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Research Article

Solventless Production of Thermoplastic Lignin Esters for Polymer Blends and Elastomers via Reactive Extrusion

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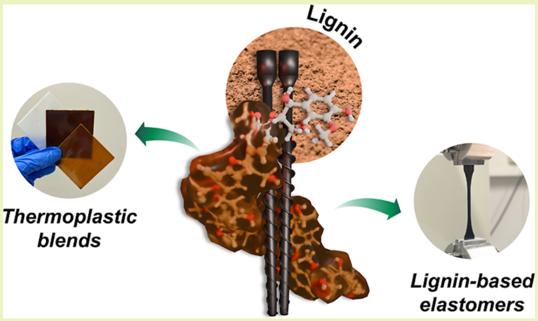
ABSTRACT: Chemical modification of lignin is needed to enhance its use in materials applications. However, traditional solvothermal methods for lignin modification often compromise the sustainability and scalability of the process. In this study, we developed a solventless approach for producing esterified lignin derivatives through reactive extrusion (REx). For the first time, we report the functionalization of lignin with octenyl succinic anhydride (OSA) via REx. We systematically explored the effects of temperature, residence time, OSA loading, and catalyst loading on lignin esterification efficiency using FTIR, 2D HSQC NMR, and ^{31}P NMR spectroscopy. Our results show preferential esterification of aliphatic hydroxyls (>80%) within minutes. Esterification of lignin with OSA yielded thermoplastic lignin esters suitable for use in polymer blends and further for producing lignin-based elastomers due to the reactivity of the added carboxylic acid functionalities. Additionally, we compared the green chemistry metrics of the REx process with the solution-state approach, highlighting the clear advantages of avoiding the use of solvent. Furthermore, we successfully esterified different biorefinery lignins through REx, demonstrating the versatility of this method. The advantageous features of REx position it as the green standard technology that could boost the integration of lignin-based materials into the market.



KEYWORDS: *reactive extrusion, lignin, thermoplastics, elastomers, green chemistry, biomass*

INTRODUCTION

Pulp and paper mills produce around 70 million tons of lignin annually,[1] most of which is incinerated to generate energy, and this supply is anticipated to increase further in the coming years with the development of lignocellulosic biorefineries.[2] Transforming lignin into high-value products would generate significant added revenue to existing pulping industries and promote the profitability of emerging biorefineries.[3,4] Lignin-based materials have the potential to replace fossil-based commodities facilitating the shift toward a circular bioeconomy. One strategy to add value to lignin is to use it as an additive or raw material in plastic production. The abundance, chemical functionality, flame retardancy, antioxidant and UV-shielding properties of lignin, among other features, make it a viable material to increase the biobased content of plastics.[5,6] However, blending hydrophobic polymers with unmodified lignin generally results in inferior mechanical properties compared to their pure counterparts.[7] This phenomenon occurs because lignin macromolecules have abundant hydroxyl moieties that exhibit a strong tendency to form hydrogen bonds, resulting in self-aggregation and weak interactions with the polymer matrix.[8,9] To circumvent this issue, lignin can be modified by functionalizing its hydroxyl groups to weaken its capabilities for hydrogen bonding and increase its affinity to the core polymers.

Esterification reactions are among the most studied approaches to increase the compatibility of lignin with various polymers including polyethylene,[10,11] polystyrene,[12] polylactic acid,[13,14] and polypropylene.[15] The resulting blends with esterified lignin present better thermal processability and mechanical properties in comparison to blends with unmodified lignin. However, in many cases, excessive amounts of solvents and reagents are used during lignin modification, which decreases the sustainability and economic feasibility of these processes. In addition, lignins from different origins have varying solubilities and chemical reactivities which can add further complexity to solution-state modifications.

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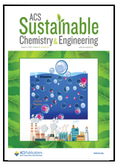

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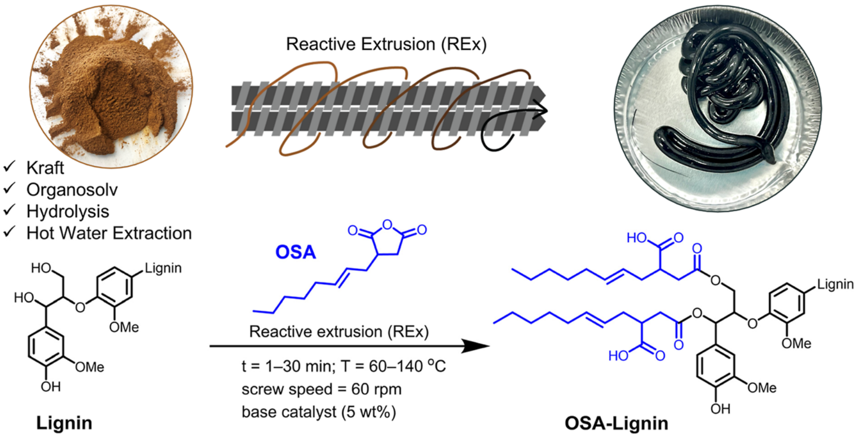

Figure 1. Schematic representation of the reactive extrusion process showing both photos of the unmodified kraft lignin and the modified lignin, referred to as OSA-lignin, as well as the modification reaction. The reaction parameters are summarized in Table S1.

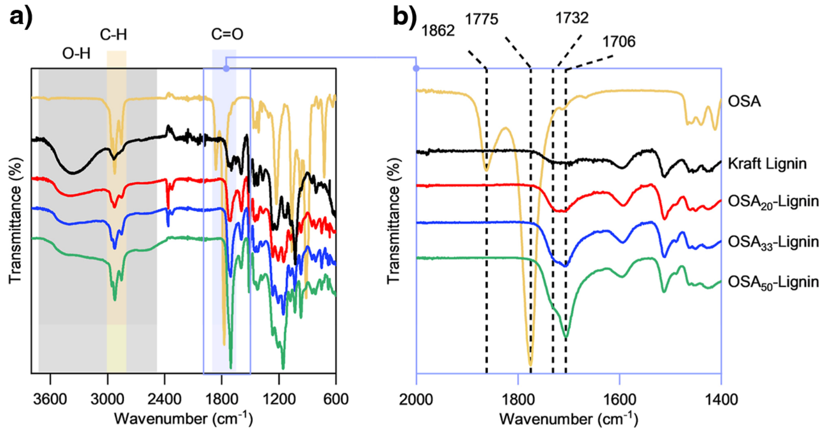

Figure 2. (a) Stacked FTIR spectra of OSA, kraft lignin, and OSA-lignins with different OSA loadings (20, 33, and 50 wt %). (b) Expanded view from the wavenumber range 2000 to 1400 cm^{-1}. The spectra were baseline corrected and normalized according to the aromatic C−C stretching band at 1510 cm^{-1}. The reaction parameters were set to 5 wt % pyridine loading, t = 10 min, T = 120 °C, and 60 rpm.

