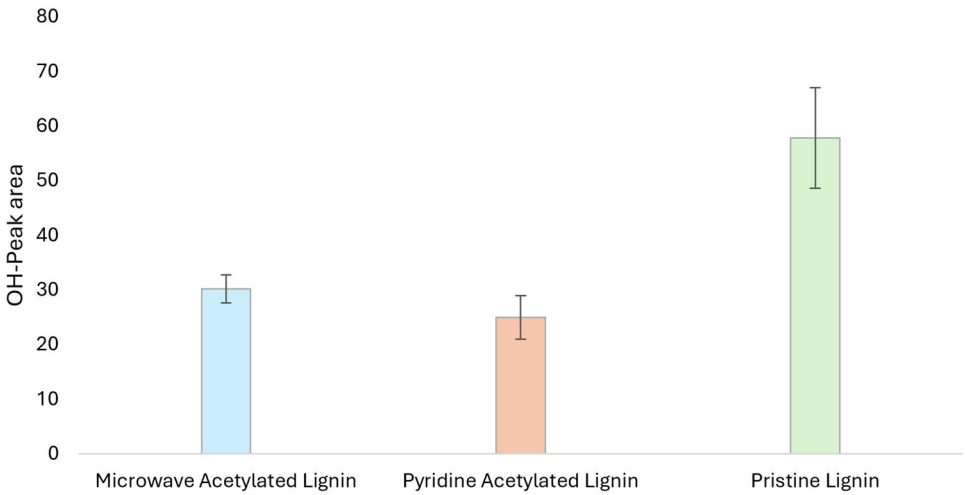

FIGURE 3 | Integrated area of the O–H stretching band obtained by ATR-FTIR analysis of pristine and acetylated lignin. Error bars represent standard deviation.

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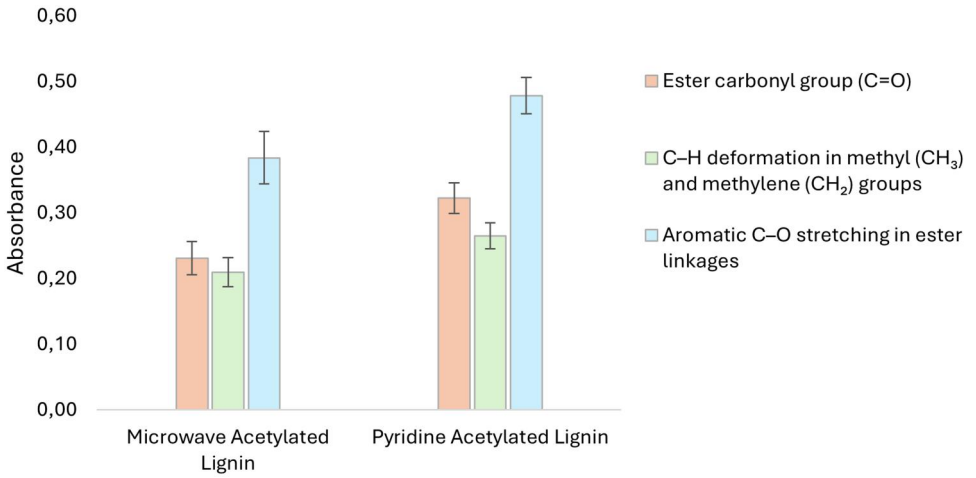

FIGURE 4 | Absorbance intensities of characteristic ester-related ATR-FTIR bands for microwave- and pyridine-acetylated lignin. Error bars represent standard deviation.

FIGURE 5 | Visual appearance of microwave-assisted acetylated, pyridine-acetylated, and pristine lignin (left to right).

microwave-assisted acetylated lignin could limit its use in applications where visual appearance or transparency is important, such as in packaging or consumer products requiring light-coloured materials. However, for applications where colour is less critical, such as automotive components or structural materials, this is unlikely to be a significant limitation.

Additionally, the darker colour may be associated with increased conjugation or structural changes during microwave treatment, which could potentially influence UV absorption. However, UV absorption and resistance were not evaluated in the present study, and further investigation would be required to determine whether these structural changes provide any functional advantage.

3.4 | ^{13}C NMR and 1H NMR Spectroscopy of Lignin Samples

The pristine lignin and the acetylated lignin samples were analysed by solid state and solution NMR, in order to confirm the acetylation reaction. The NMR analysis provides clear evidence of successful acetylation of lignin. In both solid-state and solution-state spectra, the appearance of new signals corresponding to acetyl functional groups confirms the introduction of acetyl moieties into the lignin structure. In particular, the presence of characteristic peaks associated with the acetyl carbonyl (C = O) and methyl (CH_3) groups demonstrates that hydroxyl functionalities in lignin have been successfully substituted through esterification. These spectral changes, together with shifts observed in the aromatic region, indicate structural modification of lignin consistent with acetylation.

The ^{13}C CP MAS NMR spectra for the pristine lignin is shown in Figure 6. According to the previous NMR studies of lignin [8, 30–32], the main peak at 56.0 ppm with a shoulder at 60.1 ppm belongs to the carbons of oxy-methyl groups -O-CH_3. The peak at 147.7 ppm is assigned to the aromatic ring carbons attached to the oxy-methyl groups. The asterisks in the chemical shift range of 195 to 240 ppm denote the spinning sidebands at multiple of spinning frequencies (13.5 kHz) from the main peaks.

The spectra for the pyridine catalysed acetylated lignin in Figure 7 shows the peaks belonging to the acetyl carbonyl at 169.4 ppm (C = O) and the methyl group at 20.2 ppm (CH_3). This provides clear spectroscopic evidence of successful acetylation [8]. The peaks belonging to the oxy-methyl groups at 55.9 and 61.0 ppm are almost unchanged compared to the pristine lignin. In the region of aromatic carbons, the main peak at 152 ppm belongs to the carbon of aromatic ring attached to the oxy-methyl groups, having neighbouring aromatic carbon attached to the -O-acetyl groups. The spectra for the microwave-assisted acetylated lignin in Figure 8 are very similar to the pyridine acetylated lignin. However, slightly lower relative intensities of the acetyl-related peaks were observed for the microwave-assisted acetylated lignin, indicating a somewhat lower degree of substitution compared to the pyridine-assisted method, consistent with the ATR-FTIR results. The acetylation shifts the strong peak at 148 ppm in the spectrum of pristine lignin to 152 ppm. This is due to the structural change in the neighbouring carbons by the acetylation. The effect can be easily verified by

