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Research article

Comparison of dehydration methods for untreated lignin resole by hot air oven and vacuum rotary evaporator to synthesize lignin-based phenolic foam

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ABSTRACT

We investigate two different dehydration methods to determine their suitability for preparing resoles for foam synthesis. A simplified process for synthesizing lignin foam (LF) from lignin resole (LR) dehydrated in a hot air oven (HAO) is compared with that dehydrated using a vacuum rotary evaporator (VRE). First, the LR formulation is prepared by mixing phenol with untreated lignin (0%–15% by weight), and subsequently, the prepared LRs are dehydrated using an HAO and a VRE. We find that for the same dehydration time, both techniques yield LRs with the same chemical compositions; however, the HAO technique affords a moisture removal of 13–17% by weight, whereas the VRE technique removes 9–12% moisture by weight. The LR obtained by the HAO is more viscous and maintains a circular shape after being dropped on a plate. In our experimental synthesis of LF containing VRE resole, biofoam is not formed owing to insufficient viscosity, whereas biofoam is obtained with the HAO resole. The synthesized LF exhibits a density range of 44.96–85.68 kg/m^3 and a compressive strength of 103.28–152.27 kPa. Scanning electron microscopy investigations show that the morphology of the foam is a closed-cell structure. The simplified synthesis of LF from the HAO-treated resole offers significant advantages over the complexity of the conventional VRE approach in terms of equipment cost and energy consumption. The resulting foam exhibits a thermal stability and thermal performance comparable with the counterpart properties of phenolic foam.

1. Introduction

Phenolic foam (PF) is a popular polymer material that is used for thermal insulation. PFs are mostly applied in high-rise buildings, airports, and chemical transport pipelines because of their light weight, low thermal conductivity, and high thermal stability [1]. The general foaming of PF is usually realized using resin. The mixture is prepared in two steps [2]: first, synthetic phenolic resole (PR) is obtained by the reaction between phenol and formaldehyde. Water in the obtained resole solution is removed by reducing the pressure during evaporation (using a vacuum rotary evaporator, VRE) until 80% solid content is achieved [3]. While VRE-based resole dehydration has been preferred by researchers such as Li et al. (2017) and Wang et al. (2019) [4,5], this technique suffers from certain drawbacks when compared with simpler techniques such as hot

air oven (HAO) drying. The equipment required for VRE is expensive, and VRE operation is complex and energy intensive because it requires pumping and pressure and temperature control mechanisms. In the second step of preparing PF, emulsifiers and other additives are added to the mixture, which is concurrently expanded and cured in an oven operated at a temperature of 50–80 °C [6].

In this context, we note that the production of phenol from crude oil is also severely detrimental to the environment. The resulting phenol is nonrenewable and unsustainable, and the cost of production is also affected by the oil-price volatility [7,8]. Meanwhile, phenolic compounds from natural sources can be used as alternatives to reduce phenol use in the petroleum industry. Natural phenolic compounds such as phenolic acids from gallic acid, acetophenones from gallacetophenone, and phenolic compounds from tannin and lignin have been used in the

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development of a number of polymer products [9] such as wood composites [10], acoustic absorbers [11], resins [12, 13, 14, 15], and foams [16].

Plant cells generally contain approximately 20–30% of lignin. Because lignin has phenolic structures, it can be used as a substitute for phenol [17]. In this regard, the depolymerization of lignin has been investigated toward increasing the number of reactive sites via catalysis [18,19] and varying the temperature [20] and reaction time to break the polymer structure [5]. The process can destroy lignin, thereby yielding 11.86–17.92% of monophenolic compounds [21,22]. The depolymerized lignin is widely applied to produce a range of products. Lignin foam (LF) is one of the products that makes use of treated lignin to replace ~50% by weight of phenol [4,5]. The chemical structure of LF has been found to be similar to that of PF, with LF exhibiting densities in the range of 30.96–08 kg/m^3 and compressive strengths of 0.27–0.37 MPa [4]. The final foam product can be classified as a thermal insulator with a low thermal conductivity (0.035–0.038 W/m·K) [5]. However, the process of foam production is still complicated owing to the need for lignin depolymerization. In this regard, a previous study has proposed the use of untreated lignin to replace phenol in the production of foam, and reportedly, the resulting foam can be classified as a flame retardant and insulation material with a compressive strength of up to 1.01 MPa [23].

In this context, the purpose of this study was to compare the HAO and VRE methods for the dehydration of resoles for foam synthesis. Phenol was replaced by 0–15% by weight of untreated lignin to synthesize resole for use in LF synthesis. The resulting resole was monitored for its physical appearance, and the functional groups were determined. The biofoam properties such as the characteristic functional groups, density, compressive strength, morphology, thermal stability, and thermal performance were also investigated.

2. Materials and methods

2.1. Materials and chemicals

All the chemicals used for LF synthesis included alkali lignin with a low sulfonate content (Sigma-Aldrich, product number 370959, lot #04414PE), solid crystal phenol (Fisher Scientific, UK), sodium hydroxide (NaOH solution water 50% w/w, Loba Chemie Pvt. Ltd.) and formaldehyde (solution 37%, QRëc Co. Ltd.), hexane (ANaPURE Co. Ltd.), *p*-toluenesulfonic acid (Sigma-Aldrich, #BCBS8919V), glycerol (QRëc Co. Ltd.), and Tween 80 (Ajax Finechem).