Recently, derivatizing lignin through mechanochemistry has gained popularity due to its advantages over solvothermal processing. Extruders, that are typically designed for continuous production, have been used to perform reactive extrusion (REx) to chemically modify lignin with succinic and maleic anhydride[16,17] or biobased oils.[18] The REx approach for functionalizing lignin offers several benefits such as short processing time and reduced reagent and solvent use. More importantly, it overcomes the issues with poor lignin solubility which is inarguably one of the major challenges in lignin upgrading technologies. This advantage becomes even more relevant considering the increasing diversity of technical lignins with the emergence of new biorefineries. Furthermore, most screw extruders are equipped with temperature control allowing for a convenient successive polymer blending, which makes them more desirable mechanochemical tools than ball mills.[19,20] The production of modified lignin via REx and its subsequent blending with poly(butylene adipate-*co*-terephthalate) (PBAT) was recently demonstrated on an industrial scale.[18] The wide availability of extruders in polymer processing industries and biomass deconstruction[21−24] favors the commercialization of REx for lignin modification. However, no reports have been made to objectively assess the sustainability of REx against solvothermal techniques. Additional research is warranted to investigate REx using different lignins and modification agents, as well as the applicability of the resulting lignin derivatives in material applications.

In this study, our aim was to demonstrate the use of REx as an efficient and versatile tool for preparing thermoplastic lignin esters. We used REx to functionalize lignin with 2-octen-1-ylsuccinic anhydride (OSA) (Figure 1), an alkenyl cyclic anhydride typically used to hydrophobize cellulose[25,26] and starch.[27,28] Unlike the more common succinic anhydride, which has been previously used for lignin esterification in REx,[16,17] OSA is liquid at room temperature. Hence, extrusion temperatures can be decreased and the need for plasticizers can be avoided. Moreover, we compared the advantages of using REx over the typical solution-state (SS) esterification of lignin, focusing on selected green chemistry metrics. The optimization of reaction parameters was performed on abundant softwood kraft lignin (Table S1), but the versatility of our REx esterification method was demonstrated by modifying biorefinery lignins from varying botanical sources and isolation technologies. Lastly, we showcased that this modification could open the applicability of lignin in bioplastics. We presented the improved miscibility of lignin esters with a thermoplastic biobased polyester and leveraged the added reactivity of the esterified lignin for building lignin-based elastomers.

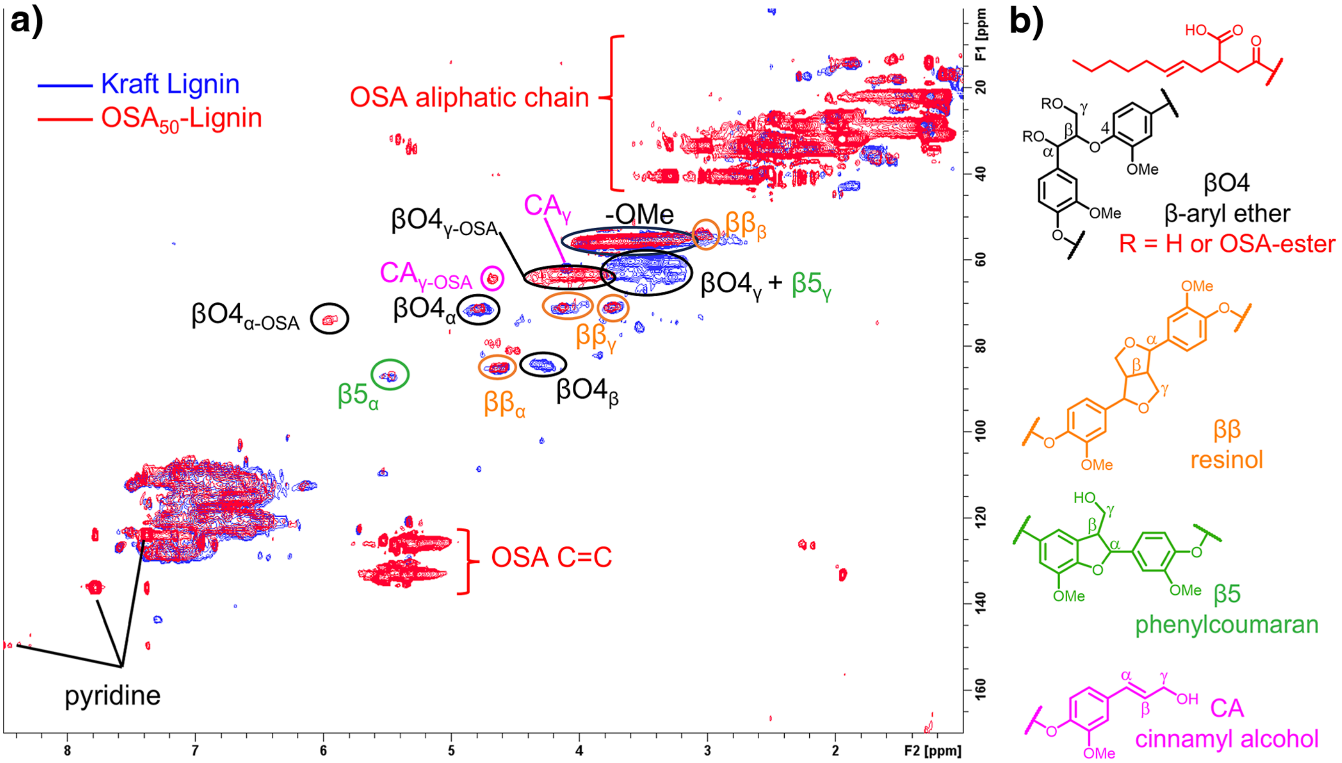

Figure 3. NMR analysis of the key structural changes in kraft lignin after esterification with OSA via reactive extrusion. (a) Stacked HSQC NMR spectra of kraft lignin (blue) and OSA_{50}-lignin (red). (b) Color-coded chemical structures to depict the linkages in the lignin samples. The REx parameters for the OSA_{50}-lignin were set to 50 wt % OSA loading, 5 wt % pyridine loading, t = 10 min, T = 120 °C, and 60 rpm.

RESULTS AND DISCUSSION

Our aim was to examine the esterification of polyaromatic lignin macromolecules using alkenyl succinic anhydrides in combination with reactive extrusion (REx), an emerging green technology for chemical synthesis, . Alkenyl succinic anhydrides such as octenyl succinic anhydride (OSA) have been shown to be efficient in modifying carbohydrate-based polymers, namely, starch[27−29] and cellulose.[25,26,30] Hill and Mallon described the esterification of wood with OSA[31] but aside from that, the esterification of lignin with this reagent has not yet been reported in the literature, to our knowledge. We envisioned that REx would facilitate a more sustainable route for functionalizing lignin with OSA than the solution-state approach.