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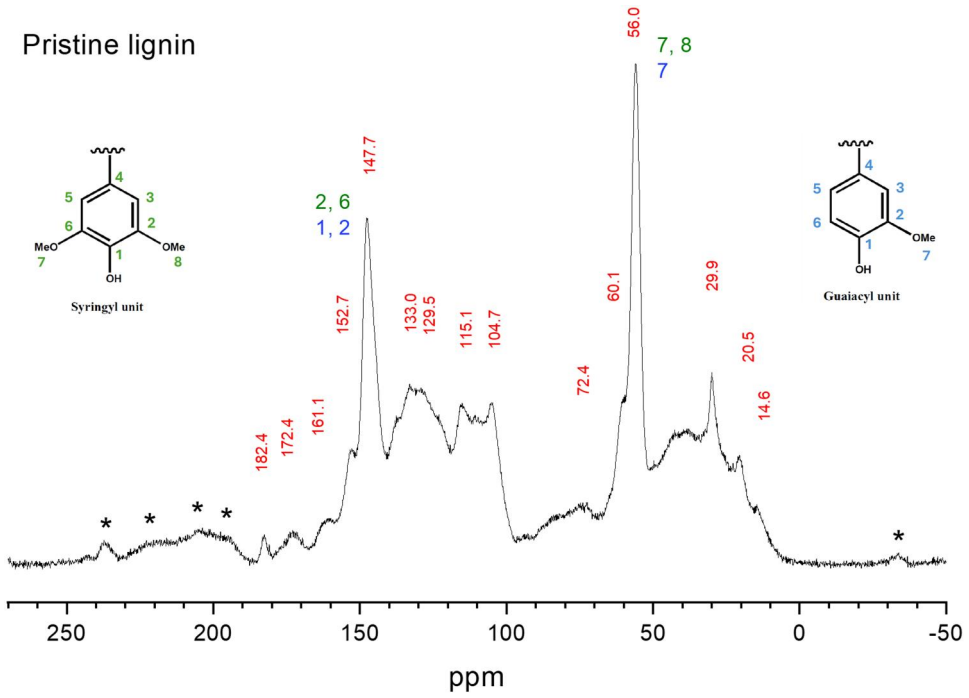

FIGURE 6 | ^{13}C CP/MAS NMR spectrum of pristine lignin with assignments of syringyl and guaiacyl units.

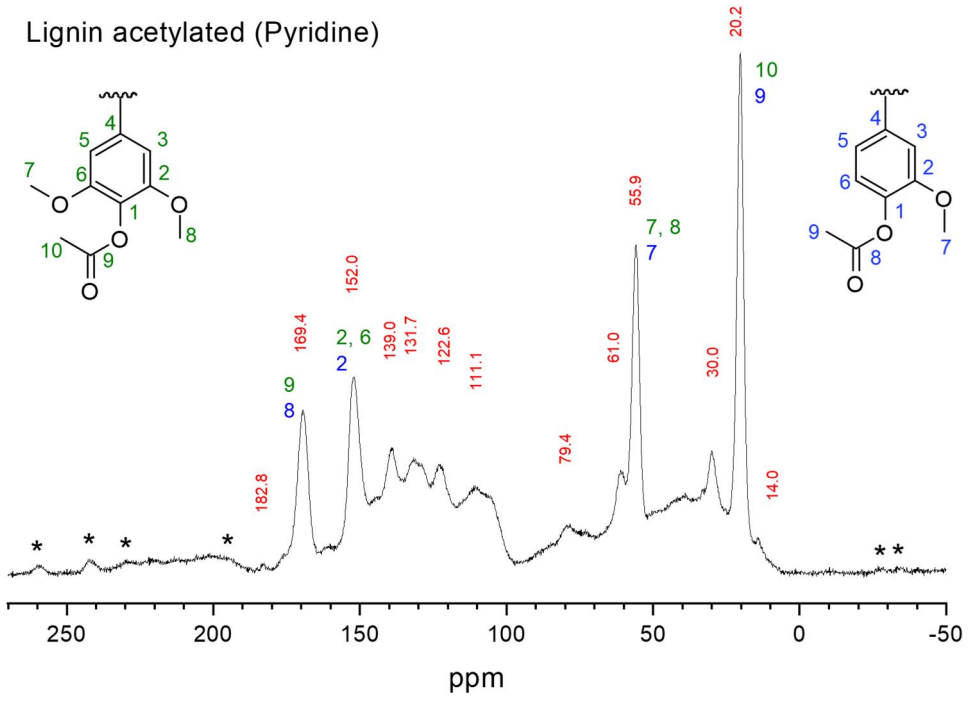

FIGURE 7 | ^{13}C CP MAS NMR spectrum of pyridine-acetylated lignin with peak assignments for the acetylated syringyl and guaiacyl units.

chemical shift prediction programmes (e.g. CNMR Predictor of ACD Labs).

The similarity is further confirmed by the spectra overlays in Figure 9. The spectra of both acetylated lignin are almost identical. Although, the relative intensities of the peaks belonging to the acetyl carbons at 169 ppm (C = O) and 20 ppm (CH_3) are about 10% higher in the spectrum of the sample acetylated with pyridine compared to that of microwave-assisted acetylation. This is also seen by the quantification of the hydroxyl group bands in the ATR-FTIR-analysis (Figure 3), where a difference in remaining hydroxyl groups of approximately 10% could be observed. The ^{13}C CP MAS NMR results were further supported by solution-state ^{1}H and ^{13}C NMR spectroscopy (Figures 10–12), which also enabled semi-quantitative evaluation of the degree of acetylation. In the ^{13}C NMR spectra for the acetylated lignin two peaks due to acetyl group (carbonyl and CH_3) were clearly identified at 20.0 ppm (-

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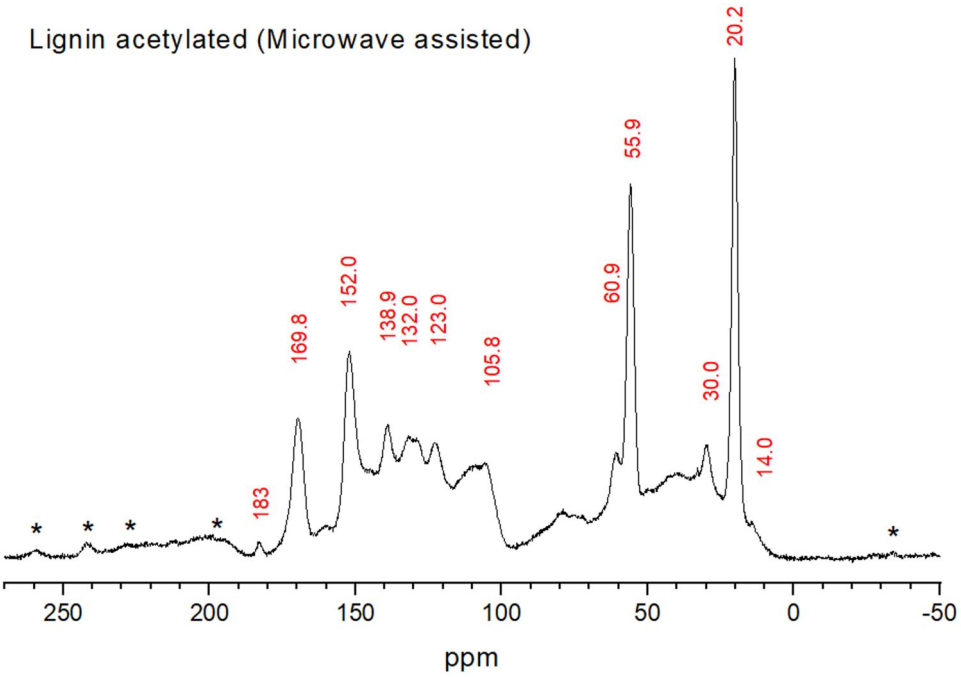

FIGURE 8 | ^{13}C CP MAS NMR spectrum of microwave-assisted acetylated lignin. Peak assignments correspond to those shown in Figure 7.

