

Tuning Eco-Foaming of Kraft Lignin through Esterification: Effects on Chemical Structures and Thermal Stability

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Cite This: *ACS Sustainable Chem. Eng.* 2026, 14, 10041–10050



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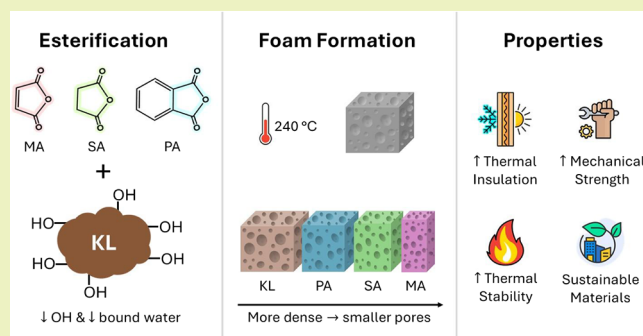
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ABSTRACT: This study explores how anhydride esterification of kraft lignin (KL) influences an “eco-foaming” process that transforms 100% KL into rigid foams. KL was reacted with maleic (MA), succinic (SA), or phthalic (PA) anhydride in acetone. FTIR analysis confirmed hydroxyl consumption (diminished 3496/3372/3280 cm^{-1} bands) and formation of ester bonds at approximately 1712/1267/1130/1030 cm^{-1} . The degrees of esterification (DE) ranged around 8.2% for MA, 7.9% for SA, and 6.3% for PA. Thermal analysis showed slightly higher glass-transition temperatures (T_g) and greater stability above 300 °C. When heated at 240 °C, the MA-KL foams exhibited smaller pores ($\sim 23 \mu\text{m}$), higher density ($\sim 0.32 \text{ g}\cdot\text{cm}^{-3}$), and more closed-cell structures, which led to increased compressive strength and reduced thermal conductivity ($0.043 \pm 0.002 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) compared to unmodified KL foams ($\sim 84 \mu\text{m}$, $0.26 \text{ g}\cdot\text{cm}^{-3}$, $0.076 \pm 0.005 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$). TGA revealed improved thermal degradation resistance between 400 and 600 °C, likely due to denser, more closed-cell architectures and potential heat-induced cross-linking. Overall, esterification provides a controllable means to modify pore structure and foam performance, yielding lignin-based foams with enhanced mechanical strength, thermal insulation, and stability, suitable for sustainable building applications.

KEYWORDS: Kraft lignin, Anhydride, Esterification, Chemical structures, Thermal stability, Thermal foaming behaviors



1. INTRODUCTION

There is increasing global interest in replacing synthetic polymers with renewable natural polymers to reduce environmental impacts linked to petroleum-based plastics.¹ Lignin, the second most abundant natural polymer and a key byproduct of pulping and biorefining industries, is a prominent biobased candidate.² Annually, around 70 million metric tons of technical lignin are produced, mostly used for energy through burning.² Creating high-value products from lignin could greatly enhance the economic prospects of paper mills and biorefineries. A more profitable lignin supply would also benefit the forestry sector, which is vital for preventing deforestation.^{3,4} These factors have driven significant research efforts to turn lignin into a sustainable substitute for synthetic plastics and polymers.

One potential application route that has recently gained attention is the utilization of lignin to produce foam materials.^{5,6} Previous studies have explored several methods such as partial substitution of polyols in polyurethane foams,^{7,8} partial replacement of phenolic components in phenol–formaldehyde and phenol–urea–formaldehyde foams,⁹ and incorporation of lignin into polystyrene-based foams.¹⁰ In these cases, lignin usually makes up less than 40 wt % of the

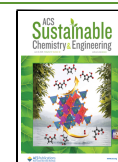
mixture, as higher lignin loading often compromises mechanical strength and processability.⁵ Recently, researchers have started to develop foams in which lignin is the main structural component. For example, Fagbemigun and Mai¹¹ prepared lignin–furfuryl alcohol foams with diethyl ether as a blowing agent, while Duarte et al.¹² produced rigid foams from lignin–tannin blends using pentane. Liang et al.¹³ directly fabricated foams by heating lignin from corn residues. In our previous work,^{14–16} we developed an eco-foaming process that converts 100% kraft lignin (KL) into rigid foams solely through compression and heat, where bound water and hydroxyl dehydration act as intrinsic blowing agents and processing parameters control pore structure.¹⁴ That process established a route to lignin-based foams without external blowing chemicals and demonstrated the influence of moisture content, preheating, and pressing conditions on the resulting