Esterification of Kraft Lignin with OSA via REx. Softwood kraft lignin was selected as the main starting material to study the esterification of lignin with OSA via REx. The extruded samples were analyzed directly without further purification. The success of esterification was initially monitored by FTIR spectroscopy (Figure 2). The OSA reagent exhibits two sharp absorption bands at 1775 and 1862 cm^{-1} corresponding to the C═O stretching of the cyclic anhydride. When kraft lignin was reacted with increasing OSA loading, progressive intensification of bands were observed at 1706 and 1732 cm^{-1}. These peaks correspond to the overlapping carbonyl groups[20,32] of the COOH (1695−1715 cm^{-1}) and the nonconjugated aliphatic esters (1732 cm^{-1}), respectively, as can be seen in Figure 2a. The carboxylic acid moiety is due to the opening of the anhydride ring of OSA during esterification (Figure 2b). Furthermore, the broad O−H stretching band of unmodified kraft lignin, centered at 3350 cm^{-1}, decreased in intensity after esterification. In addition, the signals for the O−H spanning from 2500 to 3200 cm^{-1} broadened with increasing OSA loading (Figure S1). This phenomenon is attributed to the generated carboxylic acid groups that exhibit broad O−H bands due to hydrogen bonding. Moreover, the increase of the C−H stretching band of the aliphatic chain of OSA in the 2800 to 3000 cm^{-1} region is also evident in the spectra of the OSA-lignins.

Since the FTIR analysis clearly indicated successful esterification and increasing degree of substitution with increasing amount of OSA reagent, the samples were further characterized with HSQC NMR to identify structural features of the OSA-lignins. The stacked spectra of unmodified kraft lignin and OSA_{50}-lignin are shown in Figure 3, while individual HSQC NMR spectra of all samples are shown in Figures S2−S5. The most significant changes after esterification of kraft lignin are observed in the oxygenated aliphatic region (δ_H/δ_C 2.5−6.0/50−90 ppm). The side-chain β-O-4 γ, β-O-4 α, and cinnamyl alcohol end-group γ-signals shifted from δ_H/δ_C 3.4/60.6 ppm, δ_H/δ_C 4.8/71.6 ppm, and δ_H/δ_C 4.1/62.1 ppm, respectively, to higher ppm (δ_H/δ_C 4.0/63.5 ppm, δ_H/δ_C 5.9/74.3 ppm, and δ_H/δ_C 4.7/64.6 ppm, respectively) which is a clear indication of the esterification of the hydroxyl groups at these positions. Furthermore, a cluster of signals attributed to the long aliphatic chains of OSA were detected in the aliphatic region (δ_H/δ_C 0.5−3.5/10−40 ppm). Moreover, the C═C double bond signals of OSA attached to lignin polymer are visible at δ_H/δ_C 5.3−5.4/126.1−133.1 ppm as wide signals, with four major peaks corresponding to the *cis* and *trans* isomers. In the OSA_{50}-lignin, a sharp peak was detected at δ_H/δ_C 5.5/125.4 ppm, which originates from the unreacted OSA reagent, but was not visible in the spectra of OSA-lignins with 20 and 33 wt % OSA loadings (Figures S3 and S4). The

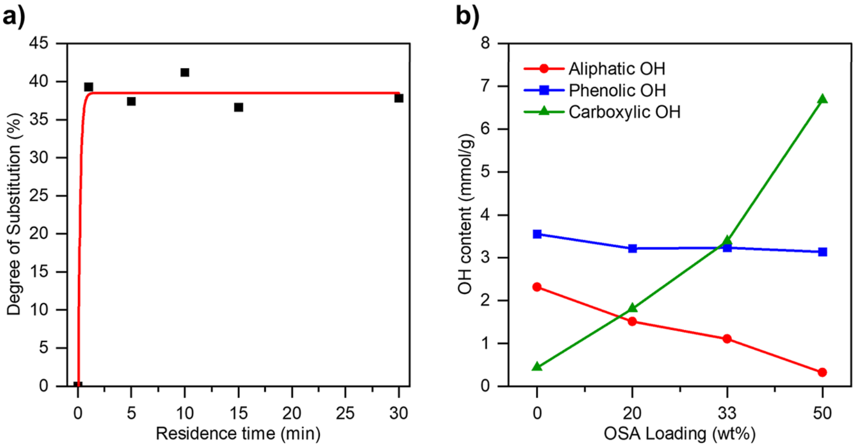

Figure 4. Effect of the different variables on the REx esterification of lignin as evaluated by quantitative ^{31}P NMR spectroscopy. (a) Degree of substitution (DS) as a function of residence time. The extrusion parameters were set to 50 wt % OSA loading, 5 wt % pyridine loading, temperature of 120 °C, and 60 rpm. (b) Free hydroxyl group content as a function of OSA loading and t = 10 min, T = 120 °C, 5 wt % pyridine loading, 60 rpm.

amount of unreacted OSA in the OSA$_{50}$-lignin was estimated to be 13 wt % according to ^{1}H NMR quantification (Figure S6). The samples with a lower initial amount of OSA contained no residual reagent based on their ^{1}H NMR spectra.

The effect of different chemical and process parameters on the degree of substitution (DS) was evaluated using FTIR and ^{31}P NMR spectroscopy as shown in Figures S7 and 4, respectively. While the esterification of lignin with OSA under REx conditions at 120 °C for 10 min proceeded even without a catalyst, the FTIR spectra of this sample still showed residual OSA carbonyl bands (Figure S7). Using pyridine as a catalyst enhanced the reaction rates significantly thereby eliminating these residual signals. However, due to the hazardous and toxic nature of pyridine, its removal and recycling are often necessary, which is typically achieved through industrial-scale distillation. Greener catalyst alternatives were explored, such as alkali salts (K_2CO_3 and Na_2CO_3), also showing successful esterification in FTIR (Figure S7).

In a lab-scale batch reactive extrusion, three main process parameters can be adjusted: temperature, residence time, and screw speed. For simplicity, we decided to keep the screw speed constant at 60 rpm and focused on the effect of temperature and residence time on the esterification procedure. When the reaction was performed at 60 °C for 10 min, signals of unreacted OSA were detected at 1775 and 1862 cm^{-1} (Figure S7b). At temperatures of 100 °C and above, the residual OSA signals disappeared, suggesting an enhancement in reaction efficiency. In further REx reactions, we selected 120 °C as the reaction temperature to keep a balance between the viscosity of reaction mixture and the potential unwanted side reactions which are more probable at high temperatures.[16−18]

Residence time refers to the duration the material circulates within an extruder via the backflow channel. To investigate the effect of residence time on the DS, samples were extruded out at various time intervals for quantitative ^{31}P NMR analysis. Strikingly, a rapid esterification was observed after only 1 min with DS reaching 39% and peaking at 41% after 10 min (Figure 4a). Increasing the residence time did not improve the DS any further. Since the DS fluctuated between 37 and 41% with residence times between 1 and 30 min, we suggest that a 1 min reaction time is sufficient. Details on hydroxyl group content and DS values at different residence times are listed in Table S2.

While varying the OSA loading, we standardized the REx conditions at 5 wt % catalyst loading, T = 120 °C, t = 10 min, and 60 rpm. Quantitative ^{31}P NMR analysis was used to compare the hydroxyl contents of the unmodified lignin and the OSA-lignins to further determine the degree of esterification. Figure 4b illustrates a substantial reduction in aliphatic hydroxyls, a slight decrease in phenolic hydroxyls, and a drastic increase in carboxylic hydroxyls as a function of OSA loading, based on the results of ^{31}P NMR quantification (Figure S8 and Table S3). Our findings showed that OSA esterification highly preferred reaction with aliphatic hydroxyls which agree with previous studies on the esterification of lignin with cyclic anhydrides.[20,32,33] This effect was most likely due to the lesser steric hindrance in the aliphatic hydroxyl position compared to its phenolic counterpart. Koivu et al. observed a similar preference for aliphatic hydroxyls during esterification with long-chain acid chlorides using pyridine as a catalyst.[10] Their findings suggest that both steric and thermodynamic effects influence reactivity, as the primary aliphatic esters are more stable and less sterically hindered. Simultaneously, the amount of carboxylic OH sharply increased as a function of OSA loading because more carboxylic acid moieties were generated from the opening of the anhydride ring during the reaction (Figure 4b and Table S3). Further, the excessive increase in carboxylic OH content at 50 wt % OSA loading is most likely due to hydrolysis of the residual OSA in the sample.