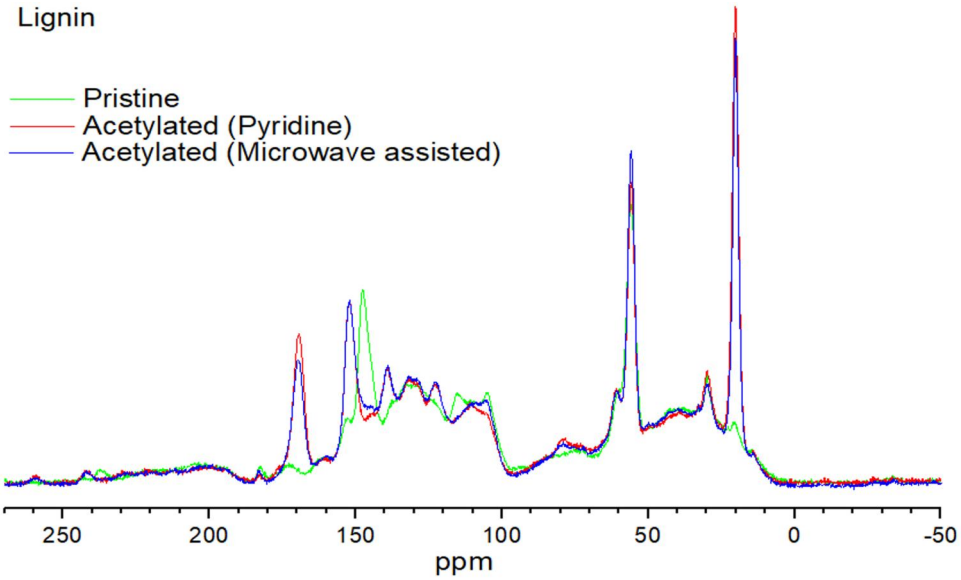

FIGURE 9 | Comparison of the ^{13}C CP/MAS NMR spectra of pristine, pyridine-acetylated, and microwave-assisted acetylated lignin.

CH_3) and at 168.4 ppm [8, 30]. In addition to qualitative confirmation, ^1H NMR spectroscopy was used to estimate the relative degree of acetylation. The extent of substitution was evaluated by comparing the signal intensity of the acetyl methyl protons (–$COCH_3$, ~2.0–2.2 ppm) with that of the aromatic protons of the lignin backbone (6.0–8.0 ppm), which were used as an internal reference (Figure 12). This approach provides a semi-quantitative measure of acetylation.

The acetylated lignin clearly exhibits the characteristic methyl signal at ~2.0–2.2 ppm, which is absent in the pristine lignin (Figure 12), confirming successful modification. The relative increase of this signal compared to the aromatic region suggests a higher degree of substitution. These observations are consistent with the trends observed in ATR-FTIR, supporting the conclusion that pyridine-assisted acetylation results in a slightly higher degree of substitution than microwave-assisted acetylation.

3.5 | Elemental Analysis

Elemental composition of the different lignin samples was quantitatively determined, and the results are presented in Table 2. The analysis of pristine and acetylated lignin shows a slight increase in carbon content following acetylation,

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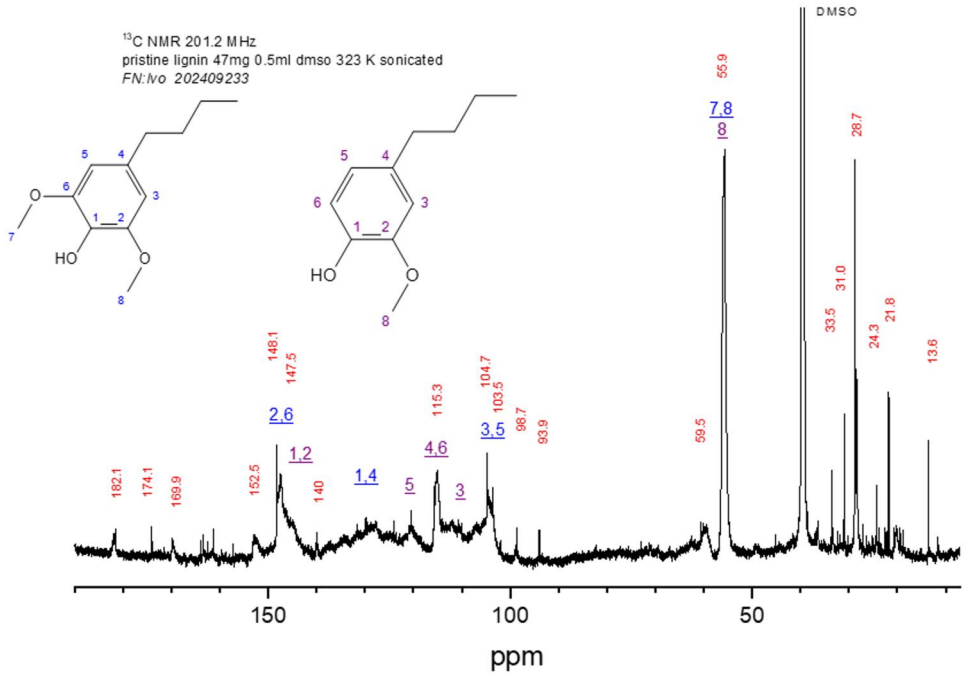

FIGURE 10 | ^{13}C NMR spectrum of pristine, nonacetylated lignin solution in DMSO. Assignment of the carbon peak positions in Syringyl (left) and Guaiacyl (right) units [8, 30, 31].