Received: November 28, 2025

Revised: March 30, 2026

Accepted: March 31, 2026

Published: May 28, 2026



morphologies.¹⁴ Building on that foundation, this study introduces an esterification step before foaming. By chemically altering lignin before thermal expansion, the hydroxyl content and bound water are reduced, while the softening behavior is also altered. This offers a second tunable factor, chemical modification in addition to processing, for controlling pore formation and material properties. As a result, eco-foaming is extended from a purely process-based to a combined chemical and process strategy, allowing property control beyond that achievable with unmodified lignin foams. However, the direct use of KL in materials is limited due to its poor thermal stability, hydrophilicity, brittleness, and low solubility in common organic solvents.^{2,17,18} To address these issues, methods such as molecular-weight fractionation, purification, and especially chemical modification are employed. Among chemical strategies, modifying hydroxyl (–OH) groups has proven particularly effective.¹⁷ Lignin contains both phenolic hydroxyls (attached to aromatic rings) and aliphatic hydroxyls (on side chains), which influence its polarity and hydrogen-bonding capacity, but also decrease compatibility with hydrophobic polymers. These hydroxyl groups can be functionalized through various reactions, including esterification, phenolation, hydroxypropylation, oxypropylation, epoxidation, nitration, sulfonation, alkylation, and silylation.¹⁸ Esterification is especially practical and effective, in which lignin–OH reacts with acid anhydrides or acid chlorides to form ester linkages, introducing hydrophobic groups that reduce hydrogen bonding and improve thermal stability.^{19–21} In some cases, longer or flexible ester chains act as internal plasticizers, lowering the glass-transition temperature (T_g) and melt viscosity, which helps in thermoplastic processing.^{19–21} Recent studies have demonstrated that anhydride esterification can significantly improve the performance of KL.²² For example, Han et al. demonstrated that succinic-anhydride-modified lignin embedded in poly(vinyl alcohol) films greatly enhances mechanical toughness and thermal stability while remaining fully biodegradable.²³ Building on this, Subbotina et al. used maleic anhydride modification to create degradable thermosets and lignin–nanocellulose biocomposites, where ester bonds enhanced compatibility and allowed for controlled hydrolytic degradation.²⁴ More recently, solvent-free reactive extrusion of lignin with octenyl succinic anhydride produced thermoplastic lignin esters with targeted esterification of aliphatic hydroxyl groups, providing a scalable route to processable lignin derivatives.²⁵ Although prior studies have shown that anhydride esterification effectively tailors lignin's chemistry and thermal stability, most have centered on films, composites, or thermoplastic processing rather than lignin's behavior during thermal foaming. In contrast, this work examines how esterification affects KL's eco-foaming behavior and foam formation during heating, addressing a gap that has received limited attention in the recent literature. A key advantage of using carboxylic acids and acid anhydrides is that many of these reagents are derived from biobased sources, which improves process circularity.²⁶ Direct esterification with carboxylic acids generally requires catalysts and high temperatures, which can lead to side reactions and degradation;¹⁸ therefore, acid anhydrides are often preferred.^{27–30} Maleic anhydride (MA), succinic anhydride (SA), and phthalic anhydride (PA) are among the most common reagents used for lignin esterification. MA introduces an unsaturated aliphatic ester, SA a saturated aliphatic ester, and PA an aromatic ester. Chen et al.³¹ demonstrated that the structure of the anhydride

significantly influences lignin properties. For example, MA and SA increase T_g and thermal stability, while PA results in lower T_g and stability. Since these anhydrides vary in rigidity, polarity, and molecular size, they provide a valuable framework for systematically exploring how chemical structure impacts processing behavior.

The eco-foaming process shares certain features with the pyrolysis process, where high temperatures facilitate the removal of volatiles and structural stabilization. However, the effects of chemical modification on such thermal foaming processes remain largely unexplored. Studies on related systems have shown that cross-linking agents such as boric acid or ammonium borate can alter the pyrolysis and foaming behavior of cellulose and lignin by modifying hydroxyl functionality.^{32,33} In contrast, anhydride esterification does not necessarily induce cross-linking but instead reduces hydroxyl content, potentially decreasing bound water and altering gas evolution during foaming. The resulting ester groups may also affect softening behavior by either plasticizing the structure or restricting molecular mobility.

Therefore, elucidating how anhydride esterification alters lignin's chemical structure, thermal behavior, and foaming response is critical for controlling foam morphology and performance. This study examines how esterification with maleic, succinic, and phthalic anhydrides affects the chemical structure, thermal characteristics, and eco-foaming behavior of KL. Using spectroscopic, thermal, morphological, and mechanical analyses, this work demonstrates that targeted chemical modification provides a versatile strategy to tune lignin foaming and tailor materials with strong potential for applications in lightweight structural components, high-performance thermal insulation (e.g., sustainable building materials), protective packaging, energy-storage platforms, and porous media for filtration and separation.

2. MATERIALS AND METHODS

2.1. Materials

KL derived from pine wood was kindly supplied by Domtar (Plymouth Mill, NC, USA). The approximate moisture content was determined according to ASTM D4442-20. The lignin sample contained 58.87% dry matter, which comprised 90.8% lignin (85.47% Klason lignin and 5.33% acid-soluble lignin), 2.76% total carbohydrates, and 0.45% ash. Maleic anhydride (MA), succinic anhydride (SA), and phthalic anhydride (PA) used for esterification were obtained from Acros Organics (Fair Lawn, NJ, USA) and used without further purification.

2.2. Esterification of Kraft Lignin

KL was oven-dried at 70 °C until a constant weight (W_1) was reached. The dried lignin was esterified separately with MA, SA, and PA. Each reaction was performed by dispersing lignin in a 10 wt % solution of the respective anhydride in acetone at a solid-to-liquid ratio of 1:20 (w/v). The mixture was heated under reflux at 60 ± 2 °C for 7 h in a stirred reactor vessel. After the reaction was completed, acetone was removed under vacuum. The solids were collected by vacuum filtration and washed to remove any unreacted anhydrides and byproducts, i.e., MA-modified lignin with distilled water, SA-modified lignin with hot water, and PA-modified lignin with toluene, and further washed repeatedly with distilled water until the pH reached 7. Finally, the modified lignin samples were dried in an oven at 70 °C until they achieved a constant weight (W_2). The weight percent gain (WPG), representing the extent of esterification, was calculated from the change in oven-dry mass before (W_1) and after (W_2) modification according to

$$\text{WPG (\%)} = \frac{W_2 - W_1}{W_1} \times 100 \quad (1)$$

Each experiment was conducted in duplicate under the same conditions, and the reported WPG values represent the average. The degree of esterification (DE), which estimates the extent of hydroxyl substitution, was determined from WPG using the molar masses of lignin repeat units and anhydride reagents^{31–34}

$$\text{DE} = \frac{\text{WPG} \times M_L}{(M_S - M_H) \times (100 - \text{WPG})} \quad (2)$$

where M_L is the molar mass of the lignin repeating unit, M_S is the molar mass of the substituting compound (anhydride), and M_H is the molar mass of hydrogen (1 g·mol^{−1}).