In terms of molar ratio, the 50 wt % OSA loading corresponded to approximately 0.8 molar equivalents of OSA for every one molar equivalent of the total aliphatic and phenolic OH groups in kraft lignin. However, we only observed a DS value of 41%, which is half of what was expected based on the loading of the reagent. Detailed information on the hydroxyl content and the calculated DS of the OSA-lignins in Figure 4b is listed in Table S3. This moderate degree of esterification observed aligns with previous studies on the esterification of lignin with cyclic anhydrides. Scarica et al. achieved a DS of 39% by esterifying lignin with succinic anhydride in THF.[33] Zhao et al. reported maximum DS values of 30% with maleic anhydride and 45% with succinic anhydride using a ball mill reactor, noting that these were lower than the DS values (up to 70−80%) obtained with noncyclic anhydrides due to the steric hindrance of the cyclic anhydride ring.[20] In our case, the reaction may be further influenced by the bulky alkenyl chain of OSA. Using microwave irradiation, Monteil-Rivera and Paquet also obtained a moderate DS value of 38% for the maleation of lignin, while having a DS of over 87% for the esterification of lignin using noncyclic anhydrides.[34] They argued that these results are due to a selective preference of cyclic anhydrides toward aliphatic hydroxyls.

Although partial esterification might lead to compatibility issues when blending OSA-lignin with nonpolar polymers, such as polyethylene and polypropylene, this selective esterification offers several advantages. The newly generated COOH groups can e.g., be exploited for further reactions, while preserving the phenolic hydroxyls that are mainly responsible for the antioxidant properties[35,36] and UV-shielding ability[37] of lignin. Since the chemical modification also changes other polymer properties like molecular mobility, a lower DS may be more desirable to retain some of the stiffness of lignin. The octenyl chain of OSA specifically introduces hydrophobicity and molecular mobility to the lignin macromolecule, potentially increasing its miscibility with less polar polymers which is further discussed in a later section.

We further studied the effect of the REX process and the esterification on the molecular weight of lignin using GPC (Figure S9 and Table S4). A reference sample (KL REx) was produced by processing kraft lignin without OSA under the standardized REx conditions (5 wt % pyridine, T = 120 °C, t = 10 min, and 60 rpm). In comparison to the unmodified kraft lignin (M_w = 4930 g/mol, $Đ$ = 4.4), we observed a slight increase in the molecular weight of the lignin after extrusion processing (M_w = 6180 g/mol, $Đ$ = 5.3). With increasing OSA loading, the distribution profile shifted to higher molecular weights—OSA_{20}-lignin, OSA_{30}-lignin, and OSA_{50}-lignin have M_w values of 6900 g/mol, 7150 g/mol, and 8950 g/mol, respectively (Figure S9). Previous studies on reactive extrusion of lignin assert this increase in molecular weight to condensation reactions occurring under elevated temperatures and shear stresses.[16−18] In contrast, we did not find increasing number of condensed units in the OSA-lignins (Table S3) hence, we attribute the progressive increase of M_w in our system mainly to the successful incorporation of the long aliphatic chain of OSA onto the lignin backbone. The use of liquid OSA as a reagent allowed the REx esterification process to be conducted at a lower temperature (120 °C) compared to previous studies that used temperatures of 140 °C and above,[16−18] consequently minimizing the competing condensation reactions. The relatively low molar mass of obtained OSA-lignins make them more applicable as functional plasticizers in thermoplastic materials rather than reinforcing additives for high-performance composites.[38] However, their increased reactivity may be exploited for cross-linking reactions to produce higher molecular weight lignin-based polyesters and epoxide resins.[39]

Improved Green Metrics of REx over Solution-State Synthesis. In the literature, reactive extrusion is often claimed to be a sustainable processing method.[16−18] However, we found no studies comparing the sustainability metrics of REx to the conventional solution-state approach for lignin modification. To address this gap, we aimed to assess our REx process and our chosen esterification chemistry using selected green metrics based on the 12 Principles of Green Chemistry.[40] We also performed lignin esterification with OSA using a solvent to serve as a solution-state (SS) counterpart to our REx method. To make the systems more comparable, dimethylformamide (DMF) was chosen as a polar aprotic high boiling point solvent to facilitate the S_N2 reactions at 120 °C. Pyridine was also used for catalysis.

Spectroscopic analyses revealed similar chemical properties regardless of the method of esterification used. The HSQC NMR spectra of SS OSA-lignin was closely alike to that of REx OSA-lignin (Figure S10). The aqueous workup to obtain the SS product was expected to hydrolyze and wash away the unreacted OSA (no peak at δ_H/δ_C 5.5/125.4 ppm) although residual DMF was still detected, highlighting the requirement of a more rigorous workup for this procedure. Quantitative ^{31}P NMR analysis also revealed a comparable degree of substitution for both methods, with SS OSA-lignin having a DS of 38.3% (Table S5).

We calculated the environmental factors (E-factor) from the data obtained on both REx and SS esterification procedures (Table S6). The E-factor measures the amount of waste generated relative to the yield of the reaction.[41] For the REx approach, the E-factor was 1.0, suggesting that 1.0 kg of waste is generated for every kilogram of product yielded. Relative to the E-factors of lignin esterification procedures reported in literature, this value is considerably low.[42] However, this "waste" was a part of the product that could not be collected from the circulation channel, which is a specific feature in a single batch of REx processing in a small-scale extruder. Large-scale extruders typically allow continuous processing such that the E-factor of this process would theoretically approach zero. At an optimal OSA loading and using greener cataysts like alkali salts (Figure S7), the purification step for the REx process may even be omitted, and the modified lignin can be readily obtained as a solid that can be used for further applications. In contrast, the SS approach resulted in an E-factor of 4.3 which is 4 times higher than that of the REx method. The solvent used in the SS approach mainly constituted the generated waste, although we note that the solvent amount was not optimized for this study. The E-factor of the SS approach may be lowered in an industrial level if the solvent is recycled. A workup auxiliary such as water is still needed to precipitate the product and to wash away the residual organic solvent. Considering the use of water to recover OSA-lignin from the solution, the E-factor of the SS process increased to 28.7.

The esterification of lignin with OSA theoretically has 100% atom economy since the ring-opening of the cyclic anhydride does not generate any byproducts. By comparison, esterification using acid chlorides and noncyclic acid anhydrides produce either hydrochloric acid or the corresponding carboxylic acid, respectively. As side products, these chemicals have corrosive properties, potentially generate emissions, and require removal from the product.[43−45] Solventless approaches for lignin modification have been reported where acid anhydrides were used both as a solvent and as a reagent.[32,34,46] However, in these studies, excess amounts of anhydride were used which required a postreaction workup to recover or quench the excess reagent. In contrast, lower anhydride loading can be used with the REx method described herein, and efficient mixing and reaction can be achieved within a significantly shorter time. Moreover, since we targeted applications in polymer blends, it is advantageous that a thermoplastic lignin ester could already be achieved with low OSA loadings.