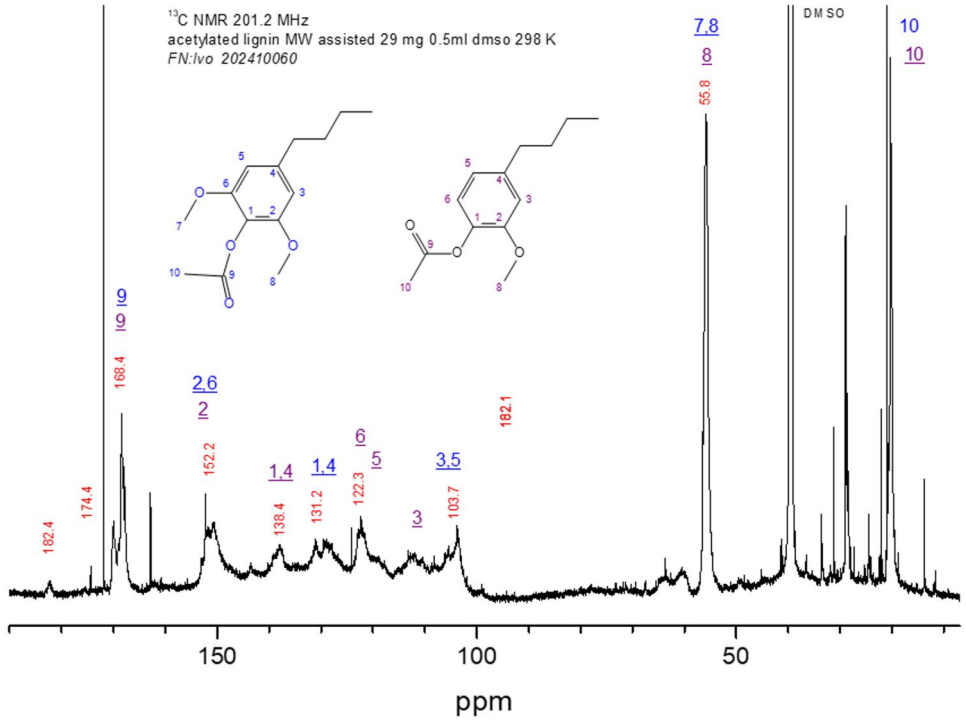

FIGURE 11 | ^{13}C NMR spectrum of acetylated lignin solution in DMSO. Assignment of the carbon peak positions in acetylated Syringyl (left) and acetylated Guaiacyl (right) units.

indicating the successful introduction of acetyl groups. As acetylation introduces additional carbon atoms into the lignin structure, an increase in the overall carbon percentage is expected [33].

The presence of nitrogen in all samples can be attributed to residual impurities originating from the biomass source, such as proteins or amino acid fragments remaining after the lignin extraction process. The slightly higher nitrogen content observed in the pyridine-acetylated lignin may be associated with residual traces of pyridine or impurities originating from the lignin source. In contrast, the microwave-assisted acetylation method does not involve nitrogen-containing reagents, resulting in a lower nitrogen content.

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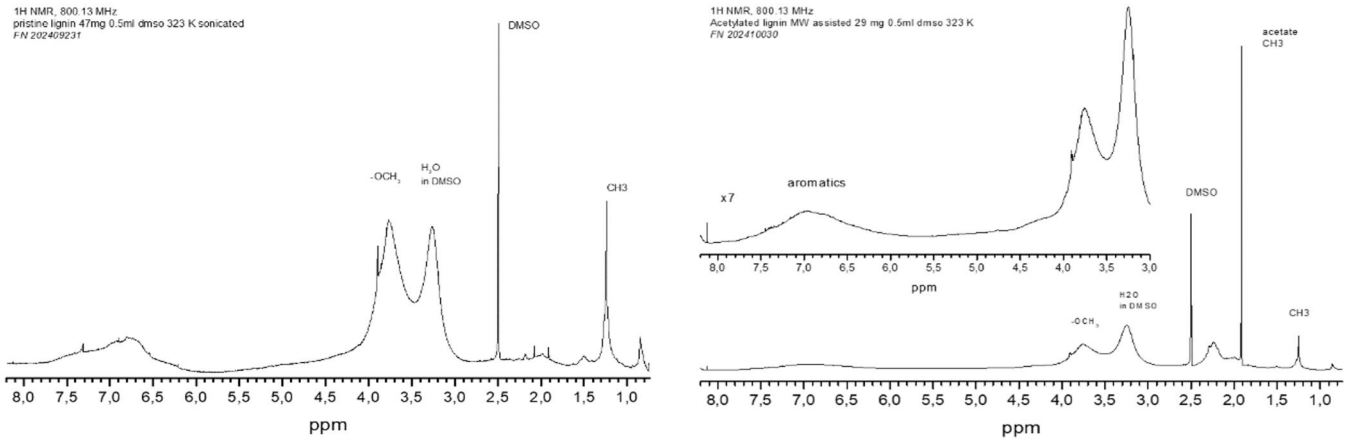

FIGURE 12 | ^{1}H NMR spectra of pristine lignin (left) and microwave-assisted acetylated lignin (right).

TABLE 2 | Elemental composition of pristine and acetylated lignin. The oxygen content was calculated from the difference between the C, H, N and S contents.

	Elemental composition (wt. %)				
Samples	**C**	**H**	**N**	**O**	**S**
Pristine lignin	62.84	5.10	0.45	31.61	n.d.
Acetylated (pyridine)	63.26	4.98	0.51	31.25	n.d.
Acetylated (microwave)	63.25	5.00	0.33	31.41	n.d.

Both acetylation methods produce similar changes in carbon and oxygen content, with minimal effect on hydrogen content. No detectable sulphur was found in any of the samples. The sulphur-free nature of these lignin samples enhances their suitability for high-purity and environmentally friendly applications.

3.6 | Charpy Impact Testing

The blends containing microwave-assisted acetylated lignin and 5% impact modifier exhibited higher impact strength than pure PLA and PLA containing 5% impact modifier alone (Figure 13). Previous studies using the same lignin–PLA system showed that acetylation of lignin increased impact strength compared with unmodified lignin [10], while the subsequent incorporation of 5% Biomax Strong into pyridine-acetylated lignin/PLA blends further increased impact strength [26]. For example, at 15 wt.% lignin, the impact strength increased from approximately 15 kJ/m^2 without impact modifier to approximately 25 kJ/m^2 with 5% impact modifier [26].

However, a control formulation containing unmodified lignin together with the impact modifier was not included in the present or previous experimental designs. Consequently, although the available results demonstrate improvements associated with lignin acetylation and with the addition of the impact modifier, their individual contributions and any potential synergistic interaction cannot be conclusively distinguished. Inclusion of such a control would enable a more complete assessment in future studies.

Increasing the lignin content from 15 to 20 wt.% resulted in a decrease in impact strength, consistent with previously reported trends [10, 26]. The microwave-assisted acetylated lignin blends also exhibited somewhat lower impact strength than the corresponding pyridine-acetylated lignin blends. This difference may be associated with the lower degree of acetylation obtained using the microwave-assisted method and resulting differences in lignin–PLA interfacial interactions. Further optimisation of the microwave-assisted acetylation process could be explored in future studies to determine whether a higher degree of acetylation improves the impact performance of these blends.