2.3. Foam Fabrication

Lignin-based foams were prepared from KL and esterified lignin derivatives using a press-molded thermal foaming process. Before foaming, all the lignin samples were dried in an oven at 70 °C until a constant mass was obtained. The dried lignin was then ground for 2 min using a multispeed blender (Hamilton Beach S0128, 10-function model) to achieve uniform particle size. The ground powder was transferred into a steel molding chamber (5 × 5 × 4 in, W × L × D) designed to control sample dimensions during foaming. The material was cold-pressed at 2.0 MPa for 30 s to form a dense lignin block. The chamber containing the pressed lignin block was then heated in an oven (Thermo Electron LED GmbH, Langensfeld, Germany) at a rate of 10 °C·min^{−1} to 240 °C, held for 60 min, and then cooled to room temperature. The resulting self-expanded foams were removed from the mold and stored in sealed containers for further testing. The foams were labeled as KLF (unmodified lignin foam), MAKLF, SAKLF, and PAKLF, corresponding to lignin esterified with maleic, succinic, and phthalic anhydrides, respectively. Detailed characterization procedures, including FTIR, TGA/DSC, microscopy, mechanical testing, and pore-size analysis methods, are provided in the Supporting Information (Section S2).

3. RESULTS AND DISCUSSION

3.1. Esterification and Characterization

3.1.1. Degree of Esterification. The chemical modification aimed to convert lignin hydroxyl groups into ester groups through reactions with MA, SA, and PA anhydrides. The DE, which indicates the fraction of hydroxyl groups replaced by ester groups, was estimated from the weight percent gain (WPG) after the reaction (Table 1). The relative DE was

Table 1. Weight Percent Gain (WPG %) and Degree of Esterification (DE) of MA-, SA-, and PA-Modified KL

Anhydride modification	WPG [%]	DE [%]
Maleic anhydride	4.26 ± 0.25	8.2
Phthalic anhydride	4.92 ± 0.37	6.3
Succinic anhydride	4.18 ± 0.23	7.9

calculated using eq 2, considering the molar masses of the repeating lignin unit and the respective anhydrides. Softwood KL mainly comprises coniferyl units (≈90%) with a molar mass of 178.2 g·mol^{−1}.³⁵ The molar masses of the anhydrides were 98.06 g·mol^{−1} (MA), 100.07 g·mol^{−1} (SA), and 148.1 g·mol^{−1} (PA).³¹ Using these values and the measured WPGs, the estimated degrees of esterification were 8.2% for MA, 7.9% for SA, and 6.3% for PA. Therefore, MA resulted in the highest extent of hydroxyl substitution, followed by SA and PA. The lower value for PA likely reflects its larger molecular size and steric hindrance, which can restrict diffusion and reaction at lignin hydroxyl sites. These relative DE values help interpret

how the type of anhydride influences lignin properties and thermal foaming behavior. Generally, a higher DE increases hydrophobicity³⁶ and can affect thermal transitions like the T_g . According to Farahani and Taghizadeh,³⁶ increasing WPG (and thus DE) significantly improves these properties. However, achieving high substitution levels in lignin remains difficult due to steric constraints and structural heterogeneity.³¹ Adjusting reaction parameters, such as reagent ratio, reaction time, temperature, and catalyst type, provides a practical route to tailor lignin modification for specific applications. The esterification step has a moderate atom economy of ~42–45% (see Supporting Information, Table S1), which is typical for acid-anhydride reactions. However, the broader sustainability of the eco-foaming route derives from the renewable lignin feedstock, mild reaction conditions, and the elimination of external blowing agents.

3.1.2. FTIR Analysis of Esterified Kraft Lignin. FTIR spectroscopy was employed to confirm esterification and to identify corresponding structural changes in KL. The spectra of the esterified samples were compared with that of unmodified lignin (Figure 1a). To semiquantitatively evaluate the reaction extent, the intensity of each relevant peak was normalized to an internal reference at 1511 cm^{−1}, assigned to the aromatic skeletal vibration of the lignin backbone (Figure 1b).

The 3700–3000 cm^{−1} region corresponds to adsorbed water and hydroxyl (–OH) stretching vibrations. It is proposed that the evaporation of bound water and dehydration of hydroxyl groups are the main blowing agents during the thermo-foaming process. Peaks near 3602 and 3555 cm^{−1} are associated with weakly bonded water, while 3496 cm^{−1} represents the valence vibration of hydrogen-bonded –OH groups, and 3372 and 3280 cm^{−1} correspond to intra- and intermolecular –OH stretching. The band at 3149 cm^{−1} arises from strongly hydrogen-bonded water.^{37–39} No significant difference in the weakly bonded water (3602 and 3555 cm^{−1}) was observed between unmodified lignin to the esterified lignin (Figure 1b). However, the esterified samples exhibited a noticeable decrease in the –OH-related bands (3496, 3372, 3280 cm^{−1}) and in the hydrogen-bonded water band (3149 cm^{−1}), indicating successful consumption of hydroxyl groups during esterification. The magnitude of these reductions aligns with the moderate substitution levels (6–8%) determined from the DE calculations.

New peaks characteristic of ester formation appeared at 1267, 1130, and 1030 cm^{−1}, corresponding to C–O stretching in ester linkages.^{31,40} These peaks increased in all esterified samples, most notably in the MA-modified lignin, consistent with its higher DE. A broad band between 1680–1750 cm^{−1}, centered at approximately 1712 cm^{−1} (shown in Figure 1b), corresponds to C=O stretching of saturated esters and carboxyl groups.⁴¹ This feature was most prominent in the PA-modified lignin, reflecting its aromatic anhydride origin, while it was less intense in MA-modified lignin due to the unsaturated nature of the maleate esters. Overall, the FTIR spectra support the WPG and DE results, confirming that hydroxyl groups in KL were successfully converted to ester functionalities.