Overall, these findings evidently show that the REx method is an extremely efficient and environmentally benign process for lignin esterification with OSA. Elimination of wastes which has been the core of Green Chemistry[41] was adequately accomplished by completely avoiding solvents and can be fully realized when REx is performed in continuous configuration. In terms of practicality, the REx process is a high-throughput method where the esterified lignin can be obtained within minutes and used directly for material applications, whereas the solution-state route requires additional time for lignin dissolution and a laborious product workup. While a detailed life cycle assessment of the scaled REx process would provide a more holistic assessment of its sustainability advantage against conventional solution-state methods, we argue that REx is significantly less energy-intensive due to its higher throughput and its avoidance of solvents, considering that solvent recovery is the most energy-intensive step in solvent-based processes.[47−49]

Scope of OSA-Esterification via REx with Other Lignins. Technical lignins have varying structures and properties that are highly dependent on their botanical origins and extraction methods. To understand whether the REx process is effective on varying lignin feedstocks, we conducted OSA-esterification of different industrial biorefinery lignins. Aside from the primary focus of this work using softwood kraft lignin, three other lignins were studied, namely, grass organosolv, hardwood hydrolysis, and softwood hot water extracted (HWE) lignin (Figure 5).

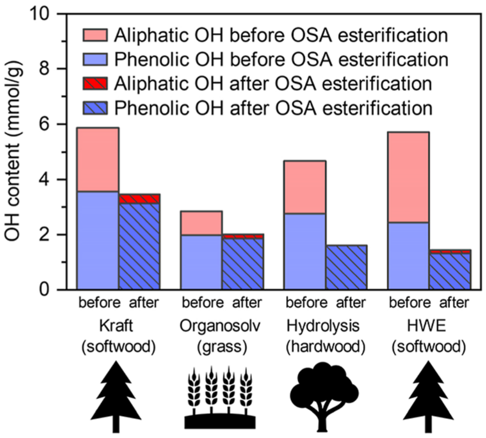

Figure 5. Hydroxyl contents of varying lignin feedstock before and after OSA modification via REx. The REx conditions were set to 50 wt % OSA loading, 5 wt % pyridine loading (based on the total mass of lignin and OSA), T = 120 °C, t = 10 min, and 60 rpm.

The successful esterification of the tested biorefinery lignins is shown in the FTIR spectra in Figure S11. All OSA-esterified lignins showed the nonconjugated C═O stretching band at 1732 cm^{-1} as evidence of the ester linkage formation. Signals from residual OSA were detected in all esterified lignins except the kraft lignin, for which the REx conditions had been developed, implying the need for future process optimization if chemically different lignins are used.

The hydroxyl contents of the different lignins were compared before and after esterification using ^{31}P NMR quantification as shown in Figure 5. The detailed values are listed in Table S7. Similar to kraft lignin, the reaction to the aliphatic OH position was favored over the phenolic OH position. Among all the lignins studied, the grass organosolv lignin obtained the lowest degree of OSA-substitution which was due to its low initial hydroxyl content. Prior to esterification, it contained a total OH content of 2.9 mmol/g with only a third of that being aliphatic hydroxyls. The low number of free hydroxyls in the organosolv lignin was mainly attributed to native acetylation characteristic of grass lignins[50] and possibly due to process-induced esterification with acetates and formates.[51] On the other hand, we calculated higher DS for both hardwood hydrolysis lignin and softwood HWE lignin (Table S6). Hardwood hydrolysis lignin possessed a high content of aliphatic OHs (1.9 mmol/g) which were completely consumed during the REx process. The more efficient esterification of this lignin could be attributed to its less-branched structure coming from a hardwood origin.[52,53] Similarly, the softwood HWE lignin was also rich in OH content (5.7 mmol/g) agreeing with a previous study on hot water extraction of spruce.[54] The hydroxyl groups of HWE lignin are predominantly of aliphatic type (3.3 mmol/g) and during the REx process, 96% of these aliphatic OHs reacted (Table S7). Moreover, the unmodified HWE lignin featured a low molar mass (M_w = 1270 g/mol). Hence, these structural features may have contributed to the high degree of OSA-substitution of HWE lignin. Surprisingly, the DS of phenolic hydroxyls in hydrolysis and HWE lignins was 42% and 46%, respectively (Table S7). We believe that the improved phenolic esterification of these lignins compared to kraft ($DS_{phenolic}$ = 12%) was due to their less-condensed structure.

In summary, these results demonstrate the successful esterification of the different biorefinery lignins via REx. The reactivity of different lignins may differ and optimizing the technical parameters is still needed to achieve higher degrees of esterification and lower levels of unreacted OSA. Nevertheless, the REx approach overcomes one of the most fundamental challenges when performing chemical modification of lignin, which is its low solubility . Based on the positive results both regarding green chemistry metrics and the versatility of REx, we continued to investigate the thermal properties of the OSA-lignins and their use in material applications.

Thermal Properties of OSA-Lignins from REx. Thermal characterization was performed on kraft lignin esterified with varying loadings of OSA. The OSA-lignins exhibited a melt-flow behavior as the extruded products became more fluid-like with increasing OSA substitution (Figure S12). These observations imply drastic changes in the thermal properties of the lignin after esterification (Figure 6a). The unmodified kraft lignin exhibited a T_g of 147 °C, which is typical of softwood kraft lignins.[10,55] With increasing OSA loading, the T_g shifted to lower temperatures, reaching as low as 17 °C for OSA$_{50}$-lignin. The softening of the OSA-lignins was attributed to the incorporation of long chain alkenyl groups into the lignin backbone. These bulky substituents weaken the hydrogen-bonding network of lignin and increase the free volume of the system, making the polymer more mobile.[7,56] Moreover, the residual OSA potentially acted as an external plasticizer in OSA$_{50}$-lignin. While the melting point (T_m) of OSA at 10 °C is absent in the OSA-lignin thermograms, it could have an influence on the extremely low T_g of OSA$_{50}$-lignin (Figure 6a). The residual pyridine may also affect the molecular mobility of the OSA-lignins as we observed a slight decrease in the T_g of the unmodified kraft lignin with 5 wt %