3.7 | Tensile Testing

The manufactured specimens were tested for tensile properties. It could be observed that the use of microwave-assisted lignin gave tensile properties on a similar level as for the pyridine acetylated lignin. In previous studies it has been observed that the acetylation process using pyridine has a positive impact on the tensile properties of the blends, when compared to blends containing unmodified lignin. The pyridine-acetylated lignin did enhance the tensile strength as well as the elongation of the resulting blends [10]. The increase in lignin load did reduce the tensile strength of the material, following the same trend as previously reported results, and that was expected, however, there is no major effect when employing microwave-assisted acetylated lignin. It should be noted that the degree of acetylation differs between the two modification methods, with pyridine-assisted acetylation resulting in a slightly higher degree of substitution compared to the microwave-assisted approach. Therefore, the observed differences in mechanical and thermal properties may reflect both the extent of acetylation and the modification method itself.

Despite the lower degree of acetylation, the microwave-assisted method yields comparable mechanical performance, suggesting that it is an efficient approach for lignin modification. However, a direct comparison at identical degrees of substitution would be required to fully isolate the effect of the modification method.

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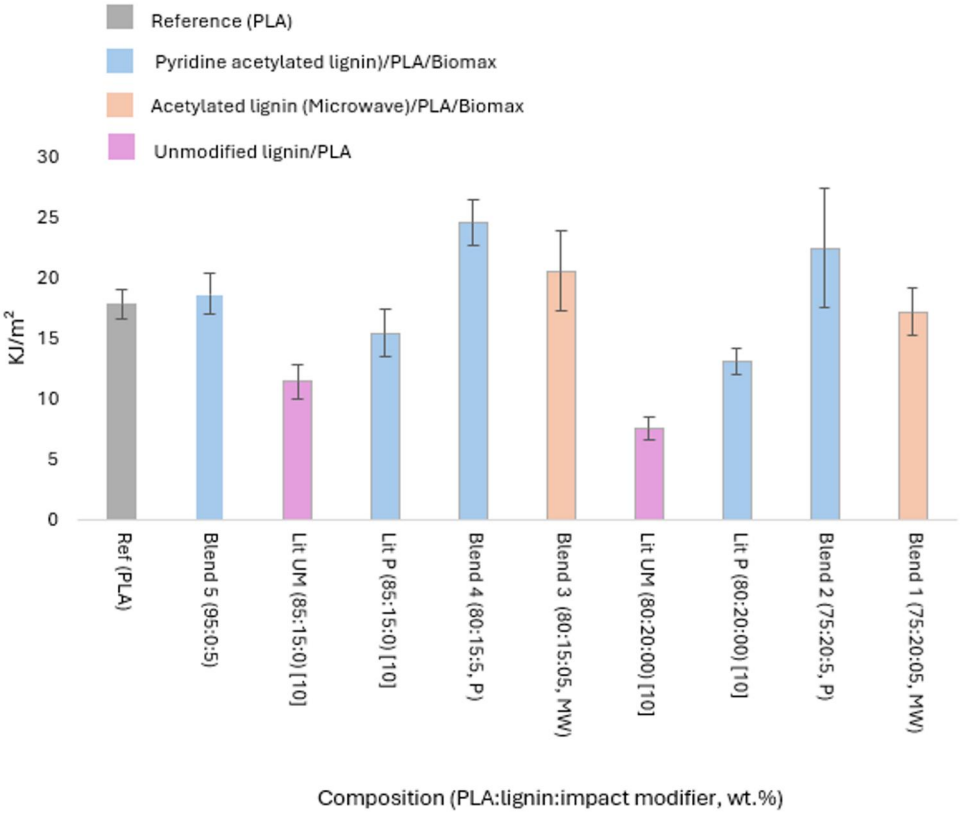

FIGURE 13 | Charpy impact strength of PLA–lignin blends. Compositions are given as PLA:lignin:impact modifier (wt.%). MW, microwave-assisted acetylated lignin; P, pyridine-acetylated lignin; UM, unmodified lignin; Lit, previously reported data [10, 26].

The relationship between the lignin loadings follows the same pattern as for previously reported pyridine-acetylated lignin (Figure 14). In the same study, it could also be observed that the incorporation of the impact modifier affected the tensile strength of the material [34], the same trend was expected to be observed for microwave-assisted lignin blends. It can therefore be concluded that microwave induced acetylation is a viable method for lignin modification.

Incorporation of lignin and impact modifiers into PLA significantly reduced tensile strength. The blends with 20% lignin (both modified by microwave-assisted acetylation and with pyridine as a catalyst) exhibited the lower tensile strengths compared to neat PLA, highlighting the trade-off between tensile strength and increased lignin content. Blends with pyridine-modified lignin showed slightly higher tensile strengths [26] compared to those with microwave-assisted acetylation. Although the incorporation of lignin reduced the tensile strength compared to neat.

PLA, this trade-off is offset by significant improvements in impact resistance, ductility, and thermal stability – properties in which PLA typically underperforms. For many targeted applications, such as automotive interior parts, durable packaging, and consumer products, enhanced toughness and heat resistance are more critical than achieving maximum tensile strength. Furthermore, lignin addition increases the renewable content of the composite, supports cost reduction, and advances sustainability targets, making the blends attractive for high-performance, eco-friendly applications despite the modest decrease in tensile strength.

Adding lignin and impact modifiers is well known to reduce the tensile modulus, but in this study, it was seen that microwave-assisted acetylated lignin blends maintained a slightly higher modulus than pyridine-modified lignin blends at comparable compositions (Figure 15). This suggests that microwave-assisted acetylated lignin may provide a more balanced stiffness in the blends. The addition of impact modifiers and lignin significantly improved the ductility of the blends when compared to neat PLA. Notably, the microwave-assisted acetylated lignin blends exhibited higher elongation at break at lignin content of 15%, compared to the pyridine-modified lignin blends. This improvement in ductility indicates that microwave-assisted acetylated lignin effectively enhances the flexibility and toughness of the material. The results indicate that while pure PLA offers excellent tensile strength and stiffness, its brittleness limits its applicability in dynamic environments. The incorporation of lignin, especially when modified through microwave-assisted acetylation, at a lignin loading of 15%, provides a more versatile material with enhanced ductility and reasonable tensile properties. These modifications enable the material to perform better in applications requiring flexibility and impact resistance. The combination of tensile strength, tensile modulus, and elongation at break data provides a comprehensive view of the mechanical performance of PLA-lignin blends. Modified lignin (via microwave-assisted acetylation) generally improves the ductility and maintains a reasonable balance between stiffness and tensile strength, making it a more suitable candidate for applications where flexibility and toughness are crucial.