3.1.3. Thermal Properties of Esterified Kraft Lignin. A key aspect of the eco-foaming process is the generation of steam from bound water and the dehydration of hydroxyl groups, which together serve as intrinsic blowing agents. Additional volatile compounds released during heating may also contribute to pore formation. To understand how

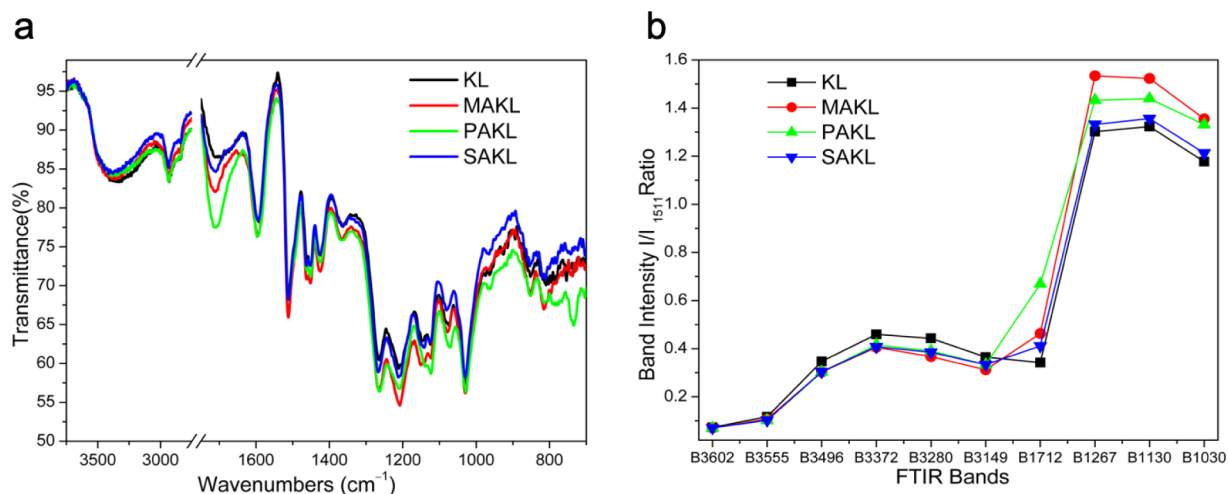


Figure 1. FTIR spectra of unmodified KL, and esterified lignins modified with maleic (MAKL), phthalic (PAKL), and succinic (SAKL) anhydrides: (a) over the range of 3750 to 700 cm⁻¹; and (b) corresponding normalized band intensity ratios for hydroxyl-, carbonyl-, and C–O-related vibrations.

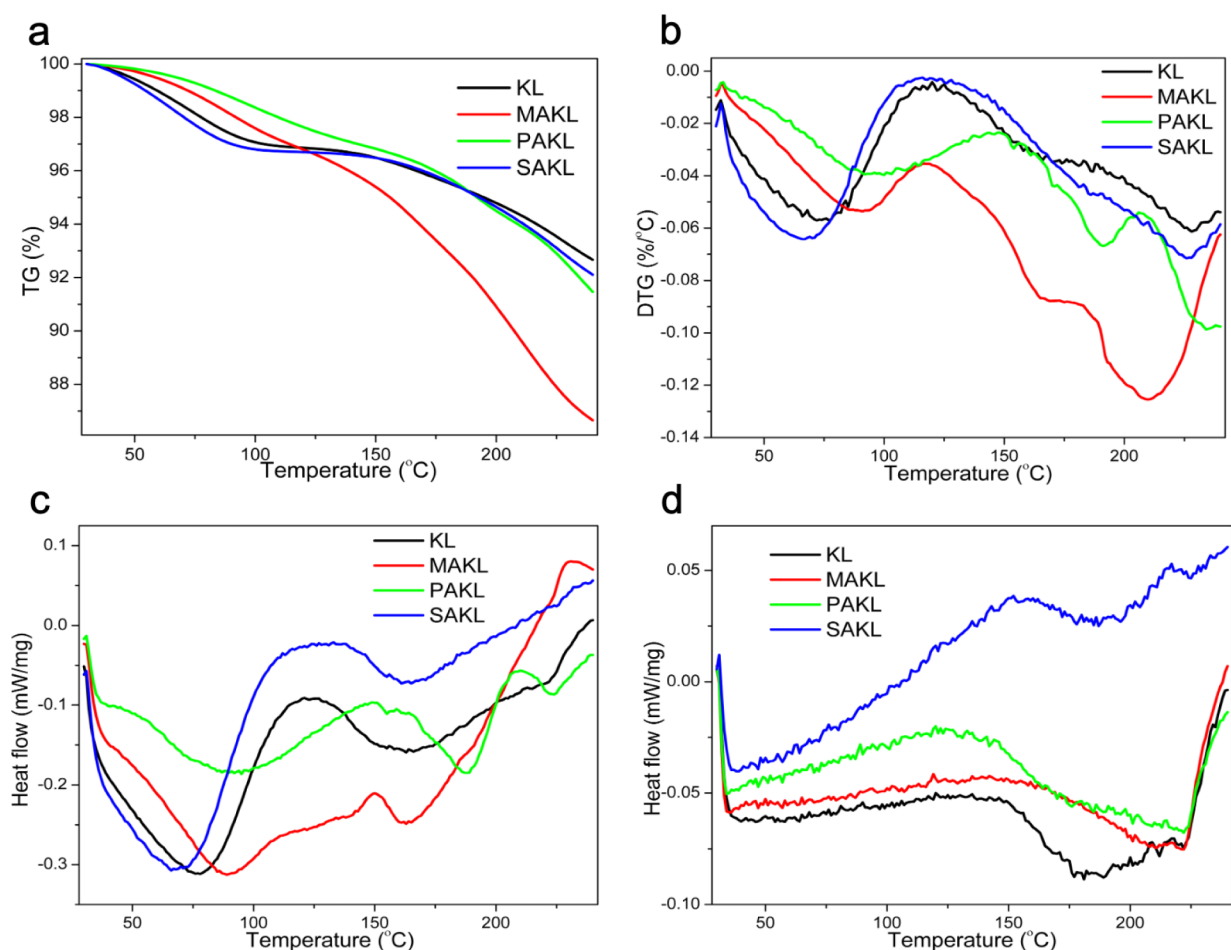


Figure 2. (a, b) TGA and derivative thermogravimetric (DTG) curves; and (c, d) DSC thermograms of unmodified KL and esterified samples MAKL, PAKL, and SAKL. Panels (a) and (b) show mass loss and decomposition rate as a function of temperature, respectively, while panels (c) and (d) present heat flow during the first and second DSC heating cycles.