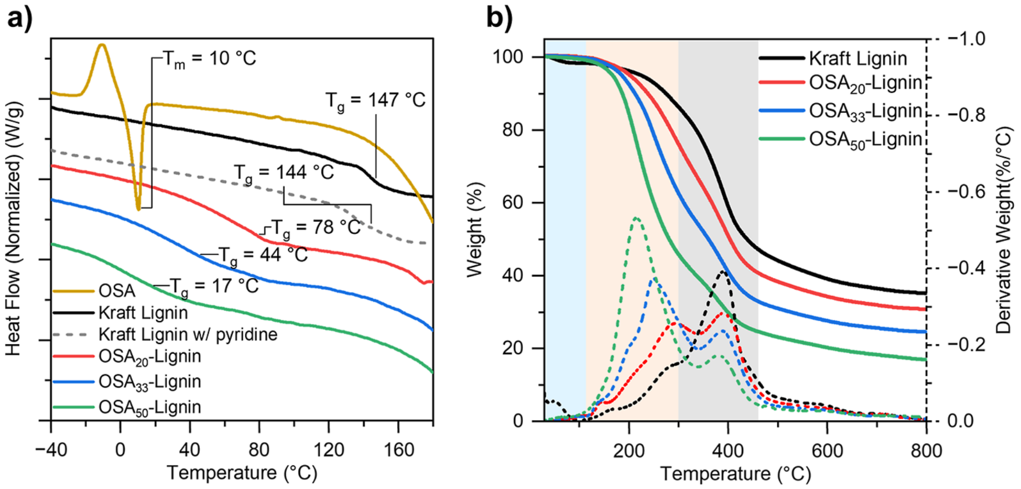

Figure 6. Thermal properties of the unmodified kraft lignin and the lignin esters analyzed via (a) DSC and (b) TGA. The REx parameters for the OSA-lignins were set to 5 wt % pyridine loading, t = 10 min, T = 120 °C, and 60 rpm.

pyridine. Overall, the thermoplastic character achievable at moderate OSA loadings suggests the potential of these OSA-lignins as additives in polymer blends.

The thermal degradation of kraft lignin and the lignin esters are shown in Figure 6b and the degradation temperatures at 5, 10, and 50 wt % losses are listed in Table S8. The thermal stability of the OSA-lignins decreased with increasing OSA loading. The degradation profile of the lignins can be divided into three stages. The first stage at temperatures below 120 °C corresponds to the loss of residual moisture. Only kraft lignin exhibited this mass loss at the first stage, suggesting that esterification increased the hydrophobic character of the samples by decreasing their hygroscopicity.[20,34] Previous studies on lignin esterification with cyclic anhydrides have found that the new carboxyl moiety increase the hydrophilic character of the lignin ester.[17,20] In our system, however, the long alkenyl chain of OSA likely counteracts this effect. The second stage from 120 to 300 °C could be attributed to the cleavage of aliphatic side chains[57] including the newly formed ester linkages,[14,58] aryl−alkyl ether linkages, and decarboxylation reactions.[33,34] For kraft lignin, the temperature at 5% mass loss ($T_{5\%}$) is 226 °C. This temperature decreased to 203 °C for OSA$_{20}$-lignin, 186 °C for OSA$_{33}$-lignin, and 168 °C for OSA$_{50}$-lignin. The same trend was observed for $T_{10\%}$ and $T_{50\%}$ (Table S8). These findings agree with previous reports where lignin esterification with cyclic anhydrides resulted in lignin derivatives with higher second-stage mass loss due to ester cleavage and decarboxylation reactions.[16,20,33,34] Lastly, rupture of C−C bonds constituted the third stage degradation events occurring above 300 °C.[57,59] The char residue at 798 °C (R_{798}) of unmodified lignin was 35.2% and a decreasing trend was observed for OSA-lignins as the degree of substitution increases.

Applications of OSA-Lignins in Bioplastics. The esterification of lignin with OSA resulted in lignin esters with thermoplastic behavior, decreased hygroscopicity, and added chemical functionality. Inspired by these observations, we explored the applicability of these OSA-lignins as a component of thermoplastic polymer blends and as a precursor for lignin-based elastomers (Figure 7a).

With the aim of developing materials with better sustainability profile, we selected polybutylene succinate (PBS) as our polymer of interest due to its biodegradability[60,61] and its mechanical properties which are comparable to fossil-based commodity plastics.[62] Our hypothesis was that, compared to unmodified lignin, OSA-lignin is more miscible with PBS due to the substitution of hydroxyl moieties of lignin which would weaken its hydrogen-bonding network. To verify our hypothesis, we produced blends of 80 wt % polybutylene succinate (PBS) and 20 wt % of lignin samples (either unmodified kraft or OSA-lignins) and evaluated their mechanical properties and morphology.

Tensile tests were performed on PBS and its blends with unmodified lignin or OSA-lignins (Figures 7b−d and S13). Pure PBS exhibited a tensile strength of 38.7 MPa, an elongation of 138%, and an elastic modulus of 793 MPa, which are consistent with values reported in literature.[63,64] The incorporation of unmodified kraft lignin into PBS resulted in a brittle material characterized by a low tensile strength (29.1 MPa), a high elastic modulus (939 MPa), and an almost 95% reduction in elongation (6.8%). These findings agree with previous reports on the tensile properties of PBS blends with unmodified lignin.[65,66]

In contrast, the mechanical properties of the PBS/OSA-lignin blends were significantly better than those of PBS blended with unmodified kraft lignin (Figure 7b−d and Table S9). While PBS/OSA$_{20}$-lignin showed little improvement in elongation over PBS/kraft lignin, PBS/OSA$_{33}$-lignin and PBS/OSA$_{50}$-lignin achieved elongation greater than 120%, which was comparable to pure PBS (Figure 7d). Despite the moderate degree of substitution, the increased miscibility between OSA$_{33}$-lignin or OSA$_{50}$-lignin and PBS was noteworthy, suggesting that partial esterification was sufficient to increase the compatibility of lignin and PBS.

Additionally, all PBS/OSA-lignin blends manifested lower modulus values compared to PBS/kraft lignin, indicating that the esterification reduced the stiffening effect of lignin (Figure 7c).[7,11] These results agree with the lower torque value of the PBS/OSA-lignin blends relative to PBS/kraft lignin and neat PBS during extrusion (Figure S14), revealing that OSA-lignin acts as an external plasticizer to improve PBS processability.[7] Interestingly, only the PBS/OSA$_{50}$-lignin blend exhibited an improvement in tensile strength (36.0 MPa) among the blends, which is comparable to the tensile strength of the pure PBS (38.7 MPa) (Figure 7b). We speculate that the residual OSA