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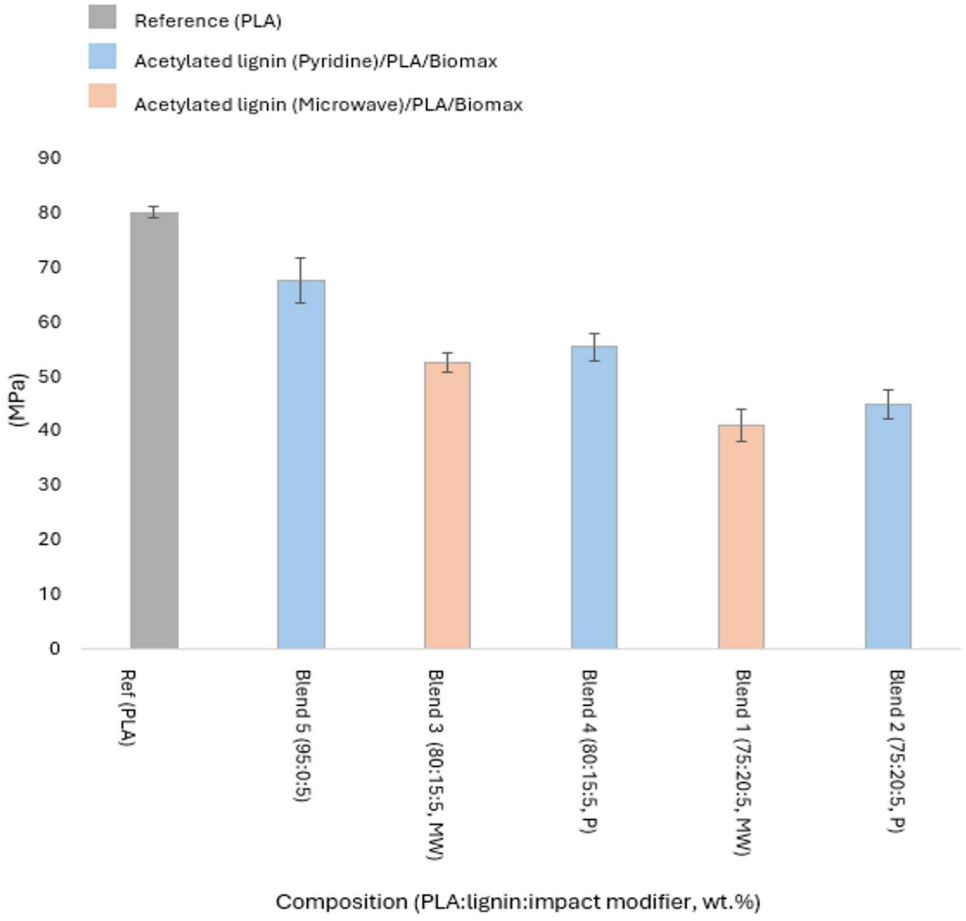

FIGURE 14 | Tensile strength of PLA–lignin blends. Compositions are given as PLA:lignin:impact modifier (wt.%). MW, microwave-assisted acetylated lignin; P, pyridine-acetylated lignin.

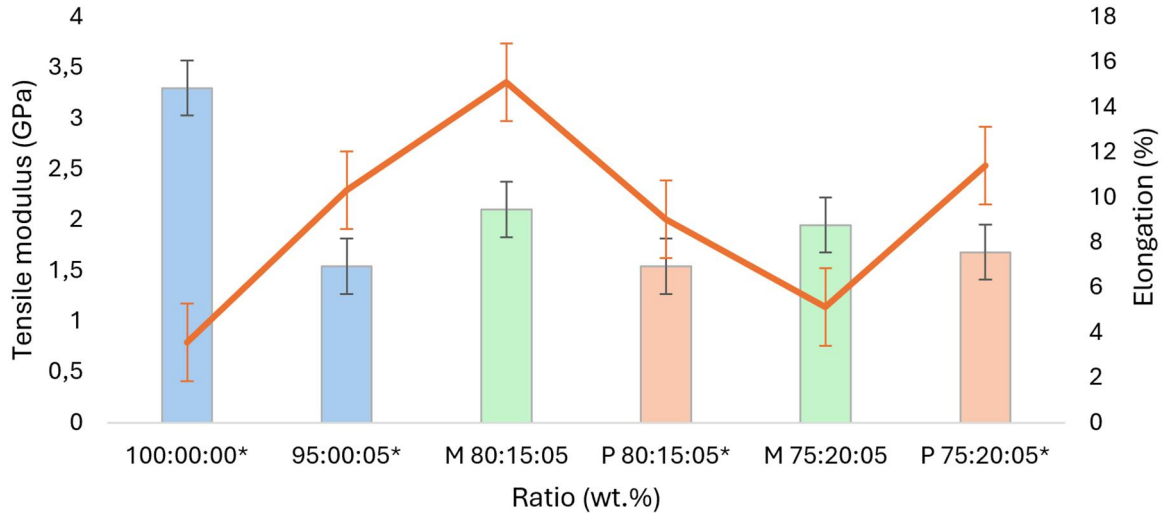

FIGURE 15 | Tensile modulus and elongation at break of PLA–lignin blends. Compositions are given as PLA:lignin:impact modifier (wt.%). MW, microwave-assisted acetylated lignin; P, pyridine-acetylated lignin. *[25].

3.8 | Thermogravimetric Analysis of Lignin

The thermal degradation properties of lignin (pristine and acetylated) were evaluated using TGA. The TGA thermograms of the acetylated lignin showed a gentle decomposition slope, regardless of acetylation method (Figure 16). The microwave-assisted acetylated lignin appears to have a slightly lower thermal stability when the point corresponding to 50 percent weight loss (T_{50}) is examined (Table 3). The lignin acetylated using pyridine reached this point at 523°C [10], whilst the microwave-assisted lignin reaches this point at 515°C, which is lower compared to unmodified lignin (542°C), indicating a