esterification changes volatilization behavior and, consequently, the foaming process, TGA was conducted (Figure 2a and b). At temperatures below 125 °C, the MA- and PA-modified lignins exhibited lower mass loss compared with unmodified KL. This decrease is attributed to a smaller amount

of bound water, indicating less steam generation during foaming. Although maleic anhydride introduces unsaturated ester groups that could potentially decompose at moderate temperatures, previous studies reported that both MA and SA modifications actually delay the onset of degradation above

300 °C.²⁸ Thus, esterification generally enhances the thermal stability of lignin, shifting volatilization and decomposition to higher temperatures.

Another key factor affecting the eco-foaming process is lignin's softening behavior at elevated temperatures, enabling thermoplastic flow during cell formation, similar to the viscoelastic behavior seen in traditional thermoplastic polymer foams. The T_g thus determines the temperature range for pore expansion and coalescence. DSC was used to assess how esterification impacts T_g (Figure 2c and d). Esterification with SA had the smallest effect, resulting in a T_g only slightly higher than that of unmodified lignin (Figure 2c, Table 2). This

Table 2. Glass-Transition Temperature of Unmodified KL, and Esterified Lignins Modified with Maleic (MAKL), Phthalic (PAKL), and Succinic (SAKL) Anhydrides Obtained from DSC during the First and Second Heating Cycles

Samples	T_g (°C)	
	1st run	2nd run
KL	141.9	163.2
MAKL	155.6	183.1
PAKL	174.1	180.2
SAKL	149.8	173.0

behavior can be rationalized by the relatively low DE in the SA-modified sample and the flexible, saturated aliphatic structure of the succinate group. FTIR analysis indicates that esterification reduces the availability of hydroxyl groups and bound water, both of which can act as plasticizers, suggesting that less plasticization should increase T_g . However, the SA moiety may also act as an internal plasticizer, counteracting this effect and leading to minimal overall change. Specifically, the succinate group adds a short, saturated aliphatic spacer between aromatic units, creating a flexible link. This enhances local chain mobility by reducing intermolecular hydrogen bonds and decreasing packing efficiency, similar to low-molar-mass plasticizers. Consequently, even though esterification typically reduces hydroxyl-driven plasticization and increases T_g , the internal chain flexibility from the succinate group counteracts this stiffening, resulting in only a minor increase in T_g . In contrast, the MA-modified lignin showed a moderate increase in T_g , which aligns with the more rigid unsaturated aliphatic structure of the maleate group that limits chain mobility. The PA modification resulted in the most significant T_g increase, due to the bulky aromatic ring of the phthalate group, which further decreases segmental movement. Overall, these findings suggest that both the DE and the chemical nature of the ester group influence lignin's softening properties. Samples subjected to a second DSC run after an initial heating cycle showed a consistent shift of T_g to higher temperatures (Figure 2d, Table 2), indicating irreversible structural changes upon heating. These changes may result from cross-linking

among ester groups, partial depolymerization, or condensation reactions within the lignin matrix. The effect of the anhydride type on T_g was more pronounced in the first cycle, while the second cycle reflected the thermally stabilized state of the material. Notably, the MA-modified sample exhibited a slightly greater T_g increase after the second run, possibly due to additional cross-linking promoted by its higher DE. Although this study examined only a single DE for each anhydride, the observed T_g shifts suggest that controlling the extent of esterification could be a practical route to tune lignin's thermomechanical behavior and, consequently, the pore morphology and density of eco-foamed lignin materials.

The observed T_g increases during both DSC cycles are directly linked to changes in functional groups identified by FTIR. The decrease in hydroxyl-related bands (3496–3280 cm^{-1}) and hydrogen-bonded water band at 3149 cm^{-1} suggests fewer hydrogen-bonding sites, which reduces external plasticization and raises T_g in the first cycle. Additionally, the growth of ester-related peaks (notably 1712, 1267, 1130, and 1030 cm^{-1}) indicates more ester linkages that limit chain mobility. Upon heating, these ester-rich regions tend to cross-link or condense, further restricting molecular motion and leading to additional increases in T_g in the second cycle. Therefore, the spectral changes offer a direct chemical explanation for the progressive T_g shifts observed in DSC.

3.2. Foam Formation and Morphology

This section aims to evaluate how esterification of KL affects the eco-foaming process, as well as the foam's structure and properties. In eco-foaming, bound water and dehydration of hydroxyl groups serve as intrinsic blowing agents, producing steam that expands the softened lignin matrix. All the lignin samples were dried at 70 °C to a constant mass prior to foaming to standardize initial moisture levels and ensure uniform foaming conditions across samples. A systematic moisture-content study, in which water content is intentionally varied to quantify its direct influence on pore formation and foam structure, remains an important direction for future studies. Therefore, foam formation is controlled by two interconnected factors: (i) the availability of hydroxyl groups and bound water, which influence gas production, and (ii) the thermoplastic flow of lignin during heating, which allows pore growth and stabilization. Esterification decreases the number of hydroxyl groups and, as a result, reduces the amount of bound water, thus altering the balance between gas generation and matrix viscosity during foaming. Table 3 presents the physical properties of the resulting foams. Compared to unmodified KL foams, all esterified lignins yielded materials with lower porosity, higher density, smaller pore sizes, and more closed-cell structures. Among the modified samples, maleated lignin (MAKL) showed the highest DE, resulting in the smallest average pore size and highest density, followed by succinated (SAKL) and phthalated (PAKL) lignins. This trend is consistent with the microstructural observations in Figure S1.