2.2. Synthesis of resole

Lignin resole (LR) was prepared as described by Li et al. (2017) [4] with slight modifications. The reactor setup included a three-necked flask equipped with a thermometer, additional chimney, cooling condenser, and preheated water bath operated at 85 °C with a magnetic stirrer. The resole compositions with different lignin-to-phenol ratios (0:100, 5:95, 10:90, and 15:85 by weight) are listed in Table 1. The resoles with different lignin contents are designated as PR, LR-5, LR-10, and LR-15, where PR refers to the resole containing 0% lignin by weight, and LR-5, LR-10, and LR-15 refer to the resoles containing 5%, 10%, and 15% of lignin, respectively. The maximum lignin content was limited to 15%

by weight because the addition of lignin beyond this amount led to an extremely high viscosity after HAO dehydration, and the resole could not be synthesized to form foam. As a representative example for formulation, to prepare LR-10, 4 g of lignin, 36 g of phenol, 10 g of distilled water, and 3.6 g of NaOH solution were loaded into the reactor and stirred for 30 min. Next, formaldehyde (62.4 g) was added dropwise into the reactor with the stirrer continuously working for 120 min. The LR was subsequently cooled to room temperature and neutralized by 5 M acetic acid to pH 5.5–6.5 with strong stirring. Two different methods were used to dehydrate the resin: VRE and HAO. The VRE was operated at 65 °C and 0.08 bar, and the HAO was operated at 105 °C. The dehydration time for both methods was 6 h.

2.3. Synthesis of lignin foam

The synthesis of the LF specimens from resoles LR-0 to LR-15 was carried out using the chemical compositions listed in Table 2. The synthesized LF was prepared with different lignin contents. For example, LF-15 was prepared from LR-15, which originally contained 15% lignin by weight. The LF was prepared in two stages. In the first stage, 20 g of resole, 0.8 g of surfactant, and 2 g of blowing agent were mixed in a paper cup using a stirrer. In the second stage, 2.8 g catalyst, 1.2 g water, and 1 g glycerol were manually blended in a beaker until the mixture formed a homo-crystal liquid. Subsequently, the crystal–liquid mixture was poured into a paper cup, vigorously stirred with a cream whipper for 1 min, and immediately placed in an oven operating at 80 °C for 60 min.

2.4. Sample testing

2.4.1. Resole testing

The pH values of the resoles adjusted with acetic acid were measured using a pH meter (HI2020, Hanna, USA) at room temperature. In the study, we defined the solid content according to Eq. (1). The initial weight of the resole before dehydration by both methods was measured using a standard weight scale with a maximum capacity of 3100 g and accuracy of up to 0.01 g. After 6 h of dehydration, the resole weight was measured again. The moisture removed by dehydration was subsequently defined using Eq. (2). The moisture removed was determined at 2 h intervals to compare the drying rates of the two methods. The chemical functional groups of samples were determined using Fourier transform infrared spectroscopy (FTIR) (Tensor 27, Bruker, Germany). All spectra were acquired with 64 scans at a resolution of 4 cm^{-1} and a spectral range of 4000–650 cm^{-1}. The physical appearance of each resole specimen was monitored by dropping it on glass plate and leaving it undisturbed on the plate for ~5 min before the visual examination of the forms of the drops with a camera (Fujifilm X-A3 digital camera, Fujifilm Japan).

$$Solid\ \ content(\%) = \frac{weight\ of\ resole\ after\ dehydration \times 100}{Weight\ of\ resole\ before\ dehydration} \quad (1)$$

$$Moisture\ \ removed(\%) = 100 - Solid\ \ content(\%) \quad (2)$$

2.4.2. Biofoam testing

The FTIR spectra of the LFs were analyzed as in the case of the resoles. All the samples were tested for the properties of interest. The density of

Table 1. Chemical compositions for the synthesis of lignin resoles.

Resoles	Weight (%)				
	Phenol	Lignin	Water	NaOH solution	Formaldehyde
PR	34.48	-	8.62	3.10	53.79
LR-5	32.76	1.72	8.62	3.10	53.79
LR-10	31.03	3.45	8.62	3.10	53.79
LR-15	29.31	5.17	8.62	3.10	53.79

Table 2. Composition of the mixture used for the synthesis of lignin foam.

Chemicals	Functions	Weight (%)
Resole	Substance	71.94
p-toluenesulfonic acid	Catalyst	10.07
Hexane	Blowing agent	7.19
Water	Solvent	4.32
Glycerol	Plasticizers	3.60
Tween 80	Surfactant	2.88

the foams was tested as per ASTM D1622 [24], and the foam compressive strength with 10% strain was measured using a universal testing machine (UTM) (5567A, Instron, USA) with a crosshead speed of 2.5 mm/s as per ASTM D1621 [25]. A desktop scanning electron microscope (MiniSEM) (SNE-4500M, SEC, Korea) was used to examine the morphology of the samples at $50\times$ magnification. The thermal stability of the foam was tested using a thermogravimetric analyzer (TGA) (DTG-60H, Shimadzu, Japan) in the range of 50–650 °C, a heating rate of 10 °C/min, and a N_2 flow rate of 30 ml/min. The thermal performance was tested using an experimental method [26]. The PF and LF-15 samples were prepared with dimensions of $2 \times 2 \times 1$ inch and placed in a wooden box with a thermal resistance test setup. Samples were heated by the radiation from a 150 W infrared lamp, and the temperature inside the box was recorded by a data logger for 120 min. Subsequently, the heat source was switched off, and the sample was left to cool at room temperature for 120 min. The porosity of foams, that is, the cumulative volume of pores between 1.70 nm and 300.00 nm, was measured using the nitrogen adsorption/desorption technique (ASPS2460, Micrometrics, USA) and calculated using the Barrett–Joyner–Halenda (BJH) method.