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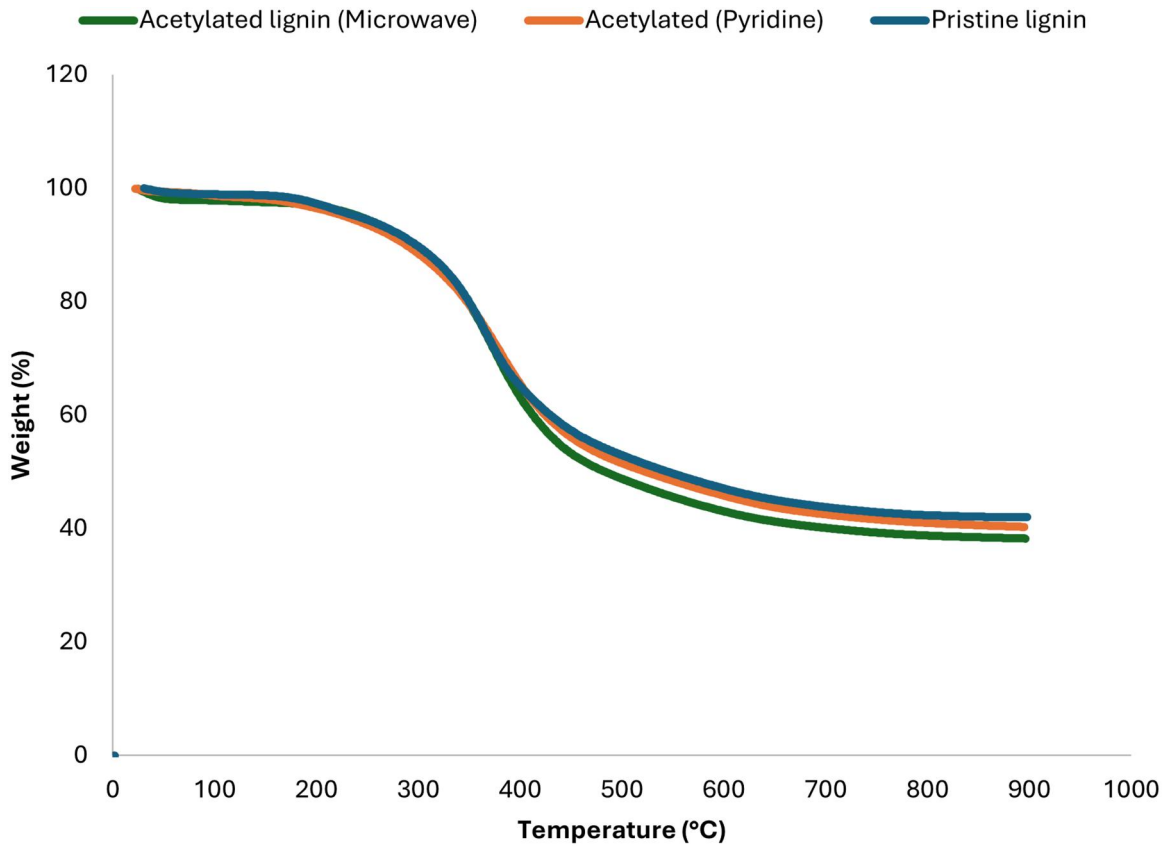

FIGURE 16 | Thermal decomposition behaviour of pristine, pyridine-acetylated, and microwave-assisted acetylated lignin.

TABLE 3 | TGA and DSC results for lignin, PLA, and PLA–lignin blends.

Modification method	RATIO(WT. %) PLA:LIGnin:imp-mod	$T_{50\%}$°C	SD	$T_{D\text{-}max}$°C	SD	Residual char (wt. %) 600°C	SD	Residual char (wt. %) 800°C	SD	Reference
	100:00:00	359	3.6	366	3.1	0.03	0.1			
	00:00:100	462	1.3	472	1.9	0.74	1.6			[26]
	95:00:05	359	1.1	364	2.1	0.15	0.4			[10]
UM	00:100:00	542				46.4		42.3		[10]
MW	**00:100:00**	515	30.7	376	1	44.5	1.7	38.2	0.5	
P	**00:100:00**	523	1.5	382	2.3	45.8	0.1	40.9	0.2	[10]
MW	**80:15:05**	367	3	369	3	4.9	1.6	0.62	3.2	
P	**80:15:05**	369	3.4	370	3.8	7.13	0.3	1.92	0.7	[26]
MW	**75:20:05**	370	2.2	369	2.5	9.33	0.5	3.1	3.4	
P	**75:20:05**	370	1.1	370	1.1	9.5	0.1	5.84	1.6	

Note:Compositions are given as PLA:lignin:impact modifier (wt.%).
Abbreviations: MW, microwave-assisted acetylated lignin; P, pyridine-acetylated lignin; SD, standard deviation; $T_{50\%}$, temperature at 50% mass loss; $T_{dd\text{-}max\text{-}max}$, temperature at maximum mass-loss rate; UM, unmodified lignin.

lower decomposition resistance than lignin acetylated using pyridine as a catalyst. However, the standard deviation for the T_{50} of microwave-assisted lignin is high in comparison to the other lignin, indicating that this is more of an area, than a fixed point where this phenomenon occurs. There was also a slightly higher char residue present for the unmodified lignin, whilst a negligible difference could be observed for the lignin that underwent acetylation.

3.9 | Thermogravimetric Analysis of Blends

The TGA thermographs and DSC results of PLA and its blends containing acetylated lignin and impact modifier were also investigated. In previous studies conducted by Johansson et al. [10, 26], it was observed that the temperature corresponding to 50% degradation (T50%) of the blends increased slightly with the incorporation of the impact modifier compared to pristine

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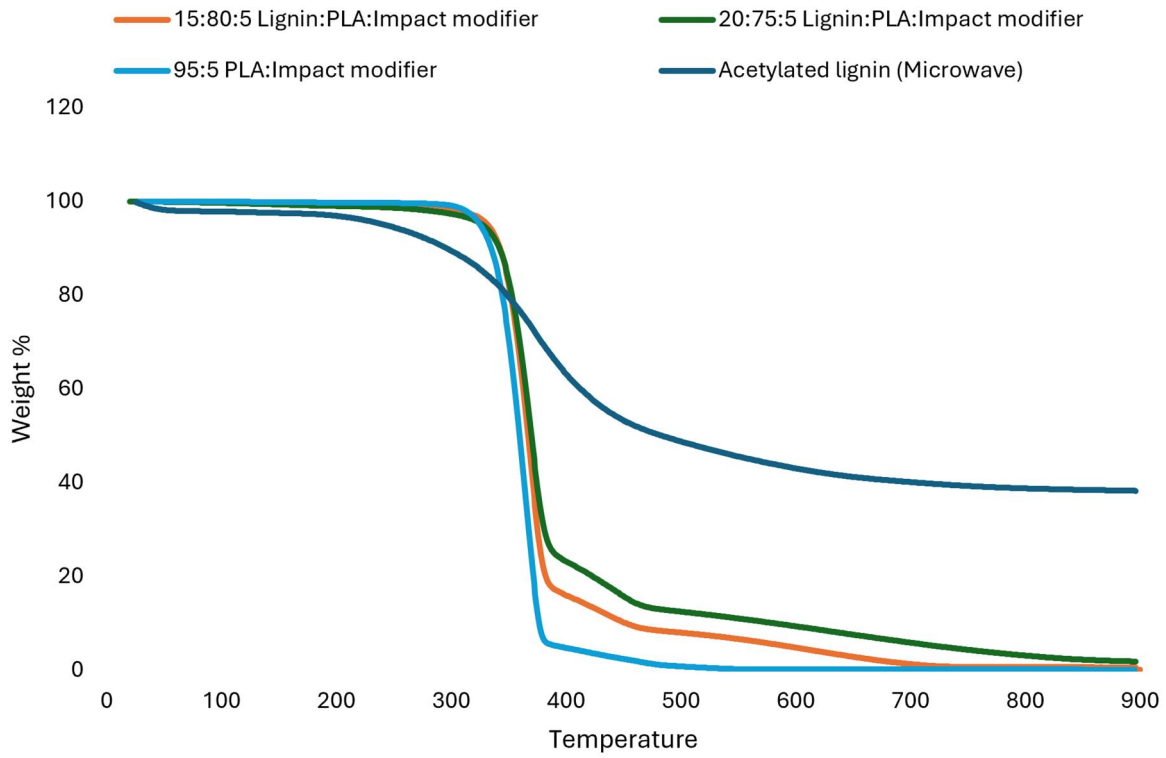

FIGURE 17 | Thermal decomposition behaviour of microwave-assisted acetylated lignin, PLA–lignin blends, and PLA containing 5% impact modifier.