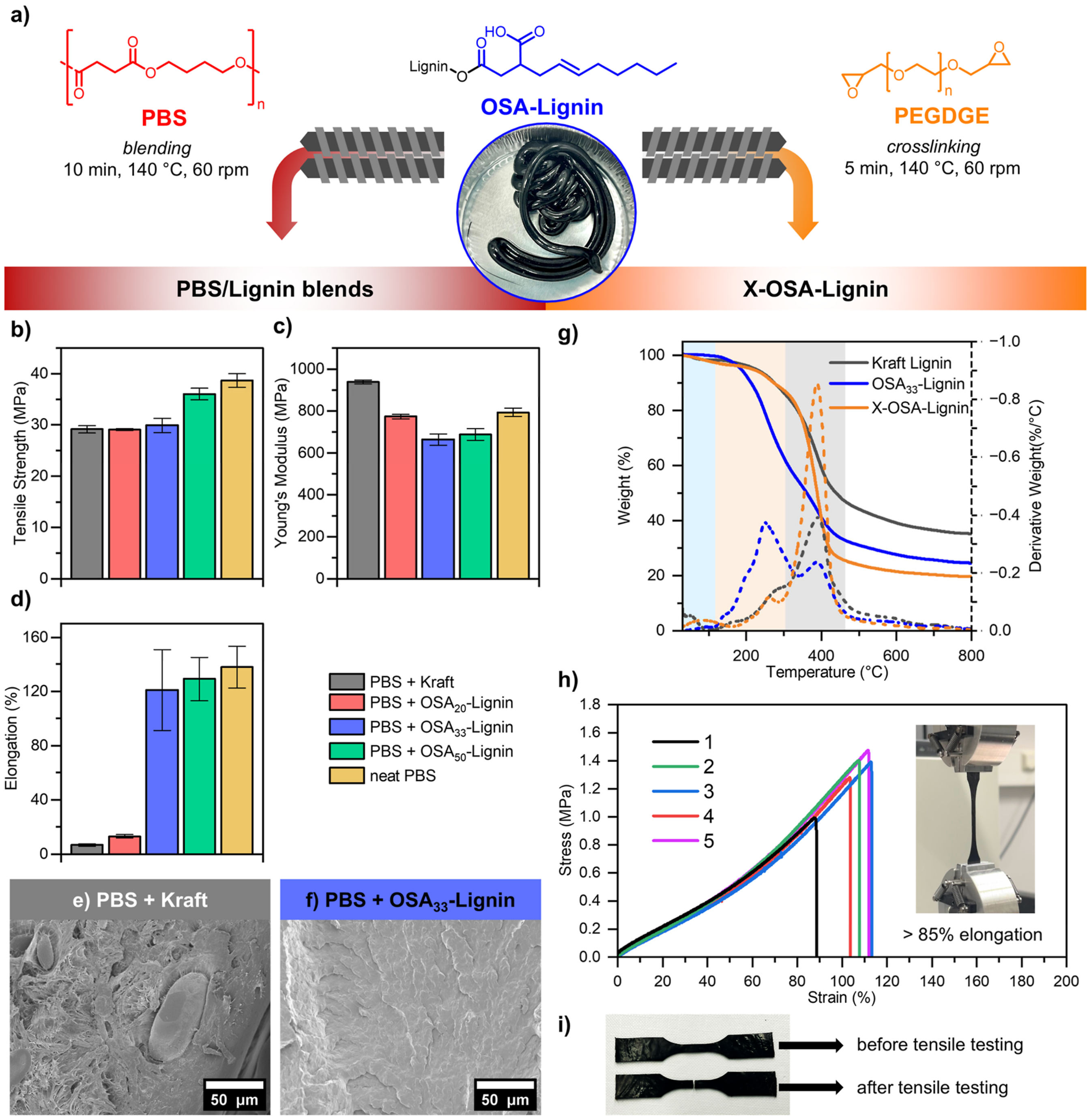

Figure 7. Performance of OSA-lignin in bioplastics. (a) Schematic illustration of the routes to transform OSA-lignin into lignin-based bioplastics either via blending with PBS or cross-linking with PEGDGE. (b−d) Tensile properties of blends with 20 wt % lignin (unmodified kraft or OSA-lignin) in PBS. (e,f) Cross-section SEM micrograph of the specimens after tensile testing. SEM images of the other blends are shown in Figure S15. (g) Thermal degradation and (h) stress−strain curves of the five specimens of the lignin-based elastomer (referred to as X-OSA-lignin) produced by cross-linking OSA_{33}-lignin with 40 wt % PEGDGE. (i) Visual appearance of X-OSA-lignin before and after tensile testing.

could potentially act as a compatibilizer between OSA_{50}-lignin and PBS.

The SEM analysis of the cross-section of the blends provided further insights on the miscibility of the lignin samples with PBS. The SEM image of PBS/kraft lignin in Figure 7e shows distinct phase separation between the two components, as large aggregates of lignin were evident in the polymer matrix. This weak interfacial adhesion likely caused ineffective stress transfer between the components, leading to the poor mechanical properties.[8] Similar results were observed for PBS/OSA_{20}-lignin (Figure S15), which explains its low elongation, suggesting that OSA_{20}-lignin had too low DS for sufficient miscibility. In contrast, almost monophasic morphologies with no discrete lignin aggregates can be observed for PBS/OSA_{33}-lignin and PBS/OSA_{50}-lignin (Figures 7f and S15). Combined with elongation data, these observations indicate that the esterification of lignin with 33 wt % OSA (DS = 26%) already led to a significant improvement in the miscibility between the modified lignin and PBS. We suggest that the OSA substituents improved the compatibility between lignin and PBS, and the low T_g of OSA$_{33}$-lignin and OSA$_{50}$-lignin facilitated efficient mixing with the matrix polymer. While DSC and FTIR analyses could provide additional insights on blend miscibility,[9] they were not useful in this study due to the low lignin content in the blends and the overlap of PBS melting and glass transition of the lignins. Since these comparisons were made at a constant OSA-lignin/PBS ratio (20 wt % OSA-lignin), identifying the optimal composition to achieve superior mechanical properties is an opportunity for future studies.

Apart from the changes in the thermal properties, the esterification of lignin with OSA resulted in new reactive sites on the macromolecule. We exploited the increased amount of carboxyl functionality in the OSA$_{33}$-lignin for preparing lignin-based elastomers. After reacting lignin and OSA in the extruder, we fed a diepoxy cross-linker, poly(ethylene glycol) diglycidyl ether (PEGDGE), to react with the OSA$_{33}$-lignin. Typically, a catalyst is needed to drive epoxy−carboxyl reactions.[67] In our case, the residual pyridine in the OSA-lignin system served as a base catalyst for cross-linking where the carboxylate anion attacks the epoxide ring, forming a β-hydroxy ester. Primarily, the intensity of the carbonyl stretching band at 1706 cm^{-1} decreased, confirming the reaction of the carboxyl groups, while the intensity of the peak at 1732 cm^{-1} increased, indicating the formation of new ester groups (Figure S16). The consumption of the epoxy groups was confirmed by the absence of the oxirane band at 910 cm^{-1}. Furthermore, C−O−C stretching at 1089 cm^{-1} and C−H stretching at 2866 cm^{-1} from the PEGDGE segments in the cross-linked samples were observed to increase with increasing epoxy loading.

The cross-linked sample exhibited noticeable changes in thermal properties compared to the unmodified lignin and the OSA$_{33}$-lignin. After cross-linking with 30 wt % PEGDGE, OSA-lignin changed from a brittle to a flexible material (Figure S17). The OSA$_{33}$-lignin cross-linked with 40 wt % PEGDGE (referred to as X-OSA-lignin) exhibited a T_g of 7 °C (Table S8). This reduction in T_g was attributed to the long PEGDGE chains that increase the mobility of the molecule. Interestingly, cross-linking also improved the thermal stability of OSA$_{33}$-lignin. Figure 7g shows that the second stage degradation from 120 to 300 °C observed in OSA$_{33}$-lignin was significantly reduced in the cross-linked product. Compared to OSA$_{33}$-lignin, X-OSA-lignin exhibited 17%, 29%, and 8% increase in degradation temperatures at 5, 10, and 50 wt % loss, respectively (Table S8). This observation suggests that the cross-linking inhibited the thermal degradation by decarboxylation reactions. The degradation rate of X-OSA-lignin peaked at 389 °C where it lost half of its mass, and a char yield of 20% was obtained at 798 °C.