3. Results

3.1. pH, solid content, and physical appearance of resoles

The pH, solid content, and physical appearance of the concentrated resoles prepared by the VRE and HAO methods are listed in Table 3. The pH values of the resoles were adjusted to suitable values and then were measured to be 5.31 for PR, and in the range of 5.20–5.23 for the LR-5–LR-15 samples. The solid contents of PR, LR- 5, LR-10, and LR-15 after HAO dehydration were 86.36%, 85.31%, 82.88%, and 83.96%, respectively, and 90.86%, 88.42%, 90.11%, and 85.84%, respectively, after VRE dehydration. Here, we note that viscosity plays an important role in the formation of foam from the resole. Resoles with low viscosity do not have the capacity to retain the blowing agent during foam formation [23]. In contrast, resoles with excessive viscosity resist the expansion of air. Therefore, an appropriate viscosity must be chosen for foam preparation from the resoles. In this study, the viscosity of the resoles was not directly measured; it was inferred by monitoring their physical appearance (Figure 1). We note from the table that the HAO resoles appear to more strongly maintain circular shapes than the VRE resoles. The HAO resoles exhibit a smoother texture and clearer and more well-defined rims. It can be seen from Figure 1, the VRE PR and LR-5 samples appear to contain excess phenol.

Figure 2 shows the moisture removal from all the resoles, recorded every 2 h for 6 h. During the first two hours, the amounts of moisture removed by VRE from PR, LR-5, LR-10, and LR-15 are 7.07%, 10.89%, 8.17%, and 10.23% by weight, respectively, and the amounts by HAO are 6.84%, 6.24%, 9.08%, and 8.31% by weight, respectively. We note here that the moisture removed by VRE is higher than that by HAO because in the VRE case, the moisture is removed under vacuum (that is, at lower pressures), and because of the rotary action, the moisture evaporates more uniformly from the resole. In the case of HAO, water evaporates from the resole (placed in a container) only from the surface exposed to the drying environment. With continued dehydration for another two hours, the amounts of moisture removal from the PR, LR-5, LR-10, and

LR-15 resoles are observed to be 8.35%, 11.09%, 9.00%, and 11.30% by weight, respectively, for VRE, and 12.16, 11.71, 16.14, and 13.67% by weight, respectively, for HAO. Between 2 h and 4 h, the amount of moisture removed by VRE changes only slightly with time, whereas the moisture removed by HAO continues to increase with time. After 6 h of drying, the amounts of water removed by VRE from PR, LR-5, LR-10, and LR-15 are 9.14%, 11.59%, 9.89%, and 12.16%, respectively, and 13.64%, 14.69%, 17.13%, and 16.05%, respectively, by HAO. Evidently, HAO affords a better performance over time, thereby indicating that this approach is more suitable for drying the resole.

Here, we note that resoles with greater amounts of lignin exhibit higher viscosity because lignin has a higher molecular weight (Mw = 2000 g/mol) than phenol (Mw = 94 g/mol) [4]. In our attempts to prepare foam from the VRE resole, we found that foam could not be formed from the resole owing to its low viscosity. However, a thin layer of foam was obtained and tested for functional groups for comparison with foam obtained from the HAO-treated resoles.

3.2. Functional groups of resole and foam

The functional groups and chemical bonds of the resoles and foams were determined by means of FTIR analysis. The infrared transmittance spectra of PR and samples LR-5–15, which were dehydrated by the HAO and VRE methods, are shown in Figure 3. The characteristic peaks of all the resoles show an absorption band of the hydroxyl group at 3320 cm^{-1} [27]. The signals between 2980 and 2805 cm^{-1} and at 1481 cm^{-1} indicate C–H stretching of the methylene bridge in the resole [28]. The peak at 1700 cm^{-1} can be attributed to the C=O bonding of reactive acetic acid with hydroxyl groups by the esterification reaction [12]. The band at 1610 cm^{-1} corresponds to C–H bending, which can be attributed to the reaction of the resole with formaldehyde [29]. The characteristic bands of phenolic hydroxyls are observed at 1365 cm^{-1}, the C–O–C skeletal vibration of polysaccharide rings from formaldehyde phenolic bonds is observed at 1034 cm^{-1}, and C–O stretching is observed at 1005 cm^{-1} [30, 31, 32, 33, 34]. The adsorption peaks of C–H appear at 1112 cm^{-1} and between 918 and 665 cm^{-1}. The peak at 1112 cm^{-1} indicates C–H stretching vibrations in different groups of lignin [34]. C–H aliphatic bonds are detected at 880 cm^{-1} and the C–H aromatic bonds of phenol can be observed at 828 cm^{-1}, 758 cm^{-1}, and 694 cm^{-1} [27,33,35].

Figure 4 shows the infrared absorption spectra of LF-5, LF-10, and LF-15 (dehydrated by HAO and VRE); these spectra are very similar to the corresponding ones of the PF, which indicates that lignin biofoams exhibit a chemical structure similar to that of the PF. All the foams exhibit typical hydroxyl-group adsorption at 3358 cm^{-1}, C–H stretching in the range of 2980–2804 cm^{-1} and at 1472 cm^{-1} and 1112 cm^{-1}, and C=O phenolic hydroxyl bonding at 1700 cm^{-1}. The bridge oxygen-carbon (C–O–C skeletal vibration) appears at 1034 cm^{-1}, C–O stretching at 1005 cm^{-1}, C–H aliphatic bonding at 880 cm^{-1}, and different groups related of C–H aromatic phenol bonding at 1365, 828, 758, and 694 cm^{-1}. All the spectra of the LRs and LFs are similar to the corresponding ones of the PR and PF, which suggests that the LRs exhibit a molecular chemical structure similar to that of pure PR, and different dehydration methods do not affect the chemical structure of the resole and foam. However, the peak at 600 cm^{-1}, attributed to S–C stretching, can be found only in the case of the LR, and the signal at 1219 cm^{-1} is assigned to the functional group C–O stretching of the syringyl ring [36,37]. This variation can be attributed to the syringyl ring being part of the lignin structure in the LR but not in the PR. Hence, the peak is not observed in the PR and PF.