PLA. However, the primary contributor to the improved thermal stability of the blends is the lignin content, as a clear trend of increasing thermal stability with increasing lignin content is observed (Figure 17).

No significant differences in decomposition behaviour were observed between blends containing pyridine-acetylated lignin and microwave-assisted acetylated lignin. Although a slight reduction in thermal stability is observed for the microwave-assisted acetylated lignin blends, the difference compared to pyridine-acetylated lignin blends is negligible (Table 3). It should be noted that the degree of acetylation differs between the two modification methods; therefore, the observed thermal behaviour reflects the combined influence of both the extent of acetylation and the modification route, rather than the processing method alone.

The improved thermal behaviour observed in the blends can be associated with the incorporation of acetylated lignin, which contributes to enhanced thermal stability through increased char formation and structural rigidity. While long-term thermal stability was not evaluated, the TGA results indicate that acetylated lignin contributes to improved thermal resistance of the material under the tested conditions.

It can also be observed that blends containing microwave-assisted acetylated lignin exhibit slightly lower residual weight content at fixed temperatures (600°C and 800°C) (Table 3) compared to blends with pyridine-acetylated lignin. This slight difference in char residue may be associated with differences in the extent of acetylation and resulting structural characteristics of the modified lignin [11].

3.10 | 3.10 Differential Scanning Calorimetry

The glass transition temperature (Figure 18) was derived from the second DSC heating cycle. All blends, regardless of modification method, showed a Tg within the same range (60°C–70°C) [26]. However, it can be observed that the DSC curves for the blends containing microwave-assisted acetylated lignin exhibit a melting peak at 150°C–160°C.

The appearance of this melting peak suggests differences in molecular organisation and phase behaviour compared to blends containing pyridine-acetylated lignin. This behaviour may be attributed to differences in dispersion and intermolecular interactions.

However, this observation does not directly indicate a higher degree of acetylation. As confirmed by ATR-FTIR and NMR analyses, the pyridine-assisted acetylation results in a slightly higher degree of substitution. Therefore, the differences observed in the DSC thermograms are more likely related to morphological and structural effects rather than the extent of chemical modification alone. In contrast, the absence of a distinct melting peak in the pyridine-acetylated lignin blends may indicate a more amorphous phase behaviour or differences in molecular packing within the PLA matrix.

4 | Conclusions

This study investigated the effects of microwave-assisted lignin modification on the mechanical and thermal properties of lignin–polylactic acid biopolymer blends for high-performance applications. Acetylation of lignin improves its compatibility

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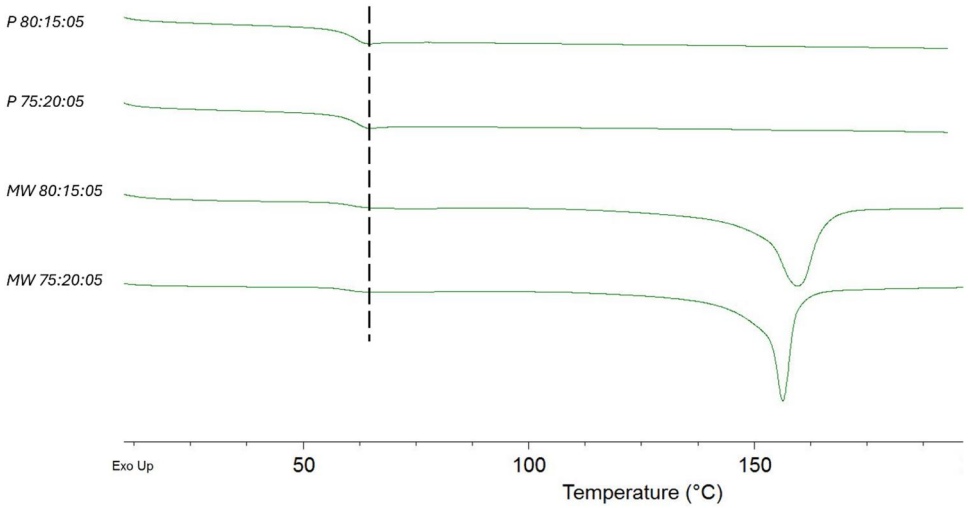

FIGURE 18 | DSC curves of PLA blends containing pyridine- and microwave-assisted acetylated lignin. Compositions are given as PLA:lignin:impact modifier (wt.%); MW, microwave-assisted acetylated lignin; P, pyridine-acetylated lignin.

with hydrophobic polymers such as PLA by replacing hydroxyl groups with acetyl groups, thereby reducing hydrophilicity, potentially improving interfacial compatibility and dispersion within the polymer matrix. These changes also increase thermal stability, reduce self-aggregation, and can enhance the mechanical performance of composites, making acetylated lignin suitable for a wide range of applications including biodegradable plastics, coatings, and bio-based composites.

Microwave-assisted acetylation offers a substantially shorter active treatment period than the conventional method and eliminates the need for a catalyst. This method provides controlled reaction conditions and shows potential for further process development and scale-up while avoiding the use of a catalyst. The blended polymers were characterised using ATR-FTIR, NMR, elemental analysis, tensile and impact testing, and thermal analyses (TGA and DSC). The successful acetylation of lignin was confirmed through spectroscopy, showing reduced hydroxyl content and the presence of ester signals. Incorporation of acetylated lignin and an impact modifier into PLA improved impact strength, ductility, and thermal stability.

The results demonstrate that microwave-assisted acetylation is a viable, sustainable alternative to pyridine-catalysed acetylation, offering comparable mechanical and thermal performance while substantially reducing the active treatment time and avoiding the use of a catalyst. It should be noted that the degree of acetylation differed between the two modification methods, and therefore the observed material properties reflect the combined influence of both the extent of acetylation and the modification route. The obtained properties indicate strong potential for producing versatile, high-performance lignin-based composites for demanding industrial applications. Future work should include comparisons at equivalent degrees of acetylation to fully isolate the effect of the modification method.

Acknowledgements

This study did not receive dedicated funding from public, commercial, or non-profit entities. Fortum is acknowledged for providing the lignin used in the study. Giulia Simao De Sousa is acknowledged for her help with the quantification of the ATR-FTIR spectra. We also thank Dr Tõnis Pehk for conducting the solution NMR measurements. The NMR measurements were supported by Estonian Research Council (Grant No PRG1702).

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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