Since cross-linking OSA-lignin yielded a flexible material, we performed tensile testing to gain insights on its mechanical properties. The average tensile strength of five specimens was 1.3 ± 0.2 MPa with a Young's modulus value of 1.7 ± 0.1 MPa (Figure 7h). Moreover, X-OSA-lignin exhibited an average elongation of 105 ± 9% demonstrating its elastomeric property. Interestingly, the material seemed to exhibit some degree of shape-memory as it returned to its original length after tensile testing (Figure 7i). Tensile properties of lignin-based epoxy resins with similar order of magnitude have been reported in literature.[68,69] Further work is ongoing to improve the mechanical properties of our prepared lignin-based elastomer. Nevertheless, this work presents a unique approach to produce elastomeric lignin-based materials in a solventless manner using an extruder.

■ CONCLUSIONS

In this study, we successfully esterified lignin with octenyl succinic anhydride (OSA) via reactive extrusion (REx). We found that the maximum degree of substitution depends on the OSA loading, with the reaction reaching completion in under 10 min at 120 °C. Spectroscopic analysis revealed that esterification primarily occurred at the aliphatic hydroxyls of lignin, and that the resulting esters were rich in carboxyl functionality. Thermal analysis showed that even partial esterification led to lignin esters with low glass transition temperatures. We emphasize that favorable thermal properties for our target applications can already be achieved at moderate OSA loadings, allowing for reduced reagent amounts, minimizing the material costs and residual byproducts. The new properties of the OSA-lignins were leveraged by demonstrating their uses as components of thermoplastics blends and as building blocks for lignin-based elastomers.

Moreover, we highlighted the benefits of REx for functionalizing lignin. Compared to the conventional solution-state approach, REx features a high-throughput route with a significantly decreased *E*-factor, which can be further reduced when done in a continuous configuration. In addition, the extruder allows for a convenient successive processing of the modified lignin into value-added materials. Furthermore, we showed the versatility of the REx approach by successfully modifying different industrial lignins from various botanical origins and isolation methods.

Overall, our work advances REx as a green technology for efficiently valorizing lignin, a highly underutilized side stream. Given its numerous advantages over conventional solvothermal methods, we envision that REx can become the standard tool for lignin modification and stimulate its application in polymeric materials, potentially replacing fossil-based resources. The adaptability of the REx method with diverse lignin feedstocks could propel its swift scale-up and easy integration as a drop-in technology in existing biorefineries. As we move toward a circular bioeconomy, further exploration of other biomass resources and the application of REx for not only biopolymer production but also polymer recycling could elevate this work significantly.

■ EXPERIMENTAL SECTION

Materials. The primary starting material of this study was softwood kraft lignin (BioPiva 395) received from UPM (Finland) in the form of a powder. Three additional industrial biorefinery lignins were used in this work: organosolv lignin from wheat straw (Fortum Bio2X, Finland), hydrolysis lignin from birch (Fibenol OÜ, Estonia), and hot water extracted lignin from spruce (Boreal Bioproducts, Finland). The lignins were dried under vacuum at 45 °C for 24 h before use. 2-Octen-1-ylsuccinic anhydride (OSA, 97% purity, mixture of *cis* and *trans* isomers) and poly(ethylene glycol) diglycidyl ether (PEGDGE, average M_n 500) were purchased from Sigma-Aldrich. Pyridine (≥99.0%) was purchased from ACS. Polybutylene succinate (BioPBS FZ91PB) was provided by Mitsubishi Chemical Group. All chemicals were used as received.

Reactive Extrusion (REx) Esterification. The synthesis of modified lignins, referred to as OSA-lignin, by REx was conducted using a corotating twin-screw micro compounder (Xplore Instruments MC 15 HT, The Netherlands). Briefly, dry kraft lignin powder, OSA, and pyridine were premixed in a beaker. The reaction mixture was fed into the extruder through a feed hopper within approximately 2 min.

The temperature profile of the liquid-tight barrel was uniformly set from the feeder to the die. The compounder featured a backflow channel, allowing the material to circulate within the system for a specified residence time. After the designated residence time, the OSA-lignin was extruded through a round hole die with a diameter of 3.00 mm. The effect of different variables such as the OSA loading (20 to 50 wt %), presence of catalyst (5 wt % of the total mass of lignin and OSA), residence time (1 to 30 min), and temperature (60 to 140 °C) were studied (Table S1). To investigate the versatility of the REx process, different biorefinery lignins were esterified at constant lignin/OSA (50:50 w/w) composition, catalyst loading (5 wt % pyridine), temperature (120 °C), and screw speed (60 rpm). To ensure reproducibility, the extrusion studies with varying OSA loadings were repeated 3 times.

Preparation of PBS Blends. To test our hypothesis that the esterification of lignin with OSA could improve its compatibility with hydrophobic polymers, we prepared blends of 80 wt % polybutylene succinate (PBS) and 20 wt % OSA-lignin using the same extruder at 140 °C and 60 rpm for 10 min. Sheets were prepared by hot-pressing the blend for 10 min at 130 °C and 150 kN. These sheets were cut into dog bone specimens for tensile testing. Specimens of neat PBS and of PBS blend with unmodified kraft lignin (80:20 w/w) were prepared for comparison.

Preparation of Cross-linked OSA-Lignins. The OSA_{33}-lignin was selected for cross-linking studies because it could be extruded as a solid material, and more importantly, it contained no unreacted OSA according to quantitative ^1H NMR analysis. After the REx esterification step to produce OSA_{33}-lignin, around 3 g of material was extruded out and an equivalent amount (3 g or 20 wt %) of epoxy cross-linker poly(ethylene glycol) diglycidyl ether (PEGDGE) was fed into the extruder. The PEGDGE loading was varied from 20 to 40 wt %. The reactions were conducted at 140 °C and 60 rpm for 5 min and the extruder torque values (N m) were monitored to observe changes in relative viscosity. Finally, the cross-linked OSA-lignin was extruded after 5 min when the torque value rose to more than 10 N m.

Characterization of Lignin and Lignin-Based Materials. The unmodified lignins and OSA-lignins were characterized using ATR-FTIR, NMR (^1H, HSQC, ^{31}P), GPC, DSC, and TGA, while the blends and elastomers were characterized using tensile tests and SEM as elaborated in the Supporting Information.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.5c04676.

> The Supporting Information contains the reactive extrusion parameters, procedure for solution-state esterification, protocols for the characterization (ATR-FTIR, NMR, GPC, DSC, TGA, tensile test, SEM) of the lignins and the lignin-based bioplastics as well as their tabulated results, full FTIR, HSQC NMR, ^1H NMR, and ^{31}P NMR spectra of the OSA-lignins, molecular weight chromatograms, *E*-factor calculations, and photographs and SEM images of OSA-lignins (PDF)

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E.M.G.: methodology, investigation, formal analysis, visualization, and writing—original draft; P.N.: conceptualization, methodology, formal analysis, and writing—review and editing; U.H.: methodology, and writing—review and editing; M.Ö.: conceptualization, supervision, funding acquisition, and writing—review and editing.

Notes

The authors declare no competing financial interest.

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