3.3. Thermal stability of resole and foam

TGA analyses of PR and LR were performed to determine their thermal stabilities. The TGA curves under a N_2 atmosphere are shown in Figure 5; these curves can be divided into three stages. The first stage corresponds to moisture removal caused by the cross-linking and

Table 3. Physical properties of the resoles prepared in the study.

Resole	pH	Solid content (%)	
		HAO	VRE
PR	5.31 ± 0.05	86.36 ± 0.64	90.86 ± 0.65
LR-5	5.23 ± 0.05	85.31 ± 0.31	88.42 ± 0.41
LR-10	5.20 ± 0.03	82.88 ± 0.13	90.11 ± 3.11
LR-15	5.20 ± 0.04	83.96 ± 1.96	85.84 ± 1.84
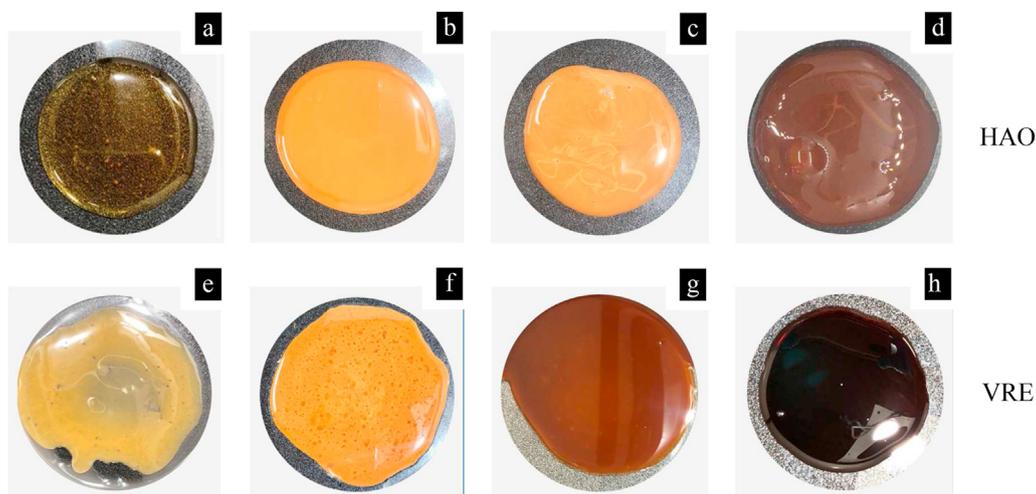
Figure 1. Physical appearance of resoles dehydrated by HAO (a) PR, (b) LR-5, (c) LR-10, (d) LR-15, and resoles dehydrated VRE (e) PR, (f) LR-5, (g) LR-10, and (h) LR-15.
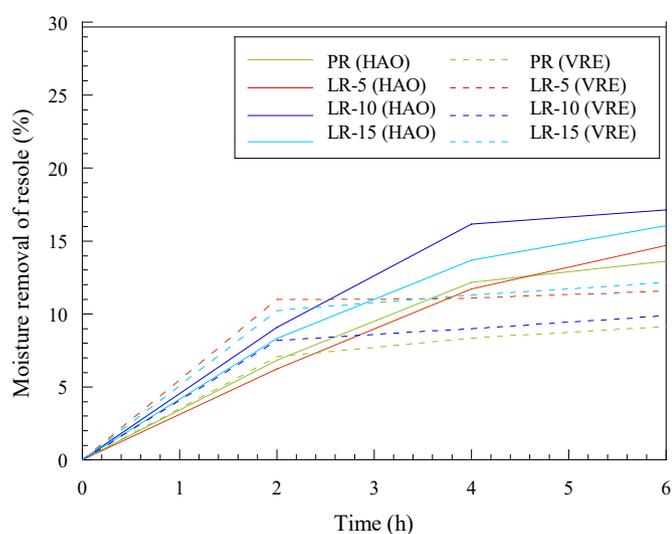
Figure 2. Moisture removal amounts from resoles with the application of HAO and VRE methods.

Figure 3. FTIR spectra of PR, LR-5–15 (HAO), and LR-5–15 (VRE) resoles.

condensation reactions of the terminal groups below 300 °C [38]. The second stage involves the second round of mass loss from PR in the temperature range of 300–450 °C, attributable to the moisture loss resulting from the condensation reaction of methylene and phenolic groups with hydroxyl groups, as well as between two hydroxyl functional groups [39]. The third stage involves the degradation of phenol in the range of 450–600 °C. This stage is the main weight-loss stage for resoles containing phenol and lignin owing to the further degradation of phenols into a carbonaceous structure [13,40]. We note from the figure that the mass residuals of PR, LR-5, LR-10, and LR-15 are 0.17%, 4.44%, 16.21%, and 5.22% by weight of the resoles, respectively. It is evident that at 650 °C, the mass residual of LR is higher than that of PR. The addition of lignin is equivalent to adding aromatic groups to the resole, rendering the resole more thermally stable [13].