Table 3. Physical Characteristics of Foams Prepared from Unmodified and Esterified Kraft Lignins

Lignin foam	Density ($\text{g}\cdot\text{cm}^{-3}$)	Average pore size (μm)	Porosity (%)	Open cell percentage (%)	Compressive strength (MPa)	Thermal conductivity ($\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$)
KL	0.26 ± 0.03	84	88.9 ± 2.1	94.6	1.57 ± 0.15	0.076 ± 0.005
MAKL	0.32 ± 0.02	23	82.7 ± 1.6	70.4	1.92 ± 0.14	0.043 ± 0.002
PAKL	0.29 ± 0.02	35	85.6 ± 1.4	81.5	1.79 ± 0.12	0.048 ± 0.003
SAKL	0.30 ± 0.02	29	84.2 ± 1.2	78.3	1.89 ± 0.12	0.047 ± 0.003

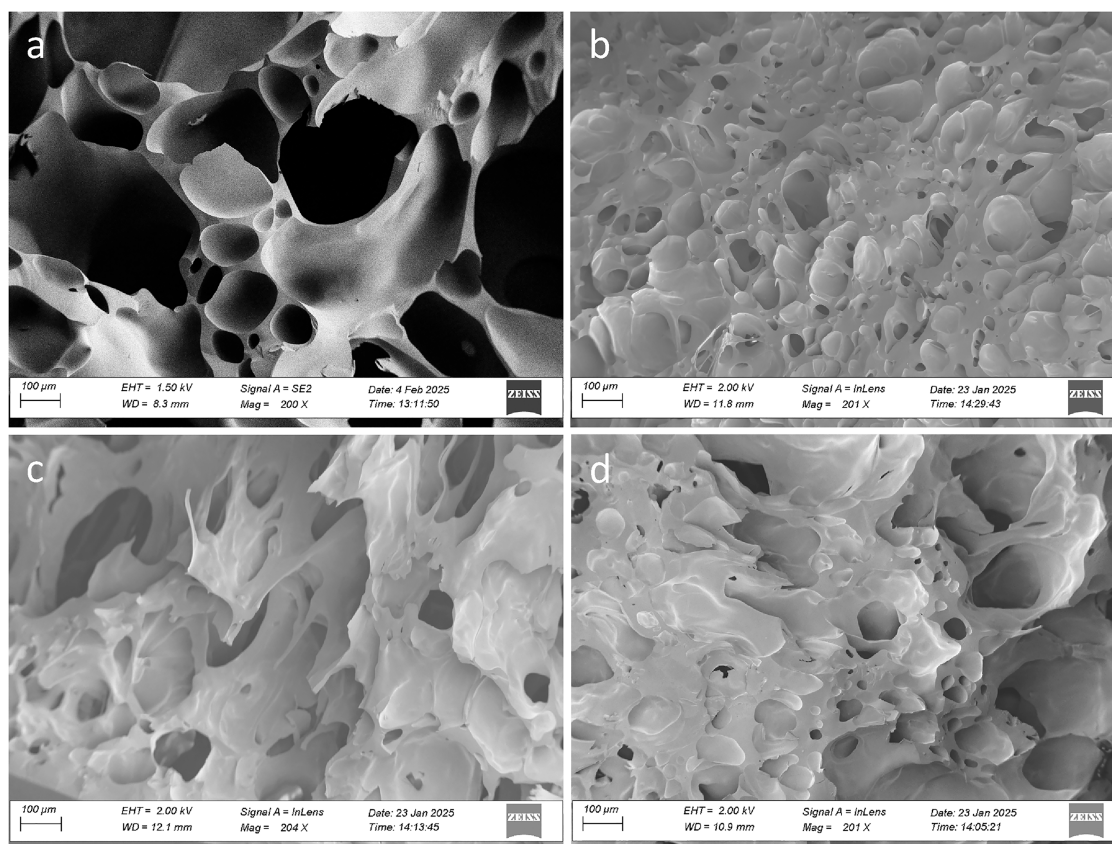


Figure 3. Scanning electron microscope images of microscale pore structure of foams: (a) unmodified KL, (b) MAKL, (c) SAKL, and (d) PAKL.

It should be noted that esterification of KL significantly increased the density of the resulting foams compared to unmodified KL foam (0.26 vs 0.29 – 0.32 g·cm $^{-3}$) ($p < 0.05$). However, no significant differences were observed between MAKL and SAKL or between PAKL and SAKL with respect to foam density ($p > 0.05$).

3.2.1. Microstructure and Pore Size Distribution. SEM revealed that the unmodified KL foam had large, interconnected pores, while esterified foams exhibited progressively smaller, more uniform pore structures (Figure 3). Quantitative image analysis confirmed a consistent decrease in both average pore size and pore-size dispersion with increasing esterification (Figure S1). For context, in our earlier eco-foaming study with unmodified KL foams,¹⁴ pore sizes averaged 350 – 152 μm, depending on the preheating temperature. In contrast, the current work produces much smaller cellular structures: unmodified KLF features pore sizes of approximately 84 μm, while esterified foams range from 23 to 35 μm at similar porosities (Table 3). This comparison suggests that incorporating a chemical modification step allows for more precise control over pore size than process tuning alone, transforming eco-foaming from a solely process-based approach to a combined chemical and process strategy. The smaller, less connected pores in MAKL align with reduced gas release during foaming. The higher T_g in PAKL did not significantly inhibit foaming, indicating that the amount of hydroxyl-derived blowing agent has a greater impact on pore formation than viscoelastic softening (e.g., T_g). This suggests that the chemical availability of hydroxyls and bound water plays a more important role than thermoplasticity in controlling the foam

morphology. Therefore, the level of esterification can be used as a molecular-level parameter to adjust pore morphology.