The thermal stabilities of PF, LF-5, LF-10, and LF-15 (HAO) are displayed in Figure 6. These results indicate a three-stage pyrolysis of the foams. In the first stage, foams are degraded in the temperature range of 0–130 °C, during which the moisture in the samples is removed [28]. In

the second stage, in the temperature range of 130–250 °C, decarboxylation of air occurs in the pores [41,42]. In the third stage, the degradation of foams occurs under a nitrogen atmosphere at temperatures in the range of 250–550 °C. In this temperature range, the terminal groups are destroyed, and the bridged methylene of phenols decomposes into carbonaceous structure [4,23]. The mass residuals of PF, LF-5, LF-10, and LF-15 at 550 °C are 0.32%, 2.99%, 6.92%, and 2.29% by weight of the foams, respectively. A comparison of the carbon residuals of PF and LF-5–15 clearly reveals that the residual weight after the burning of PF is lower than that of the LF. This can be explained by the presence of lignin, which has a more stable aromatic structure than phenol. In addition, lignin is known to be a thermostable polymer [41,43].

3.4. Proposed possible mechanism of resole synthesis

PR can be synthesized using an excess amount of formaldehyde aqueous solution and a base catalyst. Figure 7(a) shows the possible pathway of the resole synthesis. Phenol reacts with the catalyst at 80 °C

Figure 4. FTIR spectra of PF and foams prepared from PR, LR-5–15 (HAO), and LR-5–15 (VRE).

Figure 5. TGA curves of PR and LR-5–15 samples treated with HAO.

Figure 6. TGA curves of PF and LF-5–15 samples treated with HAO.

combines with phenol anions and methylol anions from the PR via crosslinking between methylene and ether linkages to yield LR (Figure 7(c)) [27].

3.5. Density and compressive strength of foam

Table 4 lists the density and compressive strength of the LF and PF prepared with the HAO resole. The density values of the "control" PF, LF-5, LF-10, and LF-15 are 35.91, 44.96, 62.40, and 85.68 kg/m^3, respectively. It should be noted that increased lignin addition correspondingly increases the LF density. Similarly, increased amounts of lignin also correspond to increased LR density. A higher LR density results in a higher LR viscosity. Because this high viscosity obstructs the expansion of air during LF synthesis, the obtained LF exhibits a high density [4]. The compressive strengths at 10% strain of PF, LF-5, LF-10, and LF-15 are 80, 103.28, 109.78, and 152.77 kPa, respectively; PF has a lower compressive strength than all the LF samples. It is noteworthy that the compressive strength of the foams increases with the amount of lignin because this strength is proportional to the density. Foams with lower densities exhibit greater porosity, with a corresponding reduction in compressive strength [45]. Moreover, we note here that the density and compressive strength of the LFs in this study are comparable with those of commercial foam and those reported in previous studies [46].

3.6. Morphology of phenolic foam

The SEM images of the PF and HAO-treated LF-5, LF-10, and LF-15 samples are shown in Figure 8. We note that the foam exhibits a closed-cell-type structure. Moreover, some of the pores are interconnected because the expanding air in the foam ruptures the thin walls between the pores or because of possible wall damage during foam cutting [23,47]. Our analysis of the pore sizes of PF, LF-5, and LF-10 revealed that the pore size increased with the amount of lignin in the foam. This result can be explained by the fact that the resole with higher lignin exhibits greater viscosity, and is hence more capable of retaining the blowing agent, which aids pore expansion in the foam [23]. The pore size of LF-15 is on average slightly smaller than that of LF-10 because

to afford a phenol anion. The reaction between the phenol anion and formaldehyde yields a methylol anion by C–C bonding at the *ortho* position of phenol [27]. The methylol group can react with the phenol anion or other methylol anions by ether linkage as *mono-*, *di-*, and *poly-*nuclear methylol phenol, all of which have more than one CH$_2$OH functional group [2].

Lignin, which contains phenolic, hydroxyl, methyl, and thiol groups, can be used to replace phenol in the synthesis of LR because its chemical structure is similar to that of phenol [44]. Figure 7(b) shows a possible mechanism pathway of LR synthesis based on our analysis and previous studies [4]. In the synthesis of LR, functional groups are crosslinked, as in the case of the PR. In this process, formaldehyde reacts with the phenolic hydroxyl group of lignin via a hydroxymethylation reaction to afford *ortho*-formaldehyde of the lignin phenolic compound. This compound

Figure 7. Proposed possible mechanism of lignin resole synthesis: (a) Reactions for the synthesis of phenolic resole, (b) hydroxymethylation reaction of lignin with formaldehyde, and (c) crosslinking of lignin resole via linkages between the lignin phenolic compound and the phenolic resole.

Table 4. Properties of HAO-treated PF and LF-5–15 foams.

Foam	Density (kg/m^3)	Compressive Strength (kPa)
PF	35.91	80.01
LF-5	44.96	103.28
LF-10	62.40	109.78
LF-15	85.68	152.27
Commercial foam [46]	15–130	1.3–31

LR-15 exhibits the highest viscosity (Figure 1). The surface tension of the resole increases with its viscosity, which resists the expansion of the pores in the foam [5]. That is, greater porosity (and hence improved thermal performance) can be achieved at the expense of compressive strength. Therefore, the LR must possess a suitable viscosity for foam synthesis.

3.7. Thermal resistance performance

Next, LF-15, whose compressive strength was the highest among all samples, was tested to determine its thermal performance with PF as the control in the temperature range of 31–66 °C. The foams were alternately tested in the same reactor. The variation curves of the inner air temperature at the center of the wooden box are shown in Figure 9. The tested foams (LF-15 and PF) received heat from the source for 2 h, and the maximum air temperatures in the cases of LF-15 and PF were 34 °C and 33.5 °C, respectively. After 2 h of heating, the foams were left in the reactor to cool at room temperature for 2 h, and the air temperatures were measured to be 31.22 °C and 30.58 °C for LF-15 and PF, respectively. The air temperature differences after heating and after cooling were only 0.5 °C, and 0.64 °C, respectively, thereby indicating a comparable thermal performance between LF-15 and PF. The morphology tests of LF-15 revealed that an increase in the lignin amount increased the
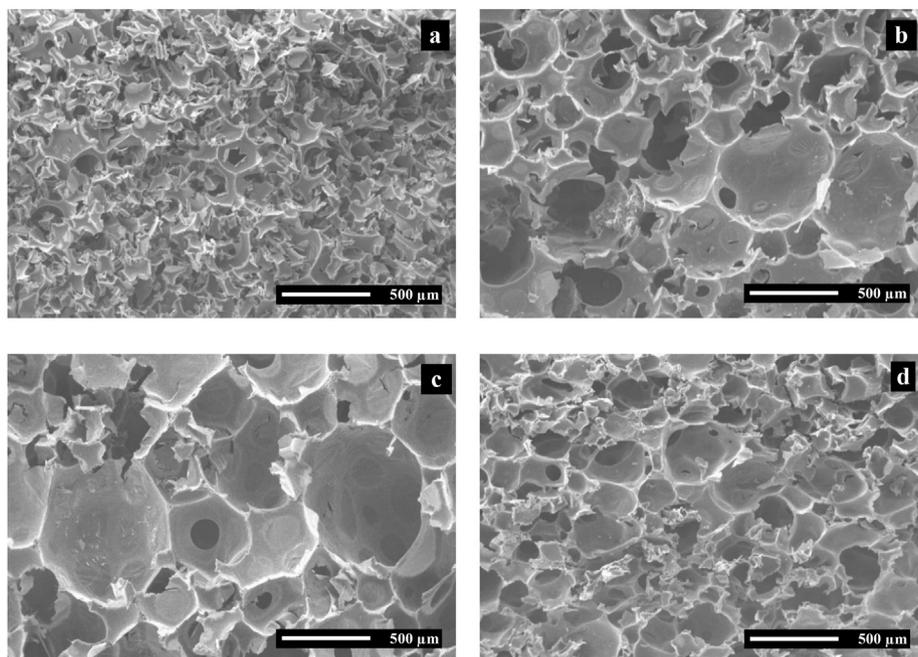
Figure 8. SEM images of specimens under 50× magnification; (a) PF, (b) LF-5, (c) LF-10, (d) LF-15.
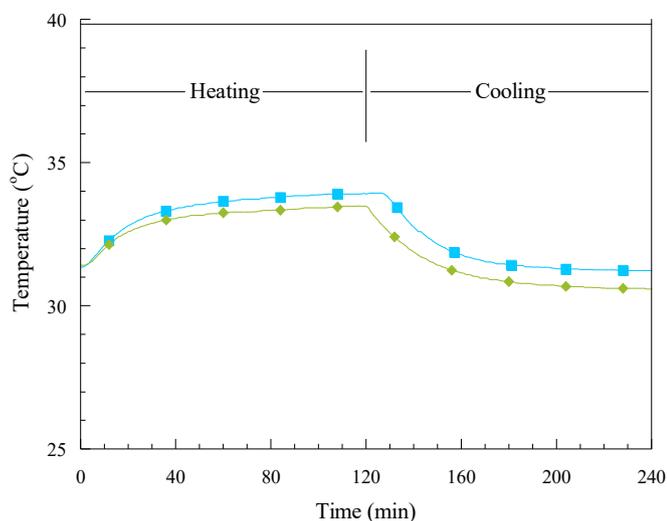
Figure 9. Thermal performance comparison between PF (- -◆- -) and HAO-treated LF-15 (– –■– –).

pore size of the foam; however, the cumulative volumes of the porosity of LF-15 and PF were 0.010918 cm^3/g and 0.037087 cm^3/g, respectively. This result explains why PF has a greater thermal resistance than LF-15.

4. Conclusions

We experimentally synthesized LF from LR by substituting phenol with untreated lignin (0–15% by weight) using two different methods of resole dehydration, namely, the VRE and HAO methods. We found that the simple HAO method could remove greater amounts of moisture from the resole than the VRE method for the same operating time. The resole obtained by the VRE method could not be used to make foam because of its low viscosity resulting from the excess moisture retained in the resole. The two dehydration methods did not transform the chemical functional groups in the resoles and foams. The addition of lignin increased the density (44.96–85.68 kg/m^3) and compressive strength (103.28–152.27 kPa) of HAO-treated LF. Our SEM examinations of the LF morphology revealed the foam to possess a closed-cell-type structure with less porosity than the PF. The biofoam with lignin content exhibited thermal stability up to a temperature of ~250 °C. The thermal performance of LF-15 was comparable with that of PF. Our findings prove that the preparation of LR by HAO dehydration is a feasible alternative to the complex VRE dehydration process. This technique may be used for the production of lignin insulation foam for commercial purposes. In addition, the use of renewable lignin can form an alternative approach for producing bio-phenolics from natural resources. However, the foam obtained from LR should further be tested for properties such as thermal conductivity, flame resistance, and the limiting oxygenation index necessary for classification according to the current standards.

Declarations

Author contribution statement

Pattaraporn Suttaphakdee: Conceived and designed the experiments; Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Sutasinee Neramittagapong: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Somnuk Theerakulpisut: Analyzed and interpreted the data; Wrote the paper.

Arthit Neramittagapong: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Tinnakorn Kumsaen: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Pornchaya Jina, Natthamon Saengkhamsuk: Performed the experiments; Analyzed and interpreted the data.