3.2.2. Mechanical Properties. The foamed materials have high compressive strength when compared to traditional polymer foams used in building applications (Table S2).^{5,11} Bulk samples of the various modified lignin foams are shown in Figure S2, with macroscale porosity shown in Figure S3. The materials are robust, as they do not crack during handling and can be cut using a bandsaw into shapes (Figure S4). However, they are highly rigid, i.e., they do not flex easily and break in a brittle manner. Foam compressive strength showed a positive correlation with foam density, as indicated in Table S2, aligning with prior studies on lignin-based foams.¹⁴ Denser foams contained a larger solid fraction capable of bearing higher loads. Although esterification changes lignin's chemical structure, the mechanical strength of the solid matrix seemed unaffected within the tested range; the overall strength trend followed density rather than chemistry. This suggests that chemical modification indirectly influences strength by controlling density, while process parameters such as precompression pressure can further adjust foam properties.¹⁴

3.2.3. Thermal Conductivity and Functional Performance. Thermal conductivity measurements revealed that open-cell foams have higher conductivity than closed-cell foams, probably because air convection occurs through interconnected pores. The MAKL foam, with its dense, closed-cell structure, demonstrated the lowest thermal conductivity, suggesting better insulating properties. This tunable behavior is useful for applications that requiring controlled vapor permeability or thermal insulation. By adjusting the level of esterification, foams can be designed for open-cell (permeable)

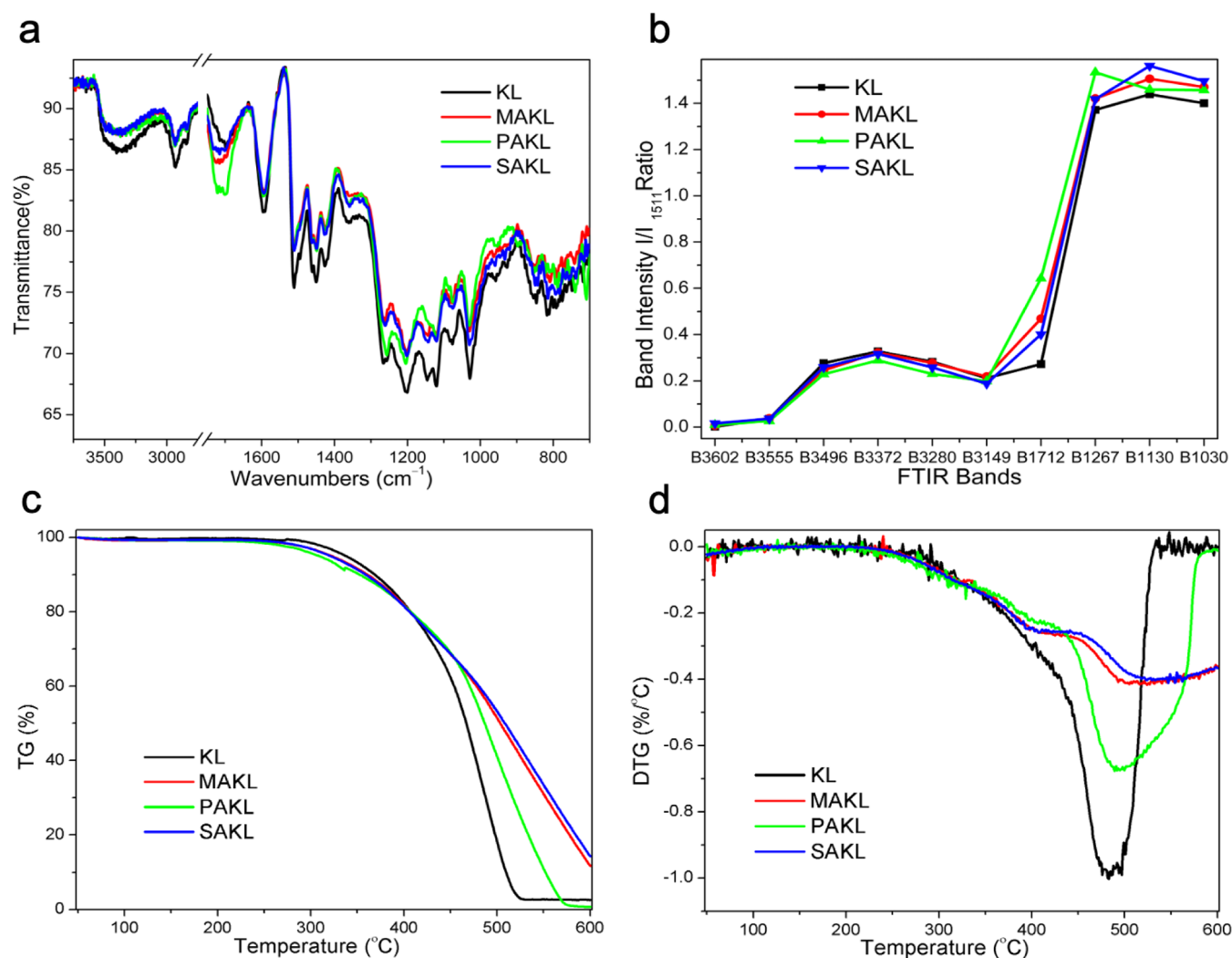


Figure 4. (a, b) FTIR spectra and corresponding band-intensity ratios of unmodified KL and esterified foams MAKL, PAKL, and SAKL, highlighting hydroxyl, carbonyl, and C–O group vibrations in the range 3750–700 cm^{-1} ; (c, d) TG and DTG curves of the same foamed materials fabricated at 240 $^{\circ}\text{C}$, showing mass-loss behavior and decomposition rates as a function of temperature.

or closed-cell (insulative) configurations, based on the specific application.