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Data availability statement

Data included in article/supplementary material/referenced in article.

Declaration of interests statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

[1] H. Shen, S. Nutt, Mechanical characterization of short fiber reinforced phenolic foam, Compos. Part A Appl. Sci. Manuf. 34 (2003) 899–906.

[2] C. Mougel, T. Garnier, P. Cassagnau, N. Sintes-Zydowicz, Phenolic foams: a review of mechanical properties, fire resistance and new trends in phenol substitution, Polymer 164 (2019) 86–117.

[3] C. Londoño Zuluaga, J. Du, H.-M. Chang, H. Jameel, R.W. Gonzalez, Lignin modifications and perspectives towards applications of phenolic foams: a review, BioRes 13 (2018) 9158–9179.

[4] B. Li, Y. Wang, N. Mahmood, Z. Yuan, J. Schmidt, C. Xu, Preparation of bio-based phenol formaldehyde foams, Ind. Crop. Prod. 97 (2017) 409–416.

[5] G. Wang, X. Liu, J. Zhang, W. Sui, J. Jang, C. Si, One-pot lignin depolymerization and activation by solid acid catalytic phenolation for lightweight phenolic foam preparation, Ind. Crop. Prod. 124 (2018) 216–225.

[6] H. Steindl, K. Hirano, L. Gollob, J. Lamb, J. McKillip, William, S. Ozeki, et al., Phenolic Resins: A Century of Progress, 2010, pp. 1–5 (9).

[7] Y. Li, A.J. Ragauskas, Kraft lignin-based rigid polyurethane foam, J. Wood Chem. Technol. 32 (2012) 210–224.

[8] B. Li, M. Zhou, W. Huo, D. Cai, P. Qin, H. Cao, et al., Fractionation and oxypropylation of corn-stover lignin for the production of biobased rigid polyurethane foam, Ind. Crop. Prod. 143 (2020) 111887.

[9] A. Crozier, I. Jaganath, M. Clifford, Phenols, polyphenols and tannins: an overview, in: Plant Secondary Metabolites: Occurrence, Structure and Role in the Human Diet, 2007, pp. 1–24.

[10] S. Jahanshahi, T. Tabarsa, J. Asghari, Eco-friendly tannin-phenol formaldehyde resin for producing wood composites, Pigment Resin Technol. 41 (2012) 296–301.

[11] C. Lacoste, M.-C. Basso, A. Pizzi, A. Celzard, E. Ella Ebang, N. Gallon, et al., Pine (P. pinaster) and quebracho (S. lorentzii) tannin-based foams as green acoustic absorbers, Ind. Crop. Prod. 67 (2015) 70–73.

[12] W. Zhang, Y. Ma, C. Wang, S. Li, M. Zhang, F. Chu, Preparation and properties of lignin–phenol–formaldehyde resins based on different biorefinery residues of agricultural biomass, Ind. Crop. Prod. 43 (2013) 326–333.

[13] M. Wang, M. Leitch, C. Xu, Synthesis of phenol–formaldehyde resol resins using organosolv pine lignins, Eur. Polym. J. 45 (2009) 3380–3388.

[14] W. Qiao, S. Li, G. Guo, S. Han, S. Ren, Y. Ma, Synthesis and characterization of phenol-formaldehyde resin using enzymatic hydrolysis lignin, J. Ind. Eng. Chem. 21 (2015) 1417–1422.

[15] F.G.C. Pinheiro, A.K.L. Soares, S.T. Santaella, L.M.A. e Silva, K.M. Canuto, C.A. Cáceres, et al., Optimization of the acetosolv extraction of lignin from sugarcane bagasse for phenolic resin production, Ind. Crop. Prod. 96 (2017) 80–90.

[16] J. Qu, Q. Han, F. Gao, J. Qiu, Carbon foams produced from lignin-phenol-formaldehyde resin for oil/water separation, N. Carbon Mater. 32 (2017) 86–91.

[17] T.K. Kirk, R.L. Farrell, Enzymatic "combustion": the microbial degradation of lignin, Annu. Rev. Microbiol. 41 (1987) 465–501.

[18] R. DiCosimo, H.C. Szabo, Oxidation of lignin model compounds using single-electron-transfer catalysts, J. Org. Chem. 53 (1988) 1673–1679.

[19] R.S. Drago, B.B. Corden, C.W. Barnes, Novel cobalt(II)-catalyzed oxidative cleavage of a carbon carbon double bond, J. Am. Chem. Soc. 108 (1986) 2453–2454.

[20] T. Yoshikawa, T. Yagi, S. Shinohara, T. Fukunaga, Y. Nakasaka, T. Tago, et al., Production of phenols from lignin via depolymerization and catalytic cracking, Fuel Process, Technol. 108 (2013) 69–75.

[21] X. Ouyang, T. Ruan, X. Qiu, Oxidative degradation of lignin for producing monophenolic compounds, J. Fuel Chem. Technol. 42 (2014) 677–682.

[22] X. Ouyang, T. Ruan, X. Qiu, Effect of solvent on hydrothermal oxidation depolymerization of lignin for the production of monophenolic compounds, Fuel Process. Technol. 144 (2016) 181–185.

[23] B. Li, Z. Yuan, J. Schmidt, C. Xu, New foaming formulations for production of bio-phenol formaldehyde foams using raw kraft lignin, Eur. Polym. J. 111 (2019) 1–10.

[24] ASTM D1622, Standard Test Method for Apparent Density of Rigid Cellular Plastics 14, Annual Book of ASTM Standards, 2004.

[25] ASTM D1621, Standard Test Method for Compressive Properties of Rigid Cellular Plastics, Annual Book of ASTM Standards, 1991.