To contextualize the performance of the lignin-based foams developed in this work, Table S2 compares key physical properties with those of representative biomass-derived and commercial foams. The esterified KL foams (MAKL, PAKL, and SAKL) exhibit a distinctive combination of relatively high density (0.29–0.32 $\text{g}\cdot\text{cm}^{-3}$), small pore sizes (23–35 μm), and high compressive strength (1.79–1.92 MPa). This combination is uncommon among most biomass-derived foams reported. In contrast, many biobased foams, such as gelatin–starch, chitosan, or cellulose nanofiber foams, typically have lower densities (≈ 0.01 – 0.11 $\text{g}\cdot\text{cm}^{-3}$) and, accordingly, lower compressive strengths (≤ 0.2 MPa).^{42–44} A key advantage of the lignin foams developed in this work is their significantly reduced pore size. Unlike many biomass and commercial foams with pore sizes between 100 and 1000 μm , the esterified lignin foams in this research have pore sizes under 35 μm . This more refined cellular structure provides a clear structural basis for the observed improvements in mechanical performance and contributes to lower thermal conductivity. The thermal conductivity of esterified lignin foams (0.043–0.048 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) is similar to that of commercial expanded polystyrene

(EPS, ≈ 0.034 – 0.038 $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$) and other biomass-derived foams, but they offer significantly higher compressive strength.⁴⁵ These findings show that adding an esterification step before eco-foaming produces lignin-based foams with a balance of strength and insulation that rivals or exceeds many other biobased foams and approaches the performance of commercial insulation materials.

3.2.4. Chemical Structure of Foamed Materials. FTIR spectra of the foams (Figure 4a) offer insights into molecular changes during foaming. The O–H and bound-water region (3600–3150 cm^{-1}) showed no significant differences in band intensity between unmodified and esterified foams, indicating that residual hydroxyls and bound water were largely consumed during the foaming process. This aligns with the higher porosity and larger pores seen in the unmodified foam. Conversely, characteristic ester peaks (1710–1030 cm^{-1}) remained visible in the foamed esterified lignins, confirming that ester functionalities partially survive the thermal process. The preserved ester groups could encourage cross-linking or contribute to enhanced thermal stability and interfacial compatibility, especially for composite or polymer-impregnated applications.

3.2.5. Thermal Degradation Behavior of Foam Materials. Thermal stability is an important material property for polymer-based systems, especially in building and construction applications. To evaluate their thermal stability, TGA was conducted on the foamed samples (Figure 4c and d). The foams exhibited excellent thermal stability up to approximately 300 °C, while the original lignins degraded significantly below 240 °C (Figure 2). Lignin typically degrades between 200 and 400 °C, involving the breaking of β -O-4 linkages, decomposition of side chains, and release of volatile compounds such as phenols, aldehydes, and ketones.⁴⁶ The foaming process seems to induce partial decomposition within this temperature range, creating a thermally stabilized structure that resists further breakdown at higher temperatures. Beyond 400 °C, notable differences appear between foams made from esterified and unmodified lignins (Figure 4d). The esterified foams retain significantly more mass in the 400–600 °C range, indicating improved resistance to high-temperature degradation. Several factors may explain this behavior. First, ester groups added during modification can facilitate cross-linking during foaming, resulting in a more interconnected molecular network that withstands thermal breakdown. Second, ester functionalities may be inherently more thermally stable than the residual hydroxyl or ether groups in unmodified lignin. Interestingly, even though the phthalate group is the most aromatic and thus theoretically the most heat-resistant, the phthalated foam was less stable than the MA- or SA-modified foams. This suggests that physical structure, rather than chemical composition alone, governs thermal resistance. The esterified foams had higher densities and more closed-cell structures, which are associated with lower thermal conductivity (Table 3). The closed-cell architecture likely limits heat transfer and volatile release, both of which slow degradation. Overall, these findings demonstrate that chemical modification combined with cellular structure works together to enhance the high-temperature stability of lignin-based foams.

4. CONCLUSION

In this study, KL was esterified using organic acid anhydrides to modify its behavior during eco-foaming. This process decreased hydroxyl groups and bound water, reducing the amount of steam acting as a natural blowing agent and slightly raising the T_g , which in turn limited molecular mobility during pore formation. As a result, the foams developed smaller pores, lower porosity, and denser, closed-cell structures. Among the samples, maleic anhydride achieved the highest esterification level, producing foams with the smallest pores, greatest density, and enhanced mechanical and thermal properties. These improvements increased compressive strength, thermal insulation, and resistance to thermal degradation, key features for building-material applications. Overall, controlled esterification is an effective method to adjust the foaming behavior and performance of lignin-based foams. Future research should focus on better understanding degradation mechanisms and refining modification parameters to enhance stability and scalability. Beyond performance, the eco-foaming route also offers practical benefits. By leveraging bound water and dehydration, it eliminates the need for external blowing agents and high-pressure equipment, reducing both material and processing costs. Moreover, esterification can be conducted at moderate temperatures using widely available anhydrides, supporting scalable production with lower energy demand.

Together, these advantages suggest that lignin-based foams could be a cost-effective insulation material with strong potential for sustainable building applications.

■ ASSOCIATED CONTENT

Data Availability Statement

Data will be made available on request.

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.5c12988>.

Green metrics for esterification: atom economy (Section S1); characterization and analytical methods (Section S2: FTIR, TGA/DSC, optical and SEM characterization procedures, mechanical and thermal-conductivity testing methods, image analysis of pore size distribution); detailed pore-size image analysis workflow; additional pore-size distribution data (Figure S1); images of bulk 40 mm diameter cylindrical foam samples (Figure S2); optical light microscope images of macroscale pore structure of foams (Figure S3); bulk foam block made of unmodified KL foam (Figure S4) (PDF)

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by the USDA Forest Service through Grant Nos. 19-JV-1111124-053, 19-JV-1111124-063, 20-JV-1111124-035, and Wood Innovations (Grant No. 20-DG-11094200-234). The authors would like to thank Domtar Corp. for providing kraft lignin and special thanks to Joseph Destree, Joshua Limbaugh, Kimberly Hoxie, Marshall M. Begel, and Will Kinney at USDA Forest Products Laboratory for their help in making this project run successfully.

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