[26] P. Suttaphakdee, N. Dulsang, N. Lorwanishpaisarn, P. Kasemsiri, P. Posi, P. Chindaprasirt, Optimizing mix proportion and properties of lightweight concrete incorporated phase change material paraffin/recycled concrete block composite, Construct. Build. Mater. 127 (2016) 475–483.

[27] B. Li, S.H. Feng, H.S. Niasar, Y.S. Zhang, Z.S. Yuan, J. Schmidt, et al., Preparation and characterization of bark-derived phenol formaldehyde foams, RSC Adv. 6 (2016) 40975–40981.

[28] H. Paysepar, Y. Hu, S. Feng, Z. Yuan, H. Shui, C. Xu, Bio-phenol formaldehyde (BPF) resoles prepared using phenolic extracts from the biocrude oils derived from hydrothermal liquefaction of hydrolysis lignin, React. Funct. Polym. 146 (2020) 104442.

[29] I. Poljanšek, U. Šebenik, M. Krajnc, Characterization of phenol-urea-formaldehyde resin by inline FTIR spectroscopy, J. Appl. Polym. Sci. 99 (2006) 2016–2028.

[30] O. Abdelaziz, C. Hulteberg, Physicochemical Characterisation of Technical Lignins for Their Potential Valorisation, Waste Biomass Valorization, 2016.

[31] A. Tejado, C. Peña, J. Labidi, J.M. Echeverria, I. Mondragon, Physico-chemical characterization of lignins from different sources for use in phenol–formaldehyde resin synthesis, Bioresour. Technol. 98 (2007) 1655–1663.

[32] M.G. Alriols, A. Tejado, M. Blanco, I. Mondragon, J. Labidi, Agricultural palm oil tree residues as raw material for cellulose, lignin and hemicelluloses production by ethylene glycol pulping process, Chem. Eng. J. 148 (2009) 106–114.

[33] S. Cheng, I. D`Cruz, Z. Yuan, M. Wang, M. Anderson, M. Leitch, et al., Use of biocrude derived from woody biomass to substitute phenol at a high-substitution level for the production of biobased phenolic resol resins, J. Appl. Polym. Sci. 121 (2011) 2743–2751.

[34] A. Boukir, S. Fellak, P. Doumenq, Structural characterization of Argania spinosa Moroccan wooden artifacts during natural degradation progress using infrared spectroscopy (ATR-FTIR) and X-Ray diffraction (XRD), Heliyon 5 (2019) e02477.

[35] X. Ren, H. Cai, H. Du, J. Chang, The preparation and characterization of pyrolysis bio-oil-resorcinol-aldehyde resin cold-set adhesives for wood construction, Polymers 9 (2017) 232.

[36] R.M. Buoro, R.P. Bacil, R.P. da Silva, L.C.C. da Silva, A.W.O. Lima, I.C. Cosentino, et al., Lignin-AuNp modified carbon paste electrodes—preparation, characterization, and applications, Electrochim. Acta 96 (2013) 191–198.

[37] I. Kubovský, D. Kačíková, F. Kačík, Structural changes of oak wood main components caused by thermal modification, Polymers 12 (2020) 485.

[38] W. Yang, J.M. Kenny, D. Puglia, Structure and properties of biodegradable wheat gluten bionanocomposites containing lignin nanoparticles, Ind. Crop. Prod. 74 (2015) 348–356.

[39] W. Yang, M. Rallini, M. Natali, J. Kenny, P. Ma, W. Dong, et al., Preparation and properties of adhesives based on phenolic resin containing lignin micro and nanoparticles: a comparative study, Mater. Des. 161 (2019) 55–63.

[40] N. Zhang, Z. Li, Y. Xiao, Z. Pan, P. Jia, G. Feng, et al., Lignin-based phenolic resin modified with whisker silicon and its application, J. Biores. Bioprod. 5 (2020) 67–77.

[41] B. Prieur, M. Meub, M. Wittemann, R. Klein, S. Bellayer, G. Fontaine, et al., Phosphorylation of lignin: characterization and investigation of the thermal decomposition, RSC Adv. 7 (2017) 16866–16877.

[42] C. Delgado-Sánchez, J. Sarazin, F.J. Santiago-Medina, V. Fierro, A. Pizzi, S. Bourbigot, et al., Impact of the formulation of biosourced phenolic foams on their fire properties, Polym. Degrad. Stabil. 153 (2018) 1–14.

[43] X. Zhang, Y. Kim, T.L. Eberhardt, R. Shmulsky, Lab-scale structural insulated panels with lignin-incorporated rigid polyurethane foams as core, Ind. Crop. Prod. 132 (2019) 292–300.

[44] D. Kai, M.J. Tan, P.L. Chee, Y.K. Chua, Y.L. Yap, X.J. Loh, Towards lignin-based functional materials in a sustainable world, Green Chem. 18 (2016) 1175–1200.

[45] L. Hu, Y. Zhou, M. Zhang, R. Liu, Characterization and properties of a lignosulfonate-based phenolic foam, BioRes 7 (2011) 554–564.

[46] C.S. Carriço, T. Fraga, V.M.D. Pasa, Production and characterization of polyurethane foams from a simple mixture of castor oil, crude glycerol and untreated lignin as bio-based polyols, Eur. Polym. J. 85 (2016) 53–61.

[47] M. Jalalian, Q. Jiang, A. Coulon, M. Storb, R. Woodward, A. Bismarck, Mechanically whipped phenolic froths as versatile templates for manufacturing phenolic and carbon foams, Mater. Des. 168 (2019) 